STUDIES ON THE REACTION OF BASE WITH POLYNITRODIMETHYLNAPHTHALENES

BY

J.E. Everard

A thesis submitted in part fulfilment of the requirements for
C.N.A.A. Ph.D Degree

KINGSTON POLYTECHNIC June, 1978

INDEX

Chapter One Survey of Spectroscopic and Kinetic Studies of the Reaction of Base with Polynitroaromatic Compounds

Chapter Two Spectroscopic Studies of the Reaction of Base with Polynitrodimethylnaphthalenes

Experimental

Chapter Three Kinetics of the Reaction of Base with Polynitrodimethylnaphthalenes

Chapter Four Discussion of Spectroscopic and Kinetic Data

ACKNOWLEDGEMENTS

This work was carried out at Kingston Polytechnic during the tenure of a Research Assistantship provided by the Royal Borough of Kingston-Upon-Thames.

I wish to express my thanks to Dr's E.Buckley and C.H.J.Wells for the guidance and advice they have provided during the course of this study.

I would like to thank Dr. B.C.Webb, Dr. S.R.Robinson and Mr. P.Golding for helpful discussions and the supply of certain compounds.

I am grateful to Mrs. J.Falla and Mr. M.Webb for recording the positive ion mass spectra used in the analysis of the compounds prepared in this work; and other technical staff for their many assistances.

I am also grateful to Dr.I.M.C.Shand and Mr.M.J.Harcourt for their advice in the preparation of the computer programmes used in this work.

I would like to thank Dr.G.R.Parlett for the provision of E.P.R facilities in the Department of Chemical Physics, University of Surrey.

Lastly, I wish to thank my parents and family for their understanding during some of the trying events which have occurred and especially my mother for partly typing this thesis.

SUMMARY

A spectroscopic and kinetic study of the reactions of base with polynitrodimethylnaphthalenes, namely the tri- and tetranitro- derivatives of 1,5-;1,8-;2,3- and 2,6-dimethylnaphthalenes has been carried out. The reactions of eleven polynitrodimethylnaphthalenes were studied and the preparation of four of these compounds had not been previously reported.

A series of ten bases was employed, five being ionic(hydroxide, methoxide, ethoxide, t-butoxide and sulphite ions) and the other five were amines(diethylamine, triethylamine, hexamethyldisilazane, benzylamine and hydrazine hydrate).

The spectroscopic studies showed that the principal reactions of base with the polynitrodimethylnaphthalenes were either proton abstraction from an α-methyl group to give a 'benzyl-type' anion or addition at a ring position to give a Meisenheimer type complex.

It has been shown that the lower the pK_a value of the base reacting with α-dimethylnaphthalenes the greater the likelyhood of an addition rather than proton abstraction reaction occuring.

Kinetic studies were mainly concerned with the reaction of base with 2,4,8-trinitro-1,5-dimethylnaphthalene. Detailed determination of the kinetic and thermodynamic parameters for proton abstraction from this compound by diethylamine and triethylamine in DMSO and several DMSO/methanol mixed solvent mixtures has been undertaken.

The reaction of hydroxide ion over a wide range of concentrations with 2,4,8-trinitro-1,5-dimethylnaphthalene in aqueous DMSO revealed a complex reaction process..

The rapid addition of sulphite ion to 2,4,6,8-tetranitro-1,5-dimethylnaphthalene and 1,4,5,7-tetranitro-2,3-dimethylnaphthalene in aqueous DMSO has revealed different relative rates of reaction.

The kinetic and thermodynamic parameters for the reaction of hydroxide ion with 1,3,5-trinitro-2,6-dimethylnaphthalene in various aqueous DMSO solvent mixtures show that one of the processes involved gives a short lived intramolecularly hydrogen bonded addition complex.

A brief spectroscopic and kinetic study of the reactions of base with polynitrodimethoxynaphthalenes has also been carried out.

CHAPTER ONE

SURVEY OF SPECTROSCOPIC AND KINETIC STUDIES OF THE REACTION OF BASE WITH NITROAROMATIC COMPOUNDS

1.1 Types of Base Interaction

1.1.1 Introduction

Several extensive reviews of the interaction of bases with polynitroaromatic compounds cover the period up to 1970[1-4], so it is intended to only consider the more interesting aspects in this reviewed work and to consider later work in more detail.

Spectroscopic techniques used for the investigation of reactions of base with polynitroaromatics are mainly NMR (proton) and UV-visible absorbtion spectroscopy and to a lesser extent IR absorbtion spectroscopy and EPR spectroscopy. Kinetic measurements almost invariably involve following the change in UV/ invisible absorbtion with time, requiring stopped flow and temperature-jump methods for the faster reactions. Recently the important new technique of flow PMR has provided both structural and kinetic data[95]. Thermodynamic parameters are normally calculated from kinetic and equilibrium measurements but some calorimetric studies have been made.

The reactions may be divided into six main categories.

1. Charge-transfer complexation.
2. Radical anion formation.
3. Proton abstraction to form an aryl carbanion.
4. Nucleophilic substitution.
5. Anionic sigma complex formation.
6. Proton abstraction from a substituent.

As the present work is concerned almost wholly with the latter two categories the first four categories will only be briefly reviewed.

1.1.2 Charge Transfer Complexation

Charge transfer complexes are formed by the weak interaction of electron acceptors and electron donors involving a partial transfer of charge from the donor to acceptor. Essentially there are two types of donor, n-donors which are able to complex through non-bonded electron pairs e.g. amines and pi- donors such as aromatic hydrocarbons with electron abundant delocalised pi- systems. Electron deficient compounds are generally acceptors such as aromatic systems containing electron withdrawing substituents, e.g. nitro and cyano groups.

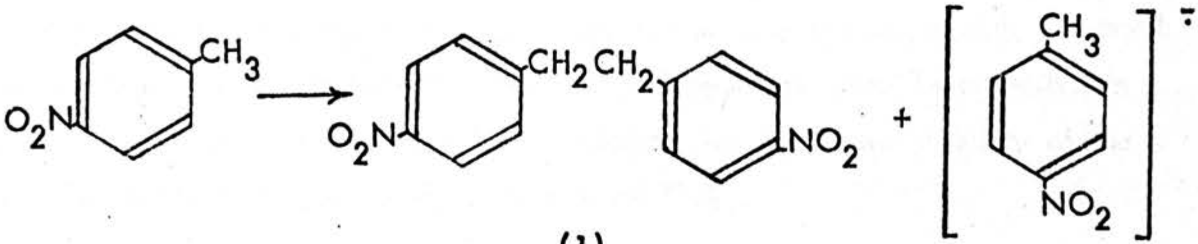
The valence bond description of charge transfer complexation by Mulliken[5] is the most generally accepted. This subject has been extensively reviewed[6-8].

1.1.3 Radical Anion Formation

Reduction of nitroaromatic compounds with alkali metals may produce radical anions which can be studied by EPR, although this method has the disadvantage that interaction with the counterion (eg Na^+ or K^+) causes line width alternation. Electrolytic and photochemical reduction have been used to overcome this.

The reaction of organometallic reagents with nitroaromatics such as n-butyl lithium and nitrobenzene in THF-hexane has been shown[9] to produce the neutral free radical, n-butylphenylnitroxide. Grignard reagents also react similarly to generate nitroxides[10]. Many studies of nitroxides derived from nitroaromatics have been made[11,12].

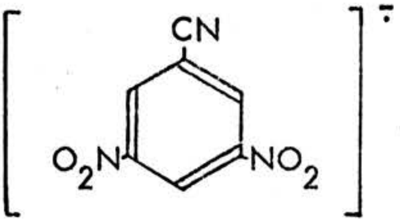
Free radicals have been observed in the reaction of nitro-compounds with alkoxide. An example is the reaction of n- or p- nitrotoluene with potassium tert-butoxide in tert-butonol/ dimethylsulphoxide (DMSO) to give nitrobibenzyls and the radical anions of n- and p- nitrotoluenes[13,14].



(1)

(2)

Russell et al[15] have also detected radical anions in basic solutions of m-dinitrobenzene (DNB). Paramagnetic species observed in the interaction of alkoxide ions with 3,5- dinitrobenzonitrile are attributed to the radical anion (3)[16].



(3)

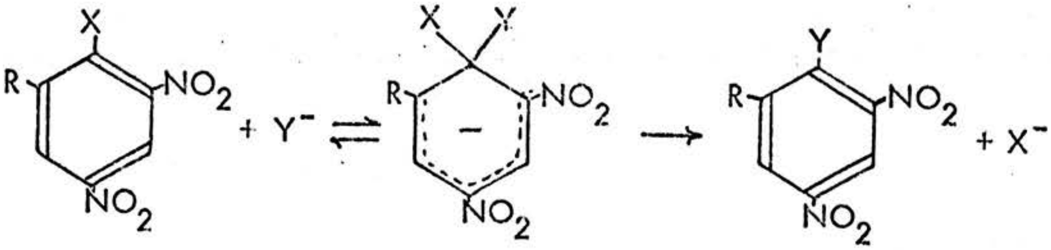
The low radical concentrations (<1% in the above case) reflect the increased stability of the sigma-addition complexes with more electron withdrawing substituents. Even small quantities of radicals are sufficient to cause such rapid proton spin relaxation that the PMR lines are broadened and no useful spectrum is obtained. This is the case for the reaction of alkoxide with 2,4,6-trinitrotoluene (TNT)[17]. Stable radicals are not formed, but they may be trapped by a radical scavenger[18].

1.1.4 Proton Abstraction to Form an Aryl Carbanion

Considerable argument occurred as to whether 1,3,5-trinitrobenzene (TNB) ionised by ring proton loss in alkaline solution. No hydrogen exchange occurred on treatment with 8M sodium hydroxide in D_2O[19] or pyridine-H_2O[20]. However, positive evidence for exchange was obtained by the action of 0.01M NaOD in dimethylformamide (DMF)/ H_2O[21] and sodium methoxide in tritiated methanol[22]. The coloured addition compound (major product) produced by base is inactive to nuclear proton exchange and the process occurs through the small residual equilibruim quantity of TNB. The C-2 hydrogen atom in m-DNB can be exchanged under milder conditions demonstrating the lower stability of the inactive addition complex relative to that of TNB.

1.1.5 Nucleophilic Substitution

Nucleophilic substitution of substituted polynitroaromatics frequently appears to occur via the formation of an intermediate of finite stability[23,24], as indicated below.



(4)

R=H, NO_2, CN X= (i) halide; (ii) alkoxide

Y= (i) alkoxide; (ii) hydroxide

Meisenheimer complexes (see section 1.2) are particularly stable forms of these delocalised sigma-addition intermediates. Base catalysis is indicative of this mechanism of substitution and is commonly observed with amine bases[25]. The rarer substitution of a nitro group with the elimination of nitrite ion[26] is possible by two processes in TNB. Gold and Rochester[27] studied the production of 3,5-dinitroanisole(DNA) by the reaction of methoxide with TNB but did not consider the major product (sigma-addition complex) to be an intermediate. This points to direct substitution. Izzo[28], however, provides strong evidence for bicarbonate addition at a carbon bearing only hydrogen and subsequent intramolecular coupling and lyate ion attack to form 3,5-DNA in the bicarbonate catalysed displacement of a nitro group by substitution[29].

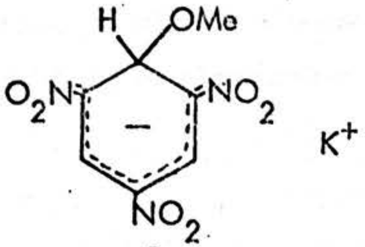
1.2 Anionic Sigma Complexes

1.2.1 1,3,5-Trinitrobenzene(TNB)

(A) Alkoxides and Hydroxide

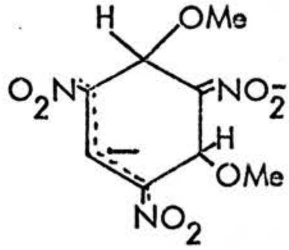
Reaction of methanolic potassium methoxide with 1,3,5-TNB to form a 1:1 anionic sigma-complex capable of isolation in the solid state, (5) was first noted at the end of the last century[30]. More recently the reaction between equimolar amounts of 1,3,5-TNB and methoxide ion in DMSO has been studied by PMR spectroscopy and the structure(5) confirmed[31].

(5)



5

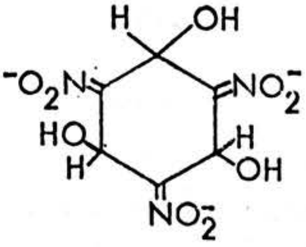
The visible absorbtion spectrum shows maxima at about 430nm and 510nm with molar extinction coefficients approximately in the ratio of 2:1 which is typical of trinitrocyclohexadienates[27,31]. With an excess of methoxide the PMR spectrum indicates a 2:1 adduct(6)[32].



(6)

Only one visible absorbtion maximum occurs at 510nm[33] due to the dinitropropenide function with the $C{=}NO_2^-$ function predicted to have no visible absorbtion.

Reaction of hydroxide ion with 1,3,5-TNB forms not only 1:1 and 2:1 adducts[34] as the hydroxide concentration is increased, but at very high concentration the colourless 3:1 complex(7)[35].

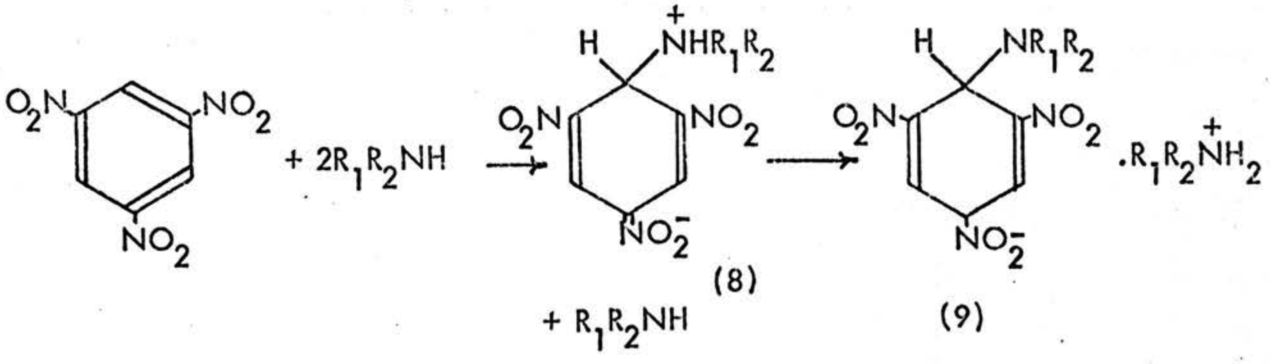


(7)

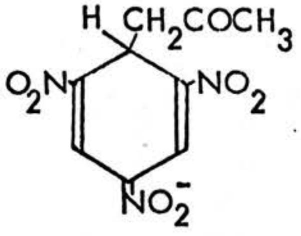
Only the 1:1[36] and 2:1[37] adducts have been observed by PMR.

(B) Aliphatic Amines

Two equivalents of primary or secondary aliphatic amine react with TNB[38] in DMSO to yield the alkylammonium salt of the covalent complex(9).

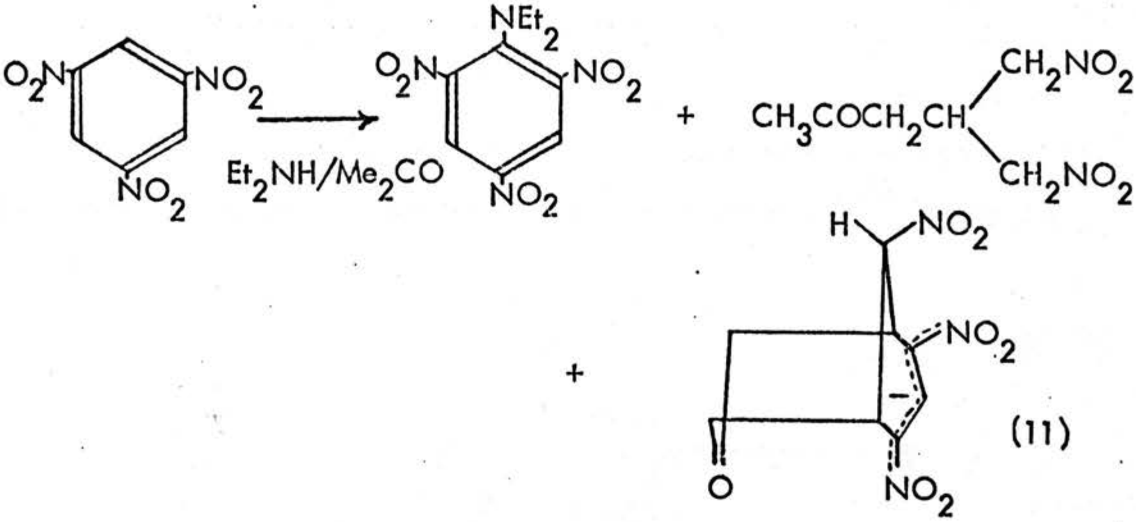


Visible spectra in either polar[39] or non-polar solvents[40] show similar features to the 1:1 alkoxide -TNB system. The sigma-addition complex is formed by attack at the 1-position to give a zwitterion(8) followed by proton abstraction[41]. Tertiary amines do not react at all in DMSO, but in acetone proton abstraction by the amine gives the acetonate anion which does form a covalent complex with 1,3,5-TNB(10)[42].



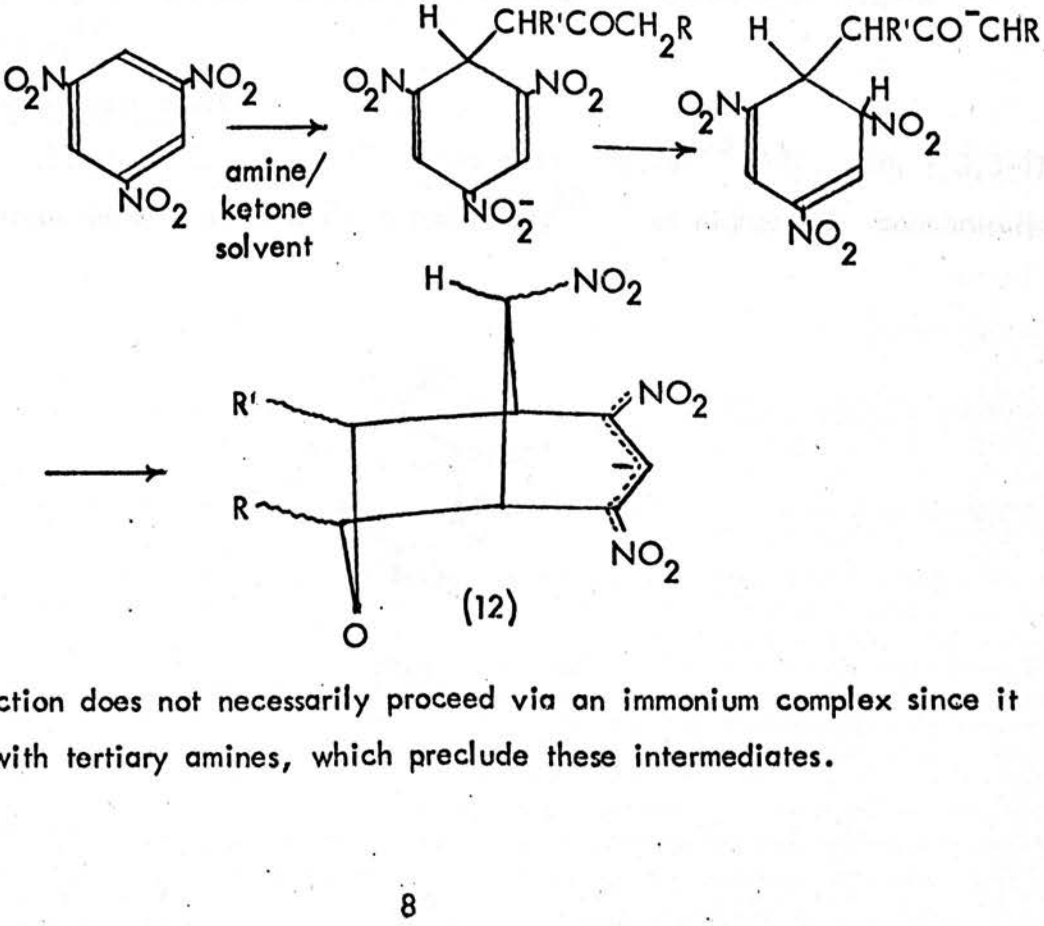
(10)

Many ketones react similarly and the 1:1 methoxide complex(5) undergoes solvolysis by acetone to give (10). (10) and the diethylamide complex ($9;R_1 = R_2 = Et$) are initially formed by the secondary amine diethylamine in acetone on 1,3,5-TNB, but ultimately besides 4-nitromethyl-5-nitropentan-2-one and p-nitro-N,N-diethylaniline a bicyclic dinitropropenide complex(11) is produced[43,44].



(11)

An immonium sigma complex has been postulated as an intermediate in the formation of (11). Solutions of 1,3,5-TNB and primary, secondary or tertiary amines in ketonic solvents such as dibenzyl ketone form only bicyclic structures like (12)[45]. The intermediate monocyclic anionic sigma complexes are detectable but cannot be isolated[45,46].

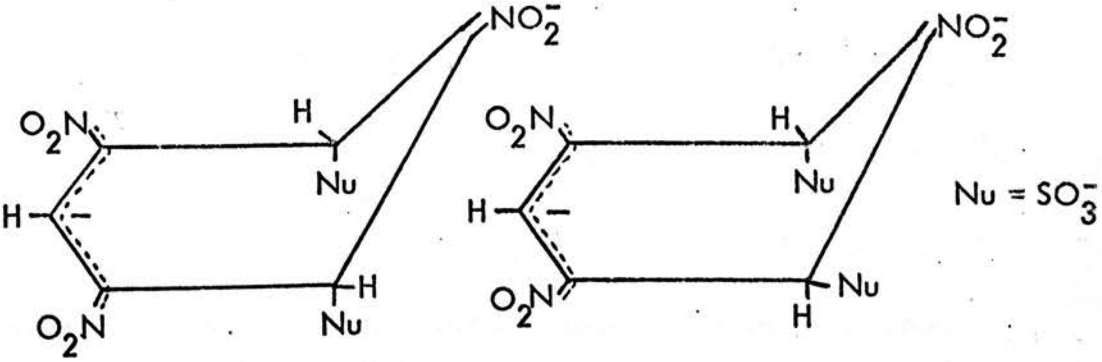


(12)

The reaction does not necessarily proceed via an immonium complex since it occurs with tertiary amines, which preclude these intermediates.

(C) Sulphite

Sulphite ion in concentrated aqueous solution reacts with 1,3,5-TNB to give a stable crystalline addition product[47] containing 2 equivalents of base to 1 of TNB. Visible spectra of the aqueous solution show the presence of 1:1[48,49] and 2:1[50] adducts depending on the concentration of sulphite. PMR confirms these results and the existence of cis-trans isomers[51,52] in the 2:1 complexes.



cis

(13a)

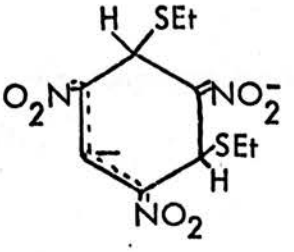
trans

(13b)

The colourless 3:1 complex is also postulated at the extreme of sulphite concentration[49].

(D) Other Sulphur Bases

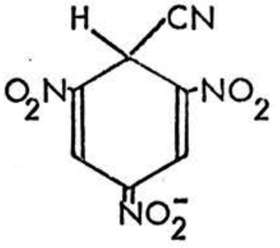
Thiophenoxide ion, PhS^- forms a 1:1 complex[53] only, with 1,3,5-TNB but thioethoxide also gives a 2:1 complex(14)[53,54] at higher EtS^- concentration.



(14)

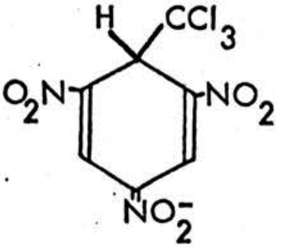
(E) Other Bases

Tetraphenylarsonium cyanide in chloroform reacts with 1,3,5-TNB to yield the 1:1 cyanide adduct(15)[55] as shown by PMR[56,57].



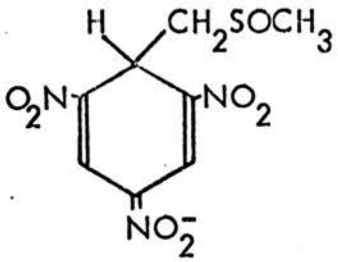
(15)

A DMSO solution of chloroform, 1,3,5-TNB and sodium methoxide produces (16)[58], as does solvolysis of (5) in DMSO by chloroform.



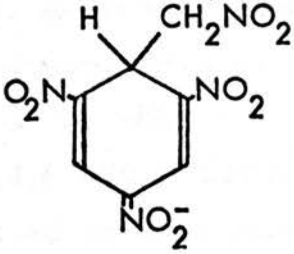
(16)

Under anhydrous conditions the conjugate base of DMSO reacts with 1,3,5-TNB to form a sigma complex (17)[59].



(17)

When a tertiary amine is added to a solution of 1,3,5-TNB in an aliphatic nitro-compound (e.g. nitromethane) an addition complex results (18)[60].

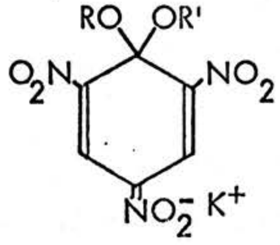


(18)

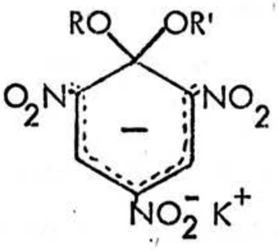
1.2.2 Picryl Ethers

(A) Alkoxides

In 1900 Jackson and Gazzolo proposed the quinoid structure (19) for the coloured adducts obtained from potassium alkoxides and picryl ethers[61]. Although Meisenheimer obtained the same product[62] from 2,4,6-trinitroanisole (TNA) and potassium ethoxide, and from 2,4,6-trinitrophenetole and potassium methoxide, it was not until 1964 that PMR provided indisputable evidence for the Meisenheimer structure[36]. The IR spectra of the solid complexes had also previously been shown to be consistent with (19)[63,64].

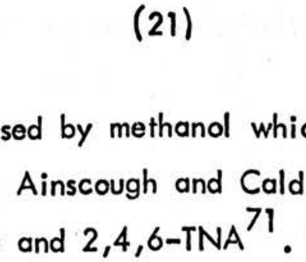


(19)



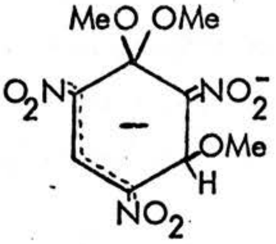
(20)

PMR spectra of adducts containing various alkoxy groups similarly indicate attack at C-1 to form an sp^3 carbon atom[32,65]. The structure (20) gained popularity in later years, but crystallographic evidence[66] and molecular orbital calculations[67,68] indicate that Jackson's original structural notation is a better representation in view of the high charge density on the nitro group para to the sp^3 hybridised carbon atom. Servis observed that the PMR spectrum showed a transient species on the addition of concentrated sodium methoxide solution to a solution of 2,4,6-TNA in DMSO[69]. This adduct was formed by attack at C-3 (21; R = Me) and gradually changed to the thermodynamically more stable C-1 complex.



(21)

The conversion was catalysed by methanol which indicates an inter- rather than intra-molecular process[70]. Ainscough and Caldin observed 2 reactions on rapid mixing of sodium ethoxide and 2,4,6-TNA[71]. The slower was considered to give the C-1 adduct (19; R = Me, R' = Et) and the faster reaction was thought to be due to charge transfer, but is very probably addition at C-3 by ethoxide (21; R = Et). The visible spectrum of (19; R = R' = Me) in methanol consists of two peaks[72] with maxima at 410nm and 486nm. The ratio of the extinction coefficients is 1.44:1, but this may vary with change of solvent[33]. These visible transitions are formulated as charge transfer between the ring and nitro-groups[68]. The high energy maxima undergo a bathochromic shift and the low energy maxima a hypsochromic shift on altering the solvent from an ether to the more ionising solvent methanol[33]. At high base concentration a 2:1 adduct with a visible band at 480nm is formed[33,72] and the structure of this 1,3-diadduct(22) is confirmed by PMR[73].

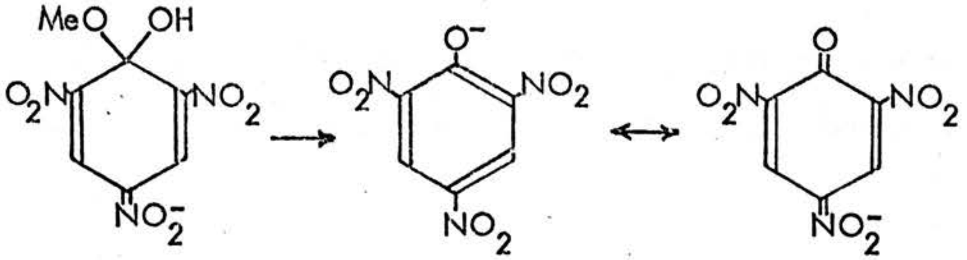


(22)

Very high methoxide concentration produces a colourless species[74], probably the 1,3,5-triadduct. Abe calculated[75] that the 1:1,2:1 and 3:1 adducts should have two, one and no visible absorbtion maxima respectively.

(B) Hydroxide

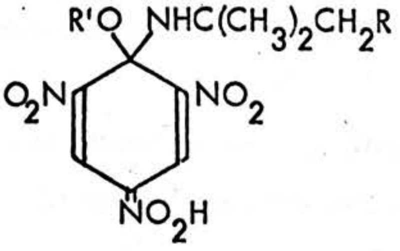
Aqueous hydroxide ion reacts with 2,4,6-TNA to form the picrate ion (24)[34] without overt formation of a stable intermediate, but it is probable that (23) would be passed through during the hydrolysis.



(23) (24)

(C) Aliphatic Amines

Similarly di-[4] and tri-[4,76] ethylamine appear to give methyldiethyl- and methyltriethyl- ammonium picrate respectively on reaction with 2,4,6-TNA. A series of neutral addition complexes(25) have been made at low temperature from hindered amines and hindered picryl ethers[77]. The series is peculiar in that the nitro-group para to the sp^3 ring carbon is protonated.

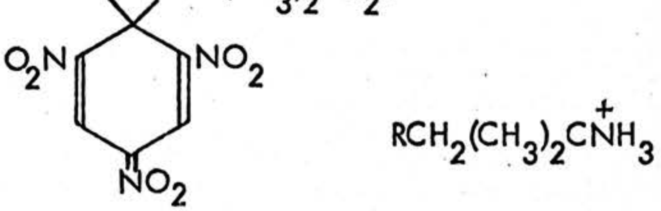


R = H, R' = Ph etc.

(25)

With excess amine anionic sigma complex salts are formed (26).

(26)



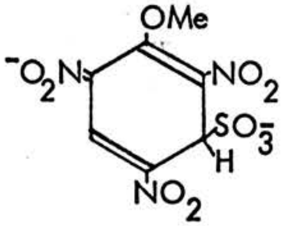
$RCH_2(CH_3)_2C\overset{+}{N}H_3$

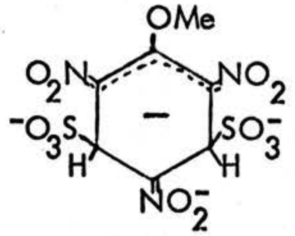
2,4,6-TNA and hindered amines give various proportions of substitution and base alkylation products depending on the actual base and solvent used.

(D) Sulphite

In aqueous DMSO sulphite ion adds to C-3(27) of 2,4,6-TNA, while in concentrated aqueous base solution a 3,5-diadduct(28) is formed[50].

(27)





(28)

(E) Other Bases

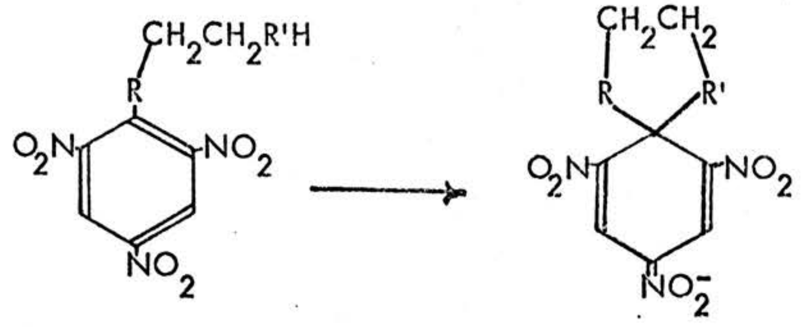
Tetraphenylarsonium cyanide and 2,4,6-TNA in chloroform react at low temperature to give a mixture of C-1 and C-3 mono-adducts[78] in the approximate ratio of 1:4. This ratio remains unchanged for several hours at -30°C. In contrast to methoxide ion adducts the C-3 cyanide adduct is more stable than the C-1 form.

Acetonate does not attack at C-1 but forms the C-3 complex[79] as does solvolysis by acetone of the C-1 methoxy adduct[32].

1.2.3 Picryl Glycol Ether

In neutral and alkaline aqueous solution picryl glycol ether (29; R = R' = -O-) forms a cyclic Meisenheimer complex(30)[80]. PMR shows the methylene protons to be equivalent[65]. Many studies[81-3] of analogous cyclic complexes with the glycol oxygen(s) replaced by thio- and methylamino- groups in various combinations have been undertaken.

(29)



(30)

R	R'	ref.
O	O	80
S	S	81
S	O	81
NMe	O	82
O	NMe	82
NMe	NMe	83

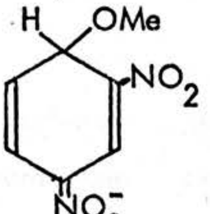
The sulphur analogue of 2,4,6-trinitrophenetole, ethyl thiopicrate reacts with sodium ethane thiolate to form the 1,1- and 1,3- mono-adducts[84]. However, in this case both isomers are present at equilibrium and the 1,3-form predominates.

1.2.4 Dinitro- and Substituted Dinitro-Benzene.

(A) 1,3-Dinitrobenzene(DNB)

(a) Alkoxides

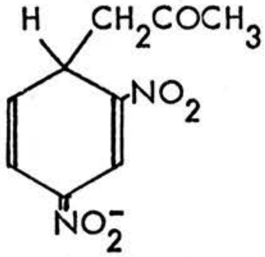
As mentioned earlier 1,3-DNB reacts with alkoxide in DMSO to give low concentrations of free radicals which preclude PMR analysis. The visible absorbtion at 516nm has been taken to indicate the formation of the C-4 rather than C-2 methoxide adduct(31)[22].



(31)

(b) Acetonate

PMR of the product given by base addition to a DMSO/acetone solution of 1,3-DNB clearly shows the acetonate C-4 complex(32)[85].

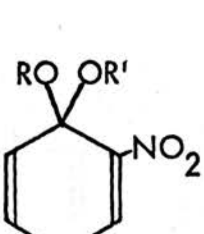


(32)

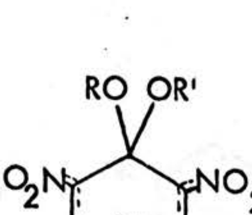
Many carbanions react similarly as was first shown by Janovsky in 1886[86].

(B) Dinitrophenyl Ethers

Various alkoxides react with 2,4- and 2,6-dinitrophenylethers to form addition products[87,88], some of which may even be isolated as solids[89]. PMR indicates the position of attack as C-1[32,37,70,90].

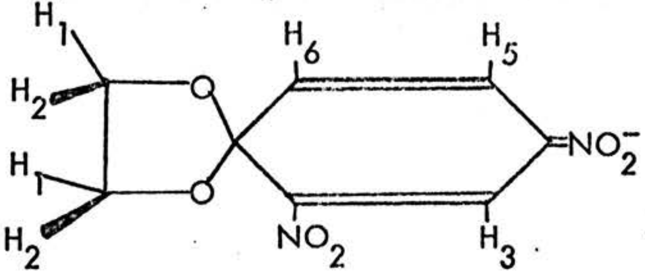


(33)



(34)

The cyclic or spiro Meisenheimer complex(35) prepared in basic solution from glycol-2,4-dinitrophenylether[91] has a PMR spectrum showing an A_2B_2 spin system for the methylene resonances[92].

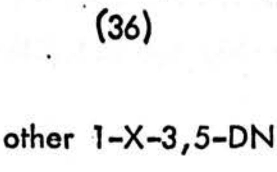


(35)

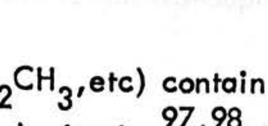
As expected the methylene protons for the 2,6-dinitro- spiro complex are equivalent and result in a singlet[42,79,92].

(C) 3,5-Dinitrocyanobenzene(DNCB)

The reaction of alkoxide ion with 3,5-DNCB has been shown by conventional PMR to give one major thermodynamically stable product(36)[93]. However, the visible spectrum shows another transient species to be formed in a kinetically controlled reaction[94] and this was studied[95] by the recently developed technique of flow NMR.[96] Rapid attack at C-4 is clearly demonstrated(37).



(36)

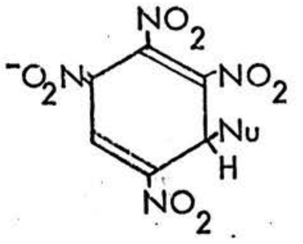


(37)

Interestingly, other 1-X-3,5-DNB's(X=CF_3,CO_2CH_3,etc) contain both isomers in the equilibrium mixture with C-2 adduct predominating[97,98] and acetonate ion appears, from visible absorbtion data, to give two species also[99].

1.2.5 1,2,3,5-Tetranitrobenzene(TETNB)

PMR shows that 1,2,3,5-TETNB reacts with aqueous hydroxide or sulphite ion in ethanol to give addition products[29] at a hydrogen-bearing ring carbon(38).

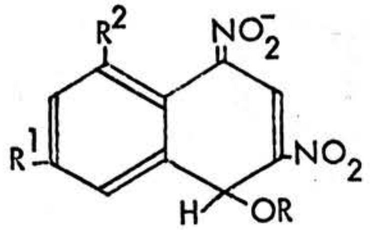


(38) Nu = OH, OEt & SO_3^-.

1,2,4,5-TETNB produces only substitution products with the bases listed above via very transient unidentified species[29].

1.2.6 Polynitronaphthalenes

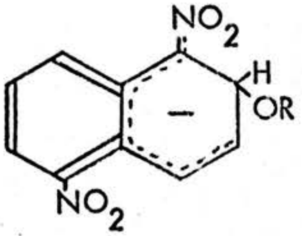
Alkoxide addition at C-4 occurs in 1,3-dinitro-(39)[79];1,3,8-trinitro-(40)[26] and 1,3,6,8-tetranitro-naphthalenes(41)[100] apparently without prior transient formation,

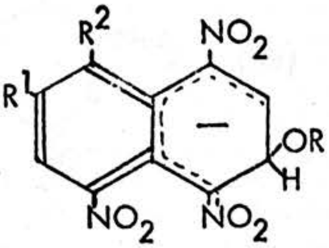


	R^1	R^2
(39)	H	H
(40)	H	NO_2
(41)	NO_2	NO_2

whereas a β -carbon adjacent to a nitro-group is attacked in 1,5-dinitro-(42); 1,4,5-trinitro-(43);1,3,5,8-(44) and 1,4,5,8-(45) tetranitro-naphthalenes[26].

(42)

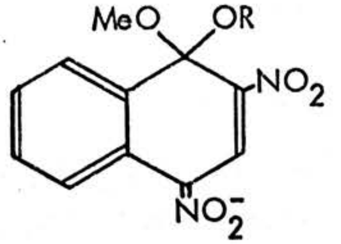




	R^1	R^2
(43)	H	H
(44)	NO_2	H
(45)	H	NO_2

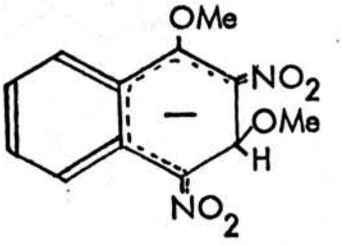
1.2.7 Polynitronaphthylalkyl ethers

As perhaps expected by analogy with dinitrophenyl ethers methoxide forms C-1 addition products(46) with 1-alkoxy-2,4-dinitronaphthalene[101]. The visible absorbtion spectrum is characteristic of naphthalene sigma-complexes showing two maxima at about 350 and 500 nm with extinction coefficients in the ratio of approximately 1:2, the opposite to trinitrocyclo-hexadienates.



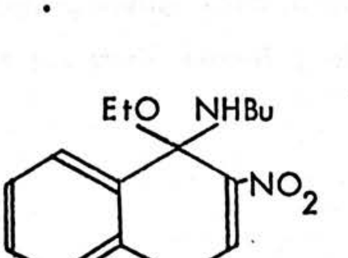
(46)

Terrier has reported formation of a transient C-3 adduct (47) using stopped-flow spectrophotometry[102].



(47)

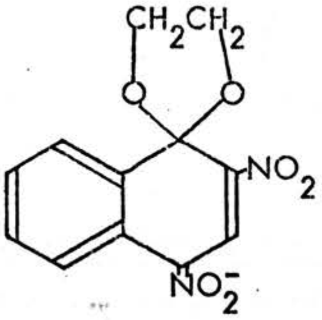
The substitution of 2,4-dinitronaphthylethyl ether by n-butylamine was postulated to occur via an intermediate (48)[103] and this has very recently been detected by flow PMR[104].

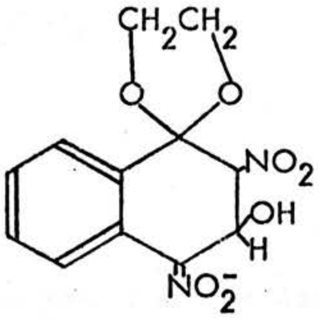


(48)

The spiro-complex (49) is readily formed[92] from the glycol ether and with concentrated hydroxide ion a higher adduct (50) is proposed[105].

(49)

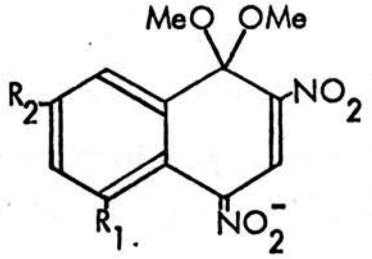




(50)

The methylene protons of (49) are only slightly non-equivalent.

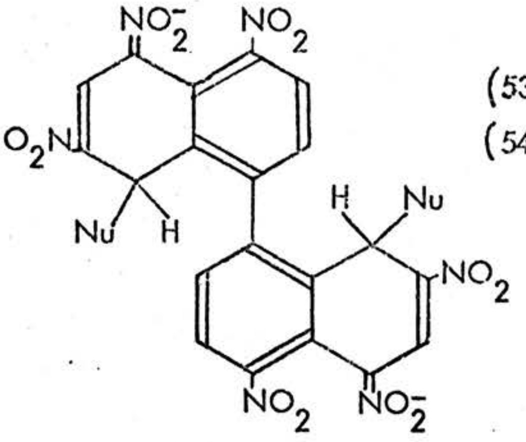
1-Methoxy-2,4,5-[106] and 2,4,7-[107] trinitronaphthalenes both yield the solid 1,1-dimethoxy adducts on reaction with potassium methoxide in dioxan. PMR in dimethylacetamide(DMA) and DMSO failed to reveal any short lived species.



	R_1	R_2
(51)	NO_2	H
(52)	H	NO_2

1.2.8 Hexanitrobinaphthyl

The 8,8'-dimethoxy sigma-addition complex (53) of 4,4',5,5',7,7'-hexanitro-1,1'-binaphthyl appears to exist in meso and racemic forms[108] in equal proportions, but the corresponding sulphite diadduct (54) occurs in only one form. This is a result of the steric crowding of the 8,8' positions and the charge on the nucleophile.

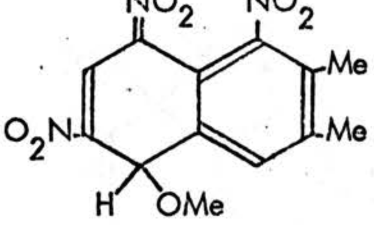


	Nu
(53)	OMe
(54)	SO_3^{--}

1.2.9 Polynitro-2,3-dimethylnaphthalenes[109]

Methoxide ion reacts with 1,6,8-trinitro-2,3-dimethylnaphthalene(55) in situ in DMSO to form the C-5 Meisenheimer complex only (56) as shown by PMR[109].

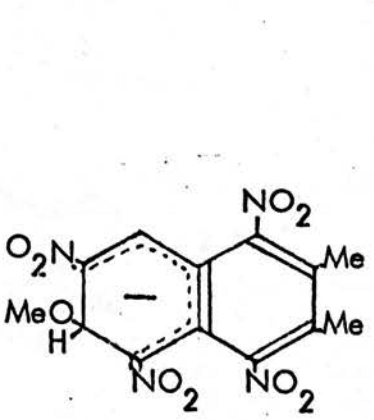
(56)



As with most polynitrodimethylnaphthalenes a solid addition product is obtained on the preparative scale in methylene dichloride under nitrogen, but this is unstable in air and when dissolved in DMSO.

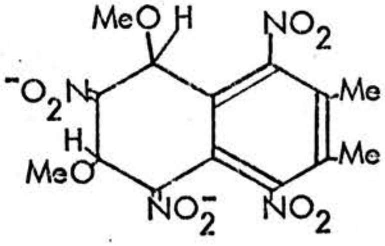
One equivalent of methoxide gives not only the C-8 adduct (57) but a small proportion of the C-6 form (58) with 1,4,5,7-tetranitro-2,3-dimethylnaphthalene.

(57)



(58)

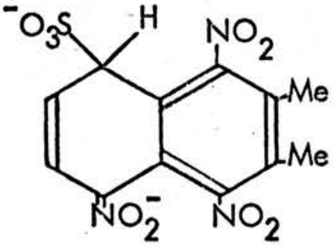
Two equivalents appear to give a mixture of the cis and trans diadducts (59a and b) and substitution product in which nitrite ion is replaced by methoxide at C-7.



(59 a & b)

On the other hand sulphite ion even in excess yields only the C-8 1:1 complex (60).

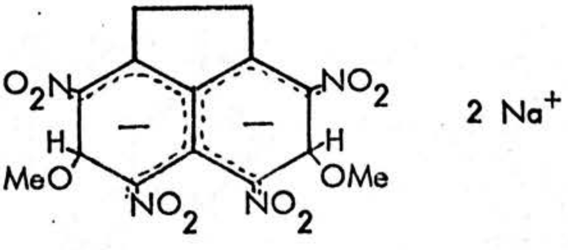
(60)



1.2.10 3,5,6,8-Tetranitroacenapthene

A dianionic sigma complex (61) is obtained by the reaction of sodium methoxide and 3,5,6,8-tetranitroacenaphthene in dichloromethane[110].

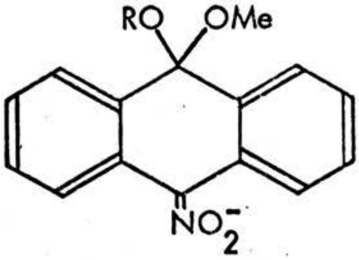
(61)



Similar treatment of 3,5,6,7-tetranitroacenaphthene gives an insoluble black precipitate[111], possibly the 7-methoxy substitution product. Reaction with methoxide in acetone produces a homogeneous deep red solution typical of an addition complex, but a broadened PMR spectrum indicates the presence of free radicals.

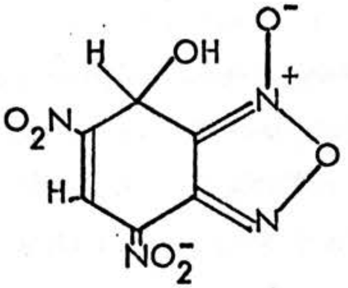
1.2.11 Nitroanthracenes

9-Nitro- and 9-nitro-10-methoxy-anthracenes undergo attack by methoxide at C-10 to form the complexes (62) and (63) first isolated by Meisenheimer[62]. Foster has confirmed the proposed structures and reports that the 9-nitro-complex has a visible maximum at 505nm[79].



	R
(62)	H
(63)	Me

Several other classes of compound besides polynitroaromatic hydrocarbons form sigma-addition complexes namely nitro-pyridines, nitro-pyrimidines and 4,6-dinitrobenzofuroxan. The last mentioned of these is particularly interesting in that the aromatic dissolves in water, yielding acidic solutions of the 7-hydroxy addition complex(64)[112].



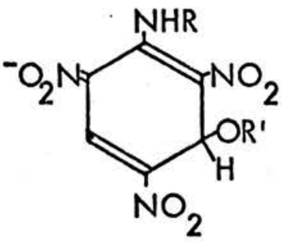
(64)

1.3 Complexes of Compounds which may involve Proton Abstraction from a Substituent

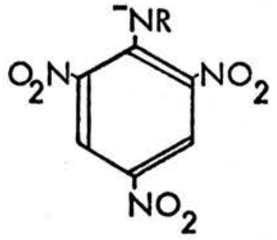
1.3.1 Picramide and N-Substituted Picramides

(A) Alkoxides and Hydroxide

Addition at C-1 is not observed with picramides, instead proton loss from the amino group and addition at C-3 usually occurs. Indeed, proton loss can become competitive with base addition, which can occur on picramide or its conjugate base. Hydroxide and alkoxide both react in this mode with picramide and substituted picramides[70,73,113,114]. The ratio of addition(65) to NH proton abstraction(69) is approximately 4:1 for equimolar amounts of methoxide and picramide in DMSO[50].

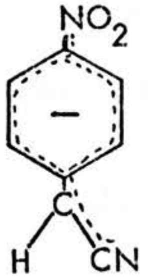


	R	R'
(65)	H	Me
(66)	Me	Me
(67)	Ph	Me
(68)	H	H



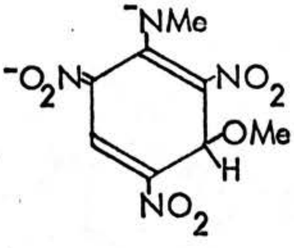
(69)	H
(70)	Me
(71)	Ph

The conjugate base (69) only is formed with t-butanol/butanol/DMSO. As the size of the nucleophile increases so the extent of complex formation decreases in the order $MeO^- > EtO^- > Bu^tO^-$. Aqueous DMSO solutions give about 70% of the C-3 adduct[70], while decreasing the water content increases the relative quantity of conjugate base. A 1:1 mixture of N-methylpicramide and methoxide contains ~80% of the conjugate base(70), the remainder being addition product (66). This greater preference for conjugate base formation with N-methylpicramide relative to picramide has been explained by the increased stability of the C-1 to nitrogen exocyclic bond, which has considerable double bond character in the conjugate base. As might be expected the PMR spectrum shows non-equivalent ring protons indicating restricted rotation about this bond. A similar effect is observed in the conjugate base of 4-nitrobenzyl cyanide(72) where an ABXY spectrum is given[115].



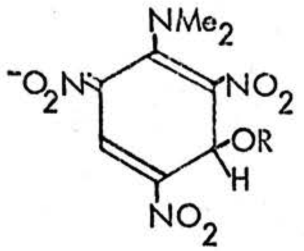
(72)

A dianion (73) is formed[70] on addition of excess methoxide to N-methylpicramide.

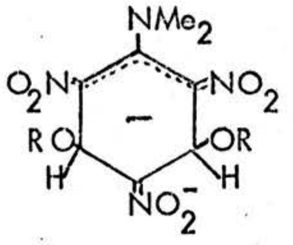


(73)

N-phenylpicramide only forms the conjugate base with one equivalent of methoxide. This is due to the stabilising effect of the phenyl attached to the amino group. N,N-dimethylpicramide does not possess an ionisable proton and so yields initially the 1:1 adduct (75) with methoxide in methanol and then the 3,5-diadduct (77) at higher base concentration[113]. Crampton and Gold confirmed this process in DMSO using PMR[116]. In aqueous sodium hydroxide solution only the diadduct (76) appears to be formed, but in aqueous DMSO PMR indicates both mono- and di-adducts[70].



R
(74) H
(75) Me

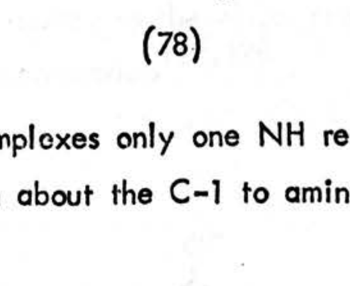


R
(76) H
(77) Me

Apparently picramides do not react with amines in DMSO solution[73,79], although it has been speculated[4] that sodium amide would proton abstract and add amide ion in accordance with the reaction of 2,4-dinitroaniline in liquid ammonia[117].

(B) Sulphur bases

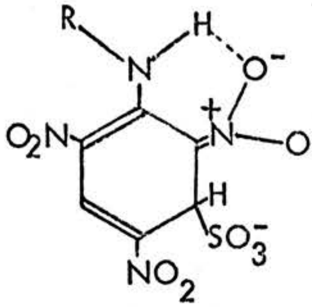
Sulphur bases add at unsubstituted positions in picramides without proton abstraction to give 1:1 and 2:1 adducts[50,53]. Separate amino proton resonances at negative τ chemical shift values for the picramide 1:1 complex with sulphite (78) support the existence of hydrogen bonding[118].

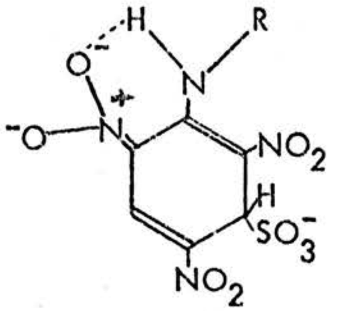


(78)

For N-substituted 1:1 complexes only one NH resonance is observed pointing to rapid rotation about the C-1 to amine-N bond in one of the isomers (79a) or (79b)[50].

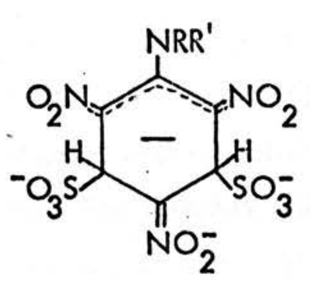
(79a)





(79b)

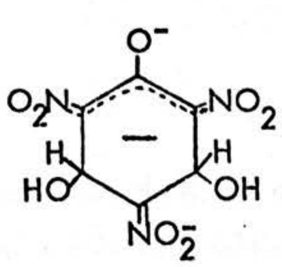
Since the nitro-group para to the sp^3 carbon carries most of the negative charge (79b) would be the more likely isomer if only one was present. Unlike 1,3,5-TNB there is no evidence of cis-trans isomerism in the diadducts (80).



(80)

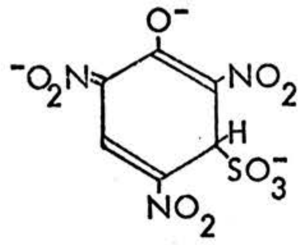
1.3.2 Picric Acid

Picric acid exists in dilute sodium hydroxide solution as the picrate ion (24) which absorbs at 360nm. In stronger hydroxide solution the 3,5-dihydroxy adduct (81) is formed as the major product with perhaps the mono-adduct present at low concentration[119,120].

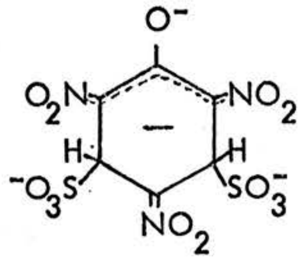


(81)

Both 1:1 (82) and (83) complexes are produced with sulphite, the latter adduct being pentavalent[120] and probably the trans-form[121].



(82)

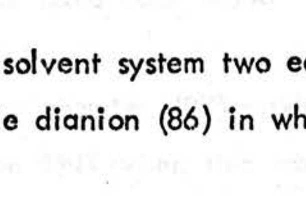


(83)

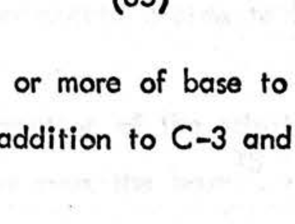
1.3.3 2,4,6-Trinitrotoluene(TNT)

(A) Alkoxides and Hydroxide

The technique of flow PMR has proven a powerful asset in the study of the reaction of 2,4,6-TNT with methoxide[17]. Rapid mixing of equimolar quantities in DMSO/methanol(7:1) initially produces a brown species identified as the C-3 addition complex (84), which is then relatively slowly replaced by a purple coloured material. This is the trinitrobenzyl anion (85) and it has even been isolated as the tetraphenylarsonium and potassium salts at low temperature under nitrogen. The PMR spectrum shows that slow decomposition reactions give a mixture of products.

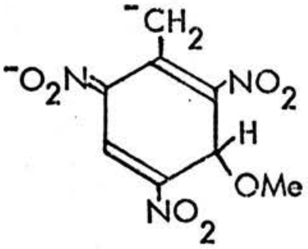


(84)



(85)

In the same solvent system two equivalents or more of base to one of TNT yield a stable dianion (86) in which both addition to C-3 and proton abstraction from the methyl group occur. The methylene proyons of the dianion are not equivalent pointing to appreciable C-C double bond character as in (69). As the methanol content is increased to 25 and 50% so a mixture of (84),(85) and (86) and then only (85) are respectively produced for the same flow rate.



(86)

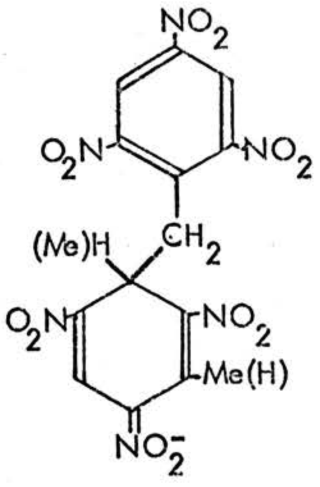
At DMSO/methanol ratios of less than 3:1 the spectra are time dependent indicating the order in which the species are formed as (84), (85) and (86). The visible absorbtions of the 3 species are given in Table 1.3.1.

Table 1.3.1 Visible absorbtion data for the products of reaction of 2,4,6-TNT with methoxide ion in DMSO/methanol solvent.

	λ_1(nm)	λ_2(nm)	$\varepsilon_1(M^{-1}cm^{-1})$	$\varepsilon_2(M^{-1}cm^{-1})$
(84)	433	505	18000	17000
(85)	520	640	17000	1
(86)	550	-	15000	-

Previous PMR studies have not been successful due to the production of free radicals. Indeed, using the flow system very large quantities of radicals were detected by EPR. Other investigations with various alkoxides and hydroxide have been made[18,122-6]. Bernasconi claims to have observed the formation

of a Janovsky complex (87) produced by reaction of the trinitrobenzyl anion (86) with free TNT when this was in excess over the base[18].

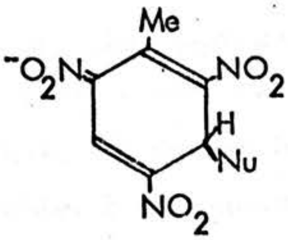


(87)

The visible spectrum had maxima at about 455nm and 530nm in methanol, ethanol or dioxane/water(1:1) solvent systems, typical of Janovsky complexes[60,127], but it is not possible to specify the position of attack which may be at C-1 or C-3.

(B) Other Bases

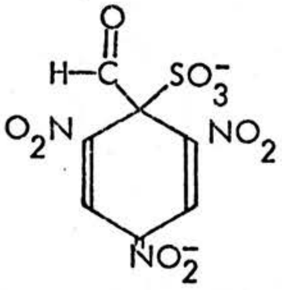
2,4,6-TNT adds cyanide[78] at C-3 (88;Nu=CN) whereas, in comparison, 2,4,6-trinitrobenzaldehyde adds at C-1[56,78]. Sulphite forms only the C-3 complex (88;Nu=SO_3^-) in 2,4,6-TNT[49,128], but with 2,4,6-trinitrobenzaldehyde in aqueous DMSO gives both C-1(89) and C-3(90) mono-adducts[129]. In water at high sulphite concentration the aldehyde yields two isomeric 2:1 sigma-complexes(91) and (92) one of which (91) appears to exist in the cis and trans forms[129]. The electron withdrawing effect of the aldehyde group would seem to tip the balance in favour of C-1 adducts.

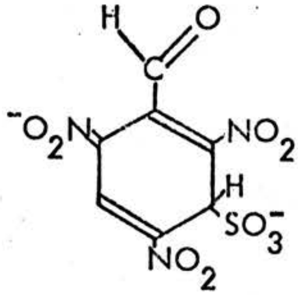


Nu
CN
SO_3^-

(88)

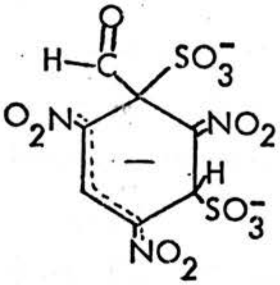
(89)

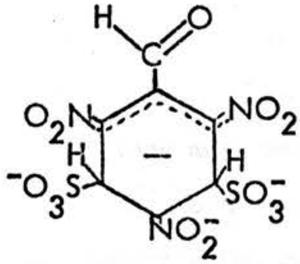




(90)

(91)





(92)

1.3.4 Polynitromethylnaphthalenes

Thompson noted the production of colour[130] on addition of sodium hydroxide to alcoholic and acetone solutions of 2,4-dinitro- or 2,4,5-trinitro-1-methylnaphthalene. Other than this no work appears to have been carried out, although 3 tetranitro isomers, of unspecified orientation, of 2-methylnaphthalene have been isolated[131].

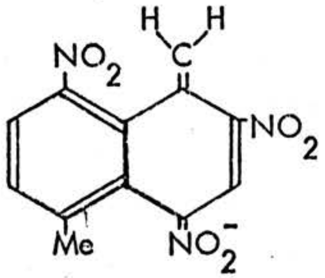
1.3.5 Polynitro-1,5-dimethylnaphthalenes

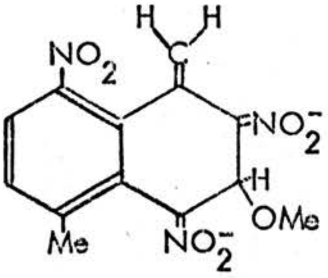
(A) 2,4,8-Trinitro-1,5-dimethylnaphthalene(93)

(a) Methoxide

One equivalent of sodium methoxide in methanol added to a DMSO solution of 2,4,8-trinitro-1,5-dimethylnaphthalene has been shown to produce a "benzyl-type" anion (94)[132]. The methylene protons in the PMR spectrum appear as widely separated singlets indicating the formation of an olefinic double bond. Unlike the trinitrobenzyl anion the coupling constant is negligible, but this has been observed in other compounds[133]. On addition of a further 2 equivalents of base a proton abstracted C-3 Meisenheimer complex is formed(95). Interestingly this does show coupling between the olefinic protons.

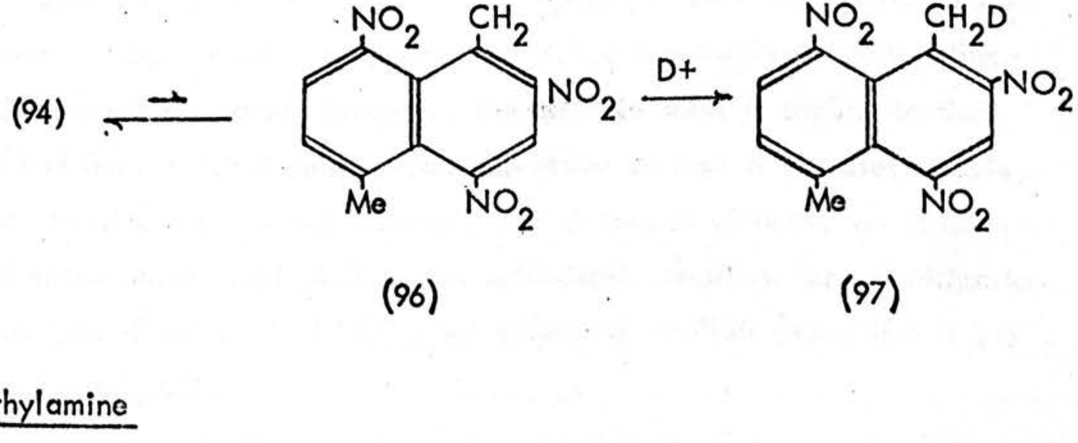
(94)





(95)

No evidence for rapid formation of a transient C-3 complex was obtained from this study. Confirmation of proton loss from the 1-methyl group comes from acidification by DCl of a solution containing (94) to yield a mono-deuterated 1-methyl nitroaromatic. Presumably D^+ ions may only be added via the non-conjugated methylene form (96), pointing to an equilibrium between (94) and (96) with almost 100% of the former being present.



(96) (97)

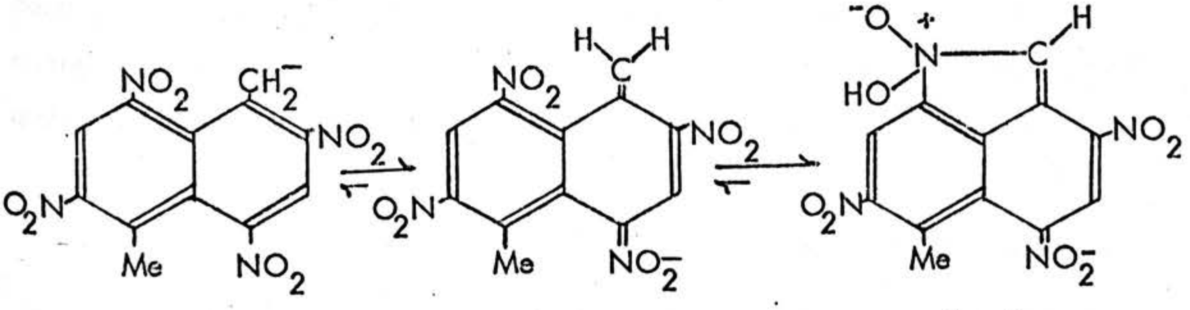
(b) Diethylamine

Addition of diethylamine even in excess to a DMSO solution of (93) produces only the benzyl-type anion (94), probably due to its lower basicity and steric hindrance to attack at C-3 by the adjacent nitro-groups.

(B) 2,4,6,8-Tetranitro-1,5-dimethylnaphthalene(98)

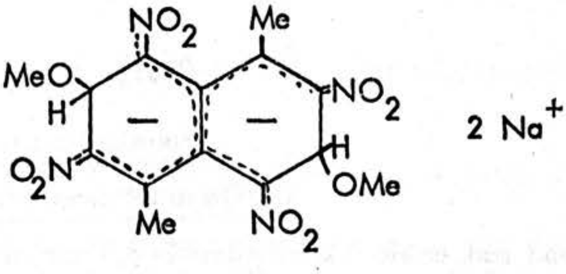
(a) Methoxide

Addition of 1 equivalent of methoxide ion to a DMSO solution of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene initially produces a "benzyl-type" anion(100)[132] by proton abstraction which then appears to undergo intramolecular reaction to form a bridged structure(101).



(99) (100) (101)

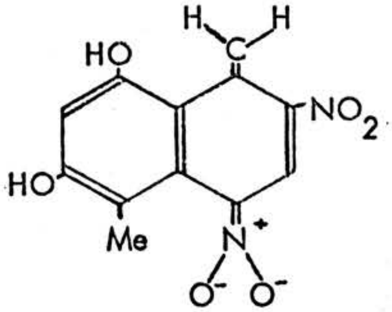
Again there was no evidence of a transient C-3 adduct prior to abstraction and addition of more base yields no new product. Acidification of a solution containing (101) gives the mono-deuteriated 1-Me form (102) of (98). Equilibrium between the three forms (99), (100) and (101), with the latter predominating, is indicated as fission of the bridge C-N bond would probably result in double deuteriation of the 1-Me group and mass spectral evidence does not support this[109]. On a preparative scale in tetrahydrofuran (THF) under nitrogen excess methoxide and 2,4,6,8-tetranitro-1,5-dimethylnaphthalene yield an orange complex. The isolated solid is similar to that obtained(61) from 3,5,6,8-tetranitroacenaphthene in that it is water soluble, hydrolyses to give the starting material, and detonates violently on touch. The PMR spectrometer used (R10) is not sufficiently sensitive for identification of the complex dissolved in DMSO, but elemental analysis shows that a 2:1 adduct is formed(103).



(103)

(b) Diethylamine and Triethylamine

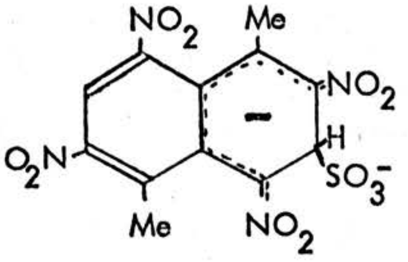
One equivalent of diethylamine or triethylamine added to a DMSO solution of (98) yields first the "benzyl-type" anion(100) which is then converted into (101), similar to the effect of methoxide. The rate of change was faster for diethylamine consistent with its higher basicity. Excess amine appears to produce a substitution product (104).



(104)

(c) Sulphite

Reaction of sulphite ion even in excess with (98) in aqueous DMSO produces the C-3 adduct (105) which is stable for a number of hours.



(105)

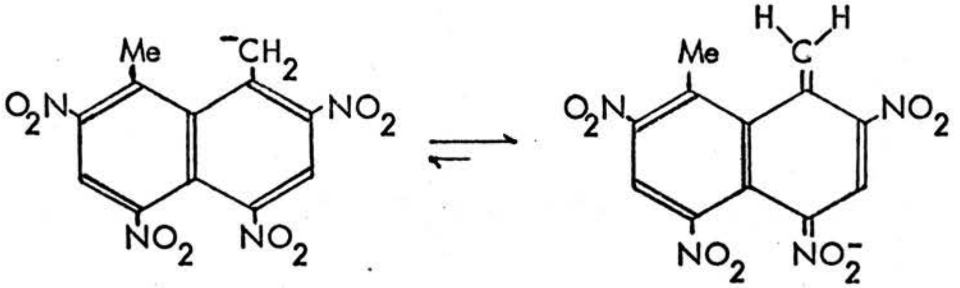
1.3.6 Polynitro-1,8-dimethylnaphthalenes

(A) 2,4,5-Trinitro-1,8-dimethylnaphthalene(106)

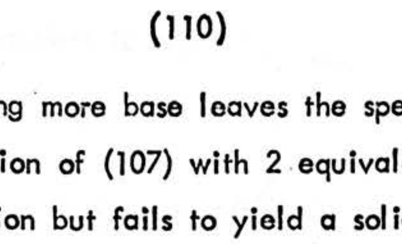
Although 2,4,5-trinitro-1,8-dimethylnaphthalene has been synthesised its reactions with base had not been studied until the present work(vide infra).

(B) 2,4,5,7-Tetranitro-1,8-dimethylnaphthalene(107)

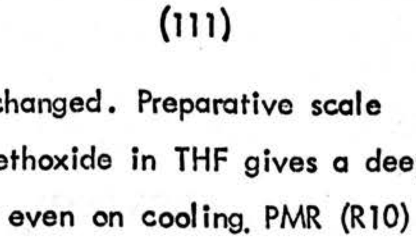
Reaction of 1 equivalent of sodium methoxide with 2,4,5,7-tetranitro-1,8-dimethylnaphthalene in DMSO forms a mixture of about 85% "benzyl-type" anion (109) and 15% addition compounds.[132] This "benzyl-type" anion exists almost entirely in the olefinic form and does not undergo any intramolecular rearrangements as the methylene is not peri to a nitro-group(cf. 98). The addition compounds appear only at low intensity in the PMR spectrum but it seems that both C-1 (110) and C-3 (111) adducts are present.



(108) (109)



(110)



(111)

Adding more base leaves the spectrum unchanged. Preparative scale reaction of (107) with 2 equivalents of methoxide in THF gives a deep-red solution but fails to yield a solid product even on cooling. PMR (R10) of the solution reveals little information.

1.4 Equilibrium and Kinetic Studies

1.4.1 Introduction

The series of successive equilibria for the interaction of a compound X with a base B to form addition complexes may be represented:-

$$X \quad + \quad B \quad \underset{k_r^1}{\overset{k_f^1}{\rightleftharpoons}} \quad XB \qquad\qquad K^1$$

$$XB \quad + \quad B \quad \underset{k_r^2}{\overset{k_f^2}{\rightleftharpoons}} \quad XB_2 \qquad\qquad K^2$$

$$XB_2 \quad + \quad B \quad \underset{k_r^3}{\overset{k_f^3}{\rightleftharpoons}} \quad XB_3 \qquad\qquad K^3$$

K^1 for reactive nitro-aromatics(e.g. TNA) in dilute solution of ionic base is simply given by $[XB]/[X][B]$. Less reactive compounds may require appreciable base concentration($>$0.1M) for significant conversion to complex or for the study of higher equilibria. Unfortunately in such solutions the basicity is not accurately described by the base concentration and acidity functions must be employed[74,134-6]. The J_- acidity function measures the ability of the medium to add base to a neutral molecule which for methoxide in methanol is given by J_{M-}:-

$$J_{M-} = p(K^1 . K_{MeOH}) + \log_{10}([XB]/[X])$$

where K^1 is the thermodynamic equilibrium constant for formation complex XB with methoxide and K_{MeOH} is the autoprotolysis constant of methanol($10^{-16.7}$).

The function is defined by studying successive overlapping equilibria with increasing pK. Addition of a second equivalent of base is covered by the J_{2-} function and for proton abstraction the first and second ionisations by H_- and H_{2-}.[74,134,137] The lack of a unique acidity function for a given base-solvent system does, however, limit the accuracy which can be obtained with this treatment.[138]

Visible spectroscopy frequently makes use of the Beer-Lambert relation for determining rate and equilibrium constants:-

$$\mathrm{OD} = \varepsilon_{XB}\,[XB]\,l$$

where OD is the optical density due to species XB, ε_{XB} is its extinction coefficient and l is the length of the absorbing path. Multiple equilibria can also be studied using this method as long as all the relevant extinction coefficients are known i.e. ε_{XB}, ε_{XB_2} .... Isobestic points are useful in such systems. For simple equilibria where the extinction coefficient is unknown the Benesi-Hildebrand method[139] may be employed to determine both ε and K. The form for Meisenheimer addition is given by:-

$$\frac{[X_0]\,l}{\mathrm{OD}} = \frac{1}{K\,\varepsilon\,[B_0]} + \frac{1}{\varepsilon}$$

A plot of $[X_0]$ l/OD against $1/[B_0]$ should be linear with intercept $1/\varepsilon$ and slope $1/K\varepsilon$. However, care must be taken as linearity does not imply that only one species is present[140]. A recent graphical method using matrix theory is suitable for determining the number(and change in number) of species in solution from spectophotometric data[141]. The method of Job[142] has long been used in ascertaining the stoichiometry of a complex by variation of the base concentration whilst keeping the sum of base and nitro-compound concentrations constant. Equilibrium constants are also given by the ratio of k_f to k_r so this value may be compared with those obtained from the spectrophotometric approach. When excess of one reactant(usually base) is used pseudo first order kinetics are observed for simple addition such that the observed rate constant, k_ψ is given by $k_f [B] + k_r$. A plot of k_ψ against $[B]$ gives a slope of k_f and intercept of k_r. Flow-NMR has very recently been used for kinetic and equilibrium studies[95], but as the reactant concentrations are high(typically 0.5M) the solutions are non-ideal making it difficult to obtain truly thermodynamic parameters. Indeed one must be very wary in comparing results from NMR and spectrophotometry due to the 10^4 factor change in concentration as there is the possibility that different processes are being observed.

1.4.2 Base addition

(A) Methoxide

(a) General Stability

A large reduction in stability is evident when an ortho-nitro group is removed from the mono-adduct of 1,3,5-TNB(5). The factor of approximately seven orders of magnitude leads to a free energy difference between the two complexes (5) and (31) of ~37kJ/mole assuming that the reactants are of similar free energy[4]. A similar change in stability occurs for the C-1 methoxy 2,4-di-(33) and 2,4,6-trinitro-anisole(19) complexes. Addition at a ring carbon carrying a methoxyl group rather than a hydrogen enhances the equilibrium constant by almost a factor of 10^3 for similarly activated substrates c.f. (19) and (21). This is interpreted as being due to reduction of steric compression between the adjacent methoxyl and nitro groups on complex formation[27]. The most effective stabilising influence in a sigma-complex is the existence of a nitro group para to the sp^3 ring carbon, with the free energy difference of the 2,6-DNA and 2,4,6-TNA C-1 adducts (34) and (19) estimated to be over 125kJ/mole.[4] Again, the three fold increase relative to an ortho nitro is ascribed to the coplanarity of the sterically unhindered para nitro group with the ring. Extending the aromatic system, as in the 2,4-dinitro-1-methoxynaphthalene complex[101](46;R=Me) enhances stability by about 31kJ/mole compared with (33), similar to the effect of an ortho nitro. Using the relation $\delta \Delta G = RT\ln(K_1/K_2)$ the approximate stabilising effect of substituents may be compared:-[150]

Table 1.4.1 Rate and equilibrium constants for complex formation with sodium methoxide in methanol at 25°C

	K^1/M^{-1}		K^2/M^{-1}	K^3/M^{-1}	$k_f^1/M^{-1}s^{-1}$	k_r^1/s^{-1}	ref
	Addition at ring carbons						
	H	OMe					
1,3,5-TNB	15.4				-	-	27
	23.1				7050	305	143
		7700			4.0	5×10^{-4}	72
		17000			17.3	1.03×10^{-3}	144
2,4,6-TNA	2.71				950	350	145
			1.3×10^{-4}	10^{-5}			74
2,4,6-TNT						600-3000	18
N,N-Dimethylpicramide	7		1				113
Picramide	38						113
Picrate	3×10^{-4}		1.6×10^{-2}				74
1,3-DNB	5×10^{-7}						22
		3×10^{-4}	10^{-5}				74
		10^{-3}	3×10^{-5}				146
2,4-DNA		2.7×10^{-4a}			7.9×10^{-3}	28.7	147
		2.5×10^{-3b}			1.9×10^{-2}	7.63	147

Table 1.4.1(contd)

2,6-DNA		5×10^{-3}	10^{-4}[c]			146
3,5-DN-Cyanobenzene	1.9(C-2)					16
	5.7(C-2)[d]					16
	31.3(C-4)[e]			0.712	0.023	95
2,4-DN-6-Cyanoanisole		2600		18.8	7.2×10^{-3}	144
2,6-DN-4-Cyanoanisole		280		6.1	0.222	144
2-Nitro-4,6-Dicyanoanisole		10		2.0	0.198	148
4-Nitro-2,6-Dicyanoanisole		34		12	0.373	148
2,4,6-Tricyanoanisole		0.4		-	-	149
2,4-DN-1-MEON		230		0.9	3.95×10^{-3}	101
1-(β-Hydroxyethoxy)-2,4-DNN		356(spiro complex)		1.28	3.6×10^{-3}	92
2,4,5-TN-1-MEON		29300		32.8	1.12×10^{-3}	106
2,4,7-TN-1-MEON		109000		62.0	0.570×10^{-3}	107
1,3-DNN	0.09			11.2	124	26
1,5-DNN	2.8			-	-	26
1,3,8-TNN	13.8			304	22	26
1,4,5-TNN	1.5			-	-	26

Table 1.4.1(contd)

1,3,5,8-TETNN	428	7900	18	26
1,3,6,8-TETNN	7700	23000	3	100
1,4,5,8-TETNN	182	1820	10	26

where DNN = Dinitronaphthalene
TNN = Trinitronaphthalene
TETNN = Tetranitronaphthalene
MEON = Methoxynaphthalene

a 0.2M $[MeO^-]$. b 1.0M $[MeO^-]$. c Determined using an acidity function.

d In DMSO/MeOH(9:1) $[X] = 1.66 \times 10^{-4}$M. e In DMSO/MeOH(7:1) $[X] = 0.5$M using Flow PMR.

Table 1.4.2 Free energies associated with various substituents of addition complexes

Complex		$-\delta\Delta G$	Position of MeO$^-$ add^n	Structural
1	2	(kJmol^{-1})	in complex 2	difference
(a) 1,3,5-TNB	2,4,6-TNA	15.5-16.3	C-1	C-1 methoxy (hindered by 2,6-NO_2's)
(b) 1,3-DNN	2,4-DN-1-MEON	19.2	α -methoxy	α -methoxy (adjacent to 2-NO_2 only)
(c) 1,3,8-TNN	2,4,5-TN-1-MEON	18.8	α -methoxy	α -methoxy (adjacent to 2-NO_2 only)
(d) 2,4-DN-1-MEON	" "	12.1	α -methoxy	5-NO_2(hindered)
(e) " "	2,4,7-TN-1-MEON	15.0	α -methoxy	7-NO_2(unhindered)
(f) 1,4,5-TNN	1,4,5,8-TETNN	11.7	β	8-NO_2(hindered)
(g) 1,3-DNN	1,3,8-TNN	12.5	α	8-NO_2(hindered)
(h) 1,3,8-TNN	1,3,6,8-TETNN	15.5	α	6-NO_2(unhindered)
(i) 1,4,5-TNN	1,3,5,8-TETNN	13.8	β	7-NO_2(unhindered)

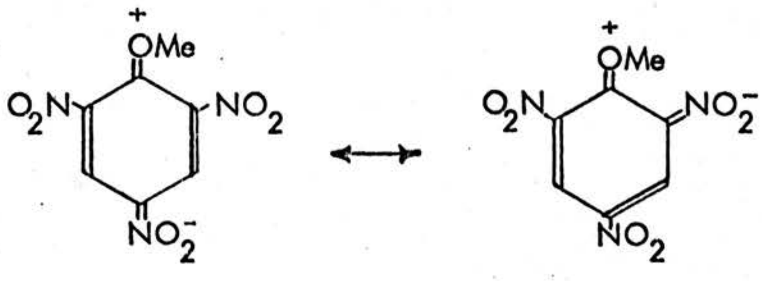
where DNN = Dinitronaphthalene
TNN = Trinitronaphthalene
TETNN = Tetranitronaphthalene
MEON = Methoxynaphthalene

Considering the approximate assumption that the nitroaromatic pairs have similar free energies these results are remarkably consistent and may be explained by steric and electronic factors. Addition at a methoxy substituted carbon is subject to more steric hindrance in (a) than (b) or (c). A nitro group on the ring not containing the sp^3 carbon has less influence than one that is. Peri nitro groups are mutually hindered and twist out of the ring plane so reducing the mesomeric electron withdrawl (d), (f) and (g). Fendler has calculated the stabilising power of various substituents from a comprehensive range of complexes[151] and considers 87.8kJ/mole to be more appropriate for a para nitro group. The decrease in equilibrium constant on replacement of nitro by less electronegative cyano groups in TNA[144,148,149] leads to a $\delta\Delta G$ of -35.1 and -77.3 kJ/mole for 2- and 4-cyano substituents respectively.

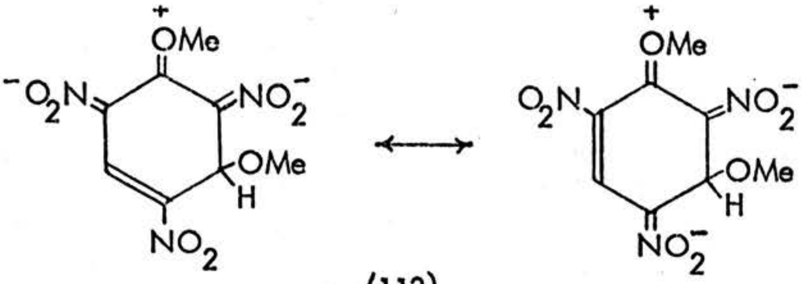
(b) Isomeric Addition

(i) 2,4,6-TNA

The rate of methoxide attack in methanol at a ring carbon attached to a proton is over fifty times faster than at C-1 in 2,4,6-TNA. The equilibrium constants for the C-1 and C-3 adducts are ~17,000 and $2.7 dm^3 mole^{-1} s^{-1}$ indicating a great difference in the corresponding rates of decomposition i.e. 10^{-3} and $350 sec^{-1}$. The faster rate of C-3 adduct (21) formation has been attributed to resonance stabilisation involving the methoxy group in 2,4,6-TNA (112), in (113) and hence also in the transition state leading to (113), whereas such resonance stabilisation is not possible in the C-1 adduct(19).



(112)



(113)

In forming (19) from 2,4,6-TNA the resonance energy of TNA which is lost in (112) has to be overcome and this reduces the rate.

The following relationship links the rate constant, k(for formation or decomposition) and corresponding thermodynamic parameters ΔS_f^* or ΔS_r^* and ΔH_f^* or ΔH_r^* which are the entropy and enthalpy of activation of the forward and reverse reactions respectively:-

$$k = k_B T/h \exp(\Delta S^*/R - \Delta H^*/RT)$$

where k_B = Boltzmann constant, h = Planck constant, R = Gas constant and T = Absolute temperature. The expression may be rewritten as the familiar Arrhenius equation $k = A\exp(-E/RT)$ where A is a constant and $E = \Delta H^* + RT$ for solution reactions where E is the energy of activation.

The higher stability of the C-1 adduct(19) is due to the small value of k_r which arises from the much higher ΔH_r^* for (19) compared with (21)[145].

Table 1.4.3 Kinetic and thermodynamic parameters for reaction of TNA with methoxide ion in methanol at 25°C

Addition at:-	C-3(21) ref 145	C-1(19) ref 144	
$k_f(M^{-1}s^{-1})$	950	17.3	
$k_r(s^{-1})$	350	1.03×10^{-3}	
$K(M^{-1})$	2.71	17000	
$\Delta H_f^*(kJmol^{-1})$	43.5 ± 4.2	53.9 ± 4.2	
$\Delta S_f^*(Jmol^{-1}K^{-1})$	-45.2 ± 14.2	-39.3 ± 14.2	
$\Delta H_r^*(kJmol^{-1})$	34.3 ± 2.1	76.9 ± 4.2	78.6^a ref 152
$\Delta S_r^*(Jmol^{-1}K^{-1})$	-80.8 ± 7.1	-20.1 ± 14.2	
$\Delta H(kJmol^{-1})$	9.2 ± 6.3	-23.0 ± 8.4	-20.3 ± 1.30 ref 153
$\Delta S(Jmol^{-1}K^{-1}$	35.6 ± 21.3	-19.3 ± 16.7	

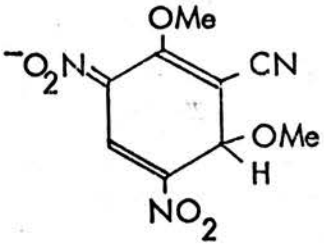
a C-1 OMe ^{14}C exchange

k_r for any complex may be determined directly by decomposition of the solid in solution, assuming a solid can be isolated. The overall enthalpy change, ΔH can be measured calorimetrically or calculated from $\Delta H_f^* - \Delta H_r^*$. Indeed, formation of transient species like (21) has been detected by calorimetric methods[154] and ΔH estimated. The total entropy change ΔS is similarly given by $\Delta S_f^* - \Delta S_r^*$.

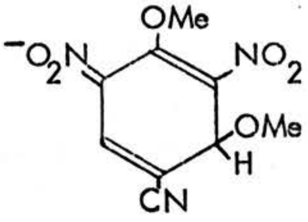
The semi-empirical method used by Miller[155-8] to calculate the relative energies of reactants, activated complex and σ-complex yields results which are in reasonable agreement with experimental data. Certainly, this produces better correspondence than Huckel Molecular Orbital (HMO) calculations which give rather disparate activation energies of formation[159]. More detailed HMO treatments[67] and Pople-Pariser-Parr SCF calculations[68] provide a more complete description of electronic structure.

(ii) Cyanodinitro- and dicyanonitro-anisoles

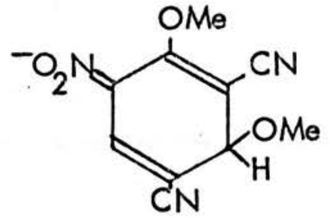
Transient 1,3-dimethoxy complexes are formed on reaction of methoxide with cyanodinitro-[144,154] and dicyanonitro-anisoles[148,154] except in the case of 2,6-dicyano-4-nitroanisole which does not possess a nitro group para to a suitable ring carbon.



(114)



(115)



(116)

The subsequently produced 1,1-dimethoxy complexes decrease in stability as the number of cyano groups increases with the tricyano-adduct being over 10^4 x less stable than (19)[149]. Terrier reports the detection by PMR of the transient 1,5-dimethoxy complex for 2-cyano-4,6-DNA in DMSO solution[160]. A kinetic study[161] of the reaction of methoxide with 2-chloro-4,6-DNA reveals all three isomeric complexes as the DMSO content of the solvent is varied.

(iii) 2,4,6-Trinitrotoluene

C-3 addition of methoxide with TNT at 25°C is so rapid, even in methanol, that it is not possible to obtain accurate kinetic data for this reaction[18].

(iv) Polynitronaphthalenes

No evidence for isomeric addition in polynitronaphthalenes has been obtained[26].

(v) 2,4-Dinitro-1-methoxynaphthalene

Terrier has employed the stopped-flow technique to study the interaction of methoxide with 2,4-dinitro-1-methoxynaphthalene in DMSO/methanol[102]. In pure methanol only 1 process is apparent, namely addition at C-1, but as the DMSO content is increased a fast step emerges due to addition at C-3.

Table 1.4.4 Interaction of methoxide with 2,4-dinitro-1-methoxynaphthalene in DMSO/methanol at 20°C.(ref 102)

	1,1-complex			1,3-complex		
% DMSO by weight	k_f $M^{-1}s^{-1}$	k_r s^{-1}	K M^{-1}	k_f $M^{-1}s^{-1}$	k_r s^{-1}	K M^{-1}
0	0.745	2.4×10^{-3}	310	-	-	-
37	4.9	8×10^{-4}	6150	-	-	-
76	178	-	-	370	65	5.7
92.6	2100	-	-	7800	8.5	916

The difference in stability of the 2 adducts is due mainly to the rates of decomposition, once again explained by lack of a nitro group para to the sp^3 carbon for the 1,3-complex.

(c) Higher Equilibria

At very high methoxide concentration in methanol using acidity functions the approximate equilibrium constants for formation of the 1,1,3-trimethoxy-diadduct and 1,1,3,5-tetramethoxy-triadduct, K^2 and K^3 of TNA have been determined as 1.3×10^{-4} and 10^{-5} dm^{3}mole^{-1} respectively[74].

(d) Solvent Effects

Stabilities of 1:1 sigma-complexes are considerably enhanced by the addition of dipolar aprotic solvents (e.g. DMSO) to protic solvents such as methanol. An example is the C-1 adduct of tricyanoanisole where an increase in k_f and decrease in k_r are observed[149], such that K^1(DMSO/MeOH(3:1)) = 20,000 K^1(MeOH). The equilibrium constants are related using the relative activity coefficients $^{MeOH}f_i^{DMSO}$ for transfer of the species involved[162]. For the reaction of TNA with methoxide ion to give the addition product $(TNA.OMe)^-$ (19) :-

$$K^1(DMSO) = K^1(MeOH)\ {}^{MeOH}f^{DMSO}_{OMe^-}\ {}^{MeOH}f^{DMSO}_{TNA} \Big/ {}^{MeOH}f^{DMSO}_{(TNA.OMe)^-}$$

A study of this reaction as the DMSO content is increased has yielded the relative activity coefficients[162]. The values for TNA and its adduct are expected to be similar[3] as they are both large polarizable species which will be better solvated in aprotic rather than protic solvents[163] and this is indeed observed. Methoxide being a small anion with high charge density forms strong hydrogen bonds in protic solvents but is unable to do so in aprotic ones. The increase in stability with DMSO content is therefore due mainly to the large increase in $^{MeOH}f^{DMSO}_{MeO^-}$. Interestingly, the activity coefficient of the transition state changes little with solvent composition. Fendler considers that in view of the complex nature of solvent effects no physical significance should be attached to the frequently observed linear relationships between rates and solvent composition, although he has noted that the relative free energies of stabilization ($\delta G = \Delta G^{DMSO} - \Delta G^{MeOH}$) by DMSO are independent of substrate.[151]

(e) Salt Effects

Even though the C-4 adduct of 3,5-dinitrobenzonitrile (37) is the thermodynamically less stable form the equilibrium constant determined by flow PMR[95] is over 5 times that for the C-2 complex measured spectrophotometrically[16]. This apparent anomaly is explained by the large difference in ionic stregth for each case. Indeed, both ionic strength and ion pairing have to be considered. A linear dependence on the ionic strength μ has been predicted[147] for ln k_f and ln k_r using the extended Debye-Huckel equation to express the activity coefficients of charged reactants and transition states and the equation of Debye and McAulay for neutral reactants.

$$\ln k_f = \ln k_f^o + b_f \mu$$

$$\ln k_r = \ln k_r^o + b_r \mu$$

The ionic strength, μ , is equal to the sodium methoxide concentration in very dilute solutions but is less than this concentration in more concentrated solutions due to ion pairing. Data for 2,4-DNA[147] show that k_r decreases with ionic strength hence $b_r < 0$. The salt effect on k_f, and thus on K, although less marked, is an even more complex function of methoxide concentration because the ion pairing not only influences the ionic strength but also reduces the nucleophilic reactivity of methoxide ions paired with cations. From the increase in k_f with $[\mathrm{NaOMe}]$ b_f is found to be positive.

(f) Cation-complex Interaction

Cation-complex association appears to increase with decrease of cationic charge density as demonstrated by the difference in stabilising effect of potassium, sodium and lithium methoxides in dilute solution[164,165]. Recent work with crown ethers in methanol which reduces the concentration of free cation show that variation of equilibrium constant is much reduced.[166] Stabilisation by small concentrations of alkaline earth cations has also been observed.[167]

(B) Other Alkoxides and Hydroxide

(a) 1,3,5-TNB

Several kinetic and equilibrium studies of the reaction of TNB with hydroxide and alkoxide ions in a variety of solvents have now been made[34,143,168-172] Perhaps the most illustrative is that of the interaction of TNB with lyate ions of water, methanol, ethanol, n- and i-propanol, and n-,i-, and t-butanol. The ratios of rate and equilibrium constants relative to the 1:1 hydroxide adduct are as follows:-

Table 1.4.5 Kinetic data for the reaction of 1,3,5-TNB with hydroxide ion in water and several alkoxide ions in the corresponding alcoholic solvents

	HO^-	MeO^{-a}	EtO^-	$n\text{-}PrO^-$	$n\text{-}BuO^-$	$i\text{-}BuO^-$	$i\text{-}PrO^-$	$t\text{-}BuO^-$
$k_f(M^{-1}s^{-1})$	1	304	1900	3660	3740	4960	3820	1500
$k_r(s^{-1})$	1	26.6	1.15	0.89	0.39	0.12	0.12	0.07
$K^1(M^{-1})$	1	9	1100	3900	7900	24400	113000	-

a See Table 1.4.1 for absolute values

The trend in k_f is understandable in terms of decreasing solvation of the lyate ion as the series is ascended. The lower values for $i\text{-}PrO^-$ and $t\text{-}BuO^-$ are due to steric effects and the decreased alkoxide solvation contributing to a more negative ΔS_f^* in these systems. The variation in k_r is less pronounced and the lower than expected value for TNB-OH^- has been attributed to intramolecular hydrogen bonding to an ortho-nitro group in the complex[143]. Both solvent and base effects, therefore, determine the stability of the complexes with basicity of the alkoxide solutions increasing from methanol to t-butanol[173]. Ion pairing effects are apparently not observed for these reactions.

(b) 2,4,6-TNT

The rapid reaction of alkoxide with TNT is difficult to study accurately[18,122,124-6] due to simultaneous proton abstraction, but the results that are available may be compared with those for 1:1 TNB and Janovsky complex formation[18](87).

Table 1.4.6 Rate and equilibrium constants for the reaction of 1,3,5-TNB and 2,4,6-TNA with alkoxides in alcohols

	EtO^- TNB add^n (ref 143)	C-3 Addition EtO^{-a} (ref 18)	 i-PrO^{-b} (ref 125)	 t-BuO^{-c} (ref 126)	JC formation in $EtOH^a$ (ref 18)
$k_f(M^{-1}s^{-1})$	33400	1500 - 3000	1580 ± 70	1400	700 ± 35
$k_r(s^{-1})$	27.5	80 - 200	3.64	1	34.5 ± 2.5
$K^1(M^{-1})$	1210	7.5 - 37.5	440 ± 40	1400	20.3 ± 2.2

a at 25°C b at 25.4°C c at 30°C using TNT-d_3

It can be seen that $k_f^{TNT} < k_f^{TNB}$, $k_r^{TNT} > k_r^{TNB}$ and $K^{1TNT} << K^{1TNB}$ for the ethoxide complexes which is consistent with the electron releasing and steric effects of the methyl group in TNT. Increasing stability of C-3 TNT alkoxide adduct appears to depend solely on reductions in k_r.

(c) Polynitronaphthalenes

It must be admitted that, contrary to the case for TNB, equilibrium constants for the formation of hydroxy σ-complexes are factors of 1.5 to 4 greater than those for 1-methoxy-cyclohexadienates in water and methanol respectively and this behaviour is also observed in polynitronaphthalene complexes[26]. The stability differences are a consequence of the slower rate of decomposition of the hydroxy than methoxy adducts.

(C) Sulphite

The kinetic and equilibrium data for the reaction of sulphite ion with several substituted TNB's in water to form 1:1 and 2:1 adducts are shown in Table 1.4.7.

Table 1.4.7 Rate and equilibrium constants for the reaction of sulphite ion with some nitroaromatics in aqueous solution

	k_f^1 $M^{-1}s^{-1}$	k_r^1 s^{-1}	K^1 M^{-1}	k_f^{2a} $M^{-1}s^{-1}$	k_r^{2a} s^{-1}	K^{2a} M^{-1}	ref
1,3,5-TNB[b]	3.5×10^4	125	290	1.2 195	0.13 21	9.2 9.3	174
2,4,6-TNA	4.8×10^3	35	140	170	0.12	1.4×10^3	121
Picrate ion	280[c]	110[c]	2.5[c]	250[d]	4[d]	60[d]	121
Picramide	5.7×10^4	7	8.6×10^3	140	7	20	175 & 121
N-Methylpicramide	1.4×10^4	0.2	6.8×10^4	330	0.16	2×10^3	175 & 121
N,N-Dimethylpicramide	4.1×10^3	0.14	3×10^4	310	0.006	5×10^4	175 & 121
2,4,6-Trinitrobenzaldehyde[e]	9×10^4 + faster add^n	- -	1.84×10^4 -	-	-	31.7	129

a Ionic strength(μ) 0.3M except where indicated. b Both cis and trans isomers formed. c $\mu = 0.3$M, k_f and K at zero ionic strength will be lower than values given. d $\mu = 2.1$M. e $\mu = 0.14$M. 2 isomeric 1:1 adducts formed.

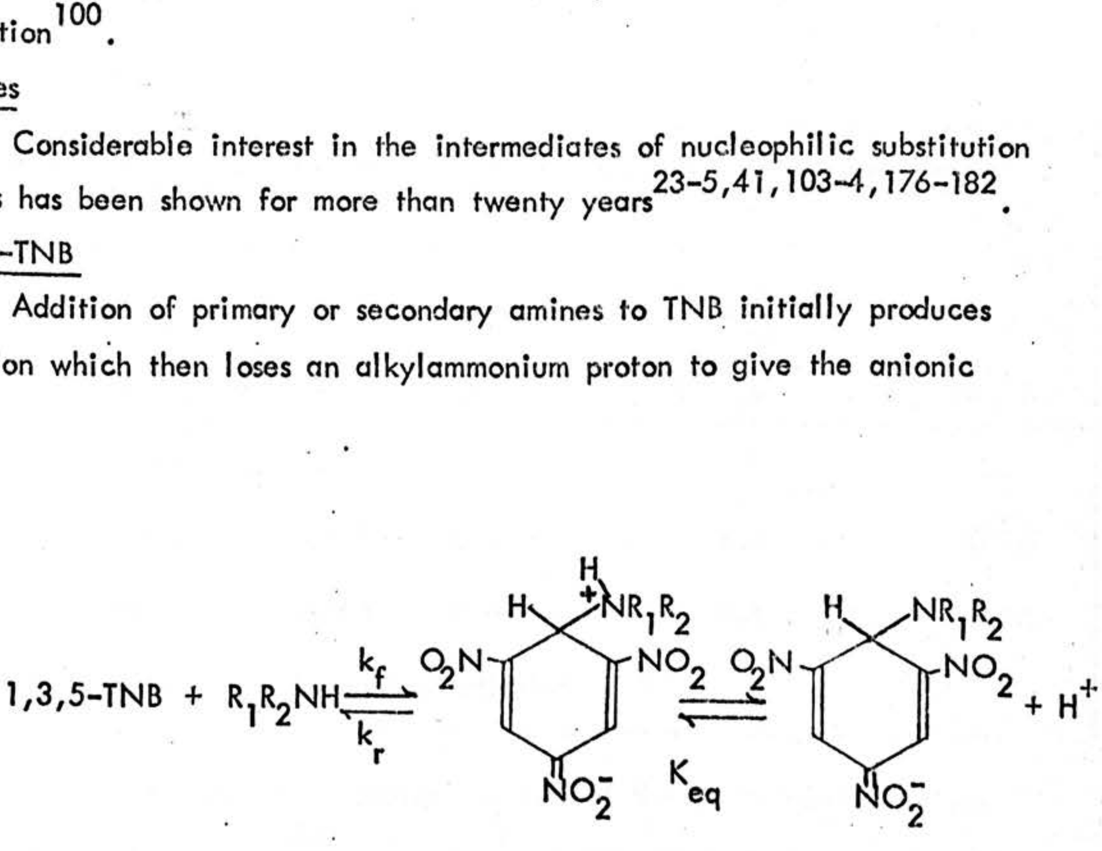
As 2:1 adducts contain more localised negative charge than 1:1 complexes they are formed most easily in protic solvents. Higher equilibria require large base concentrations for their study and are strongly dependent on ionic strength. Besides the effect of solvation and hydrogen bonding in the picramides stability seems to be determined by relief in steric strain on complex formation for substrates with bulky C-1 substituents. This would be particularly operative in the 2:1 adducts where ring planarity is not required. Except for picrate ion changes in the value of K^1 with substituent derive mainly from change in k_r^1; k_r^2 however varies to a greater extent than k_f^2. The reaction of 2,4,6-trinitrobenzaldehyde with sulphite is likened to that of TNA with methoxide where formation of the C-3 adduct is more rapid than the C-1 form. The C-4 mono-adduct of 1,3,6,8-tetranitronaphthalene is formed very rapidly in aqueous solution with K^1 approximately 2.5×10^{-4} mole dm^{-3} and it appears that a diadduct(117) may be formed at high base concentration[100].

(D) Amines

Considerable interest in the intermediates of nucleophilic substitution by amines has been shown for more than twenty years[23-5,41,103-4,176-182].

(a) 1,3,5-TNB

Addition of primary or secondary amines to TNB initially produces a zwitterion which then loses an alkylammonium proton to give the anionic complex.



(118)

A temperature jump study in 90% aqueous dioxane measures a relaxation time[183], τ, using excess amine:-

$$\frac{1}{\tau} = k_f\left[R_1R_2NH\right] + k_r\frac{\left[H^+\right]}{\left[H^+\right] + K_{eq}}$$

Plotting $1/\tau$ against $[R_1R_2NH]$ gives straight lines with slopes, k_f and intercepts dependent on $[H^+]$ such that:-

$$\frac{1}{\text{intercept}} = \frac{1}{k_r} + \frac{K_{eq}}{k_r\,[H^+]}$$

Plotting reciprocal intercepts against $1/[H^+]$ gives new intercepts equal to $1/k_r$ and slope K_{eq}/k_r. The results for pyrrolidine, piperidine and n-butylamine are shown in Table 1.4.8.

Table 1.4.8 Rate and equilibrium constants for the reaction of some amines with 1,3,5-TNB in aqueous dioxane(9:1)

	k_f $M^{-1}s^{-1}$	k_r s^{-1}	k_f/k_r M^{-1}	K_{eq} $10^{11}\,M^{-1}$	K^a_{diss} $(R_1R_2NH_2^+)$ $10^{11}\,M^{-1}$
n-Butylamine	123	20000	0.006	52.8	2.1
Piperidine	3000	14900	0.2	1.5	0.76
Pyrrolidine	8100	25000	0.3	2.1	0.50

a Measured in aqueous solution

The rates of nucleophilic attack, k_f reflect the established reactivity pattern of these three amines[23] whilst the k_r values are similar to each other. The equilibrium process K_{eq} is a fast proton transfer reaction with the participation of solvent and all acids and bases present and is even too fast for the temperature-jump technique. The zwitterion n-butylammonium complex ($118; R_1 = \text{n-Bu}, R_2 = H$) is some 25 times more acidic than the free butylammonium ion(K_{eq}/K_{diss}) and has been attributed to the inductive effect of C-1, which may be electron deficient[67], compensated to some extent by intramolecular hydrogen bonding with the ortho-nitro groups, which weakens acid strength[184].

(b) 2,4-Dinitro-1-naphthylether with n- and t-butylamine in DMSO solution has been shown to form an anionic complex by a mechanism[103] similar to that for 1,3,5-TNB, followed by base catalysed loss of ethoxide ion to yield the substitution product.

(E) Other Bases

Many bases other than those mentioned above have been used in kinetic studies with polynitroaromatic compounds, perhaps the most notable being cyanide[55,185-7] and thiolate ions[53-4,188-9]. The equilibrium constants for 1:1 1,3,5-TNB complexes have been used as a measure of carbon basicity, which is the thermodynamic affinity of the base for an aromatic carbon atom[190], and differs from the Bronsted basicity or affinity for hydrogen. The relative carbon and Bronsted basicities in methanol for some sulphur and oxygen bases are $EtS^- > MeO^- > PhS^- > PhO^-$ and $MeO^- > EtS^- > PhO^- > PhS^-$ respectively, however the order may vary in different solvents. One interesting recent study[191] has reported the formation of Meisenheimer complexes from 1,3,5-TNB and very weak bases (e.g. F^-, NO_2, HCO_3^-) in benzene, a non-polar solvent. The presence of a crown-ether to solvate the counter-ion is required and only potassium cations seem to be easily solvated.

(F) Spiro-complexes

Spiro-Meisenheimer complexes[81-3,92,105,192-9] provide a means of studying the intermediates of nucleophilic aromatic substitution without the effect of a leaving group to complicate the kinetics. Cyclic complexes tend to be more stable[92] than their acyclic analogues. The fastest rate of nucleophilic attack on an aromatic carbon is observed in catechol-2,4,6-trinitrophenyl ether($k_f = 1.2 \times 10^9 s^{-1}$) where, unusually, proton transfer is rate limiting in the formation of the spiro σ-complex[192].

1.4.3 Proton Abstraction

The most studied proton abstraction process involves the reaction of alkoxides with 2,4,6-TNT[18,122-6].

See table 1.4.9

It has been noted that the rate coefficients for deprotonation of nitromethane by methoxide in methanol and ethoxide in ethanol are practically the same for deprotonation of TNT[124]. The very low rates indicate that the proton

Table 1.4.9 Kinetic and thermodynamic parameters for the reaction of 2,4,6-TNT and 2,4,6-TNT-d_3 with hydroxide ion in water and alkoxide ions in the corresponding alcohols[a]

	$^-$OH in 1:1 dioxane/water	MeO$^-$ in MeOH	EtO$^-$ in EtOH		n-PrO$^-$ in n-PrOH	n-BuO$^-$ in n-BuOH	i-PrO$^-$ in i-PrOH		t-BuO$^-$ in t-BuOH	
Substrate	TNT	TNT	TNT	TNT-d_3	TNT	TNT	TNT	TNT-d_3	TNT	TNT-d_3
$k_f/M^{-1}s^{-1}$	2.42	13.3	82;138 ±4 ±3	39.1 ±0.8	-	-	7140^b	850^b ±100	6000^b ±400	750^b
k_r/s^{-1}	7.5×10^{-3}	1.07	0.045;0.08 ±0.005 ±0.02	0.02 ±0.005	-	-	-	-	-	-
K/M^{-1}	323	12.4	1820;1700 ±270 ±500	2000 ±500	6500 ±500	12300 ±1000	2.4×10^5 $\pm4\times10^4$	-	$>5\times10^{4\,b}$ $<10^6$	-
ref	18	18	18 124	124	126	126	125 & 126		126	
$\Delta H_f^*/kJmol^{-1}$	-	-	54.5^c - ±0.33	-	-	-	-	62.3 ±4.6	17.6 ±1.3	-
$\Delta S_f^*/Jmol^{-1}K^{-1}$	-	-	23.2^c ±0.84	-	-	-	-	21.3 ±12.1	-113 ±8.4	-
ref			122					125	126	

a at 25°C unless indicated. b at 30°C. c at 19.1°C.

transfer is accompanied by a significant electronic rearrangement and that the charge in TNT$^-$ (85) is strongly delocalised. A kinetic isotope effect is observed on changing substrate from TNT to TNT-d_3 ($k^{TNT} / k^{TNT\text{-}d_3} \sim 8$ for EtO$^-$, i-PrO$^-$ and t-BuO$^-$). The interaction of sodium isopropoxide with TNT-d_3 has shown that the free alkoxide ion rather than ion pair is the more reactive species in deuteron transfer[125]. However, the converse is apparently true for proton abstraction involving sodium or potassium t-butoxide and TNT as evidenced by the thermodynamic parameters for this reaction[126]. The value of ΔH_f^* is reduced as the major barrier to reaction of alkoxide ion is desolvation of the ion and here abstraction requires less energy due to the base existing mainly as ion aggregates. The large negative activation entropy is also in agreement with this postulate.

1.4.4 Higher Adducts

Little kinetic work on the formation of sigma-complexes from proton abstracted substrates has been performed, although the higher equilibria of various picramides have been studied employing acidity functions[74].

CHAPTER TWO

SPECTROSCOPIC STUDIES OF THE REACTION OF BASE WITH POLYNITRODIMETHYLNAPHTHALENES

2.1 Introduction

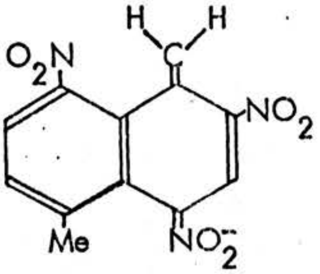
The reactions of several polynitrodimethylnaphthalenes with base have been studied using PMR and UV/visible absorbtion spectrophotometry and the results are given below.

2.2 Polynitro-1,5-dimethylnaphthalenes

2.2.1 2,4,8-Trinitro-1,5-dimethylnaphthalene(93)

(A) Deuterioxide and hydroxide

The reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with deuterioxide ion was performed by dissolving the nitroaromatic in d_6-DMSO and adding the calculated equivalent of sodium deuterioxide in D_2O. This provided a deuterated system which allowed the reaction to be followed by PMR spectroscopy. The spectrum of a reaction mixture is shown in fig.2.2.1(b). Comparison of this spectrum with that of compound (93)(resonances denoted by letter a) shows a product is formed which gives rise to a singlet and AB quartet in the aromatic region; 2 singlets in the mid-field region and 1 methyl resonance. The new lines may be assigned to the 'benzyl-type' anion (94)[132] (resonances denoted by letter b). Addition of more base gradually converts all unreacted compound (93) to (94), but no other products are observed.



(94)

The visible absorbtion spectrum resulting from the addition of up to one equivalent of hydroxide ion to a DMSO solution of compound (93) shows a major peak at 560nm with another at about 400nm, overlapped by a peak due to unreacted nitroaromatic which has an absorbtion maximum at 350nm

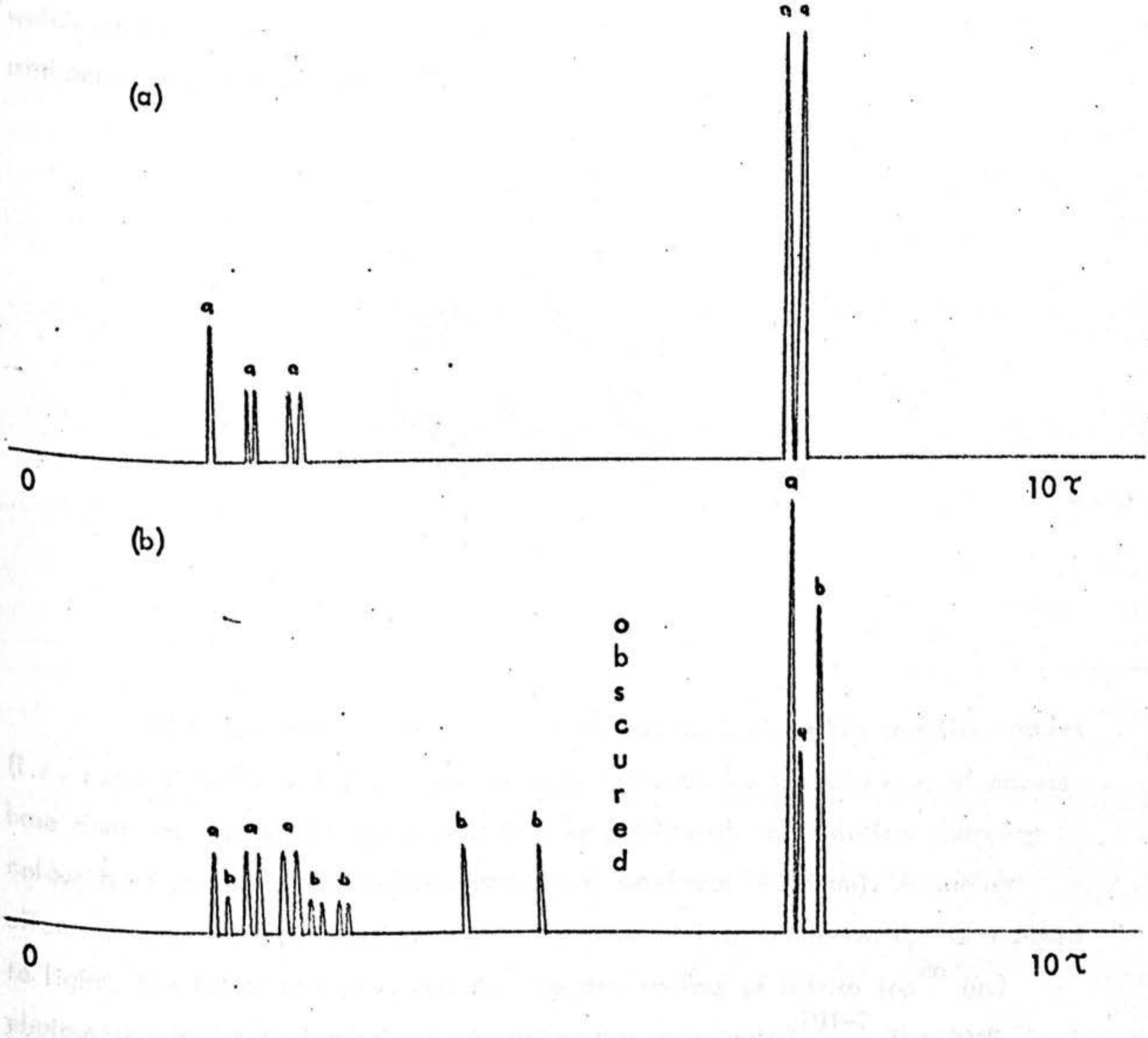
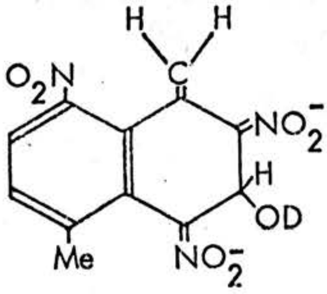


Fig.2.2.1 (a) PMR spectrum of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) in DMSO-d_6. (b) Spectrum after the addition of one equivalent of sodium deuterioxide.

(fig.2.2.2(a)). By analogy with the PMR spectrum, the visible spectrum is assumed to be due to compound (94). The visible absorbtion spectrum resulting from the addition of 10 equivalents of hydroxide ion to a DMSO solution of compound (93) is shown in fig.2.2.2(b) and displays a major peak at 560nm. The absorbtion maximum at 400nm is diminished compared to the spectrum obtained for the product of the reaction of 1 equivalent of hydroxide ion with compound (93). This is probably due to reaction of most of the residual compound (93) to form (94) or the proton abstracted Meisenheimer dianion (119) which might be expected to be formed by analogy with the reaction of methoxide ion with compound (93).[132]



(119)

With 100 equivalents of hydroxide ion an irreversible reaction occurs (i.e. neutralisation of the solution by acid followed by the addition of excess base does not regenerate compounds (94) or (119) with the solution changing colour from purple to yellow(i.e. absorbtion maximum $<$350nm). A similar effect is observed if a solution containing base at low concentration is exposed to light. The latter two processes may be due to loss of nitrite ion[26] and photosensitivity of Meisenheimer complexes has been noted.[201-2] The PMR spectrum of the products of the reaction of deuterioxide ion with compound (94) in d_6-DMSO (compound (94) is generated by reaction of diethylamine with compound (93)) is not well resolved. However, the low-field resonance due to

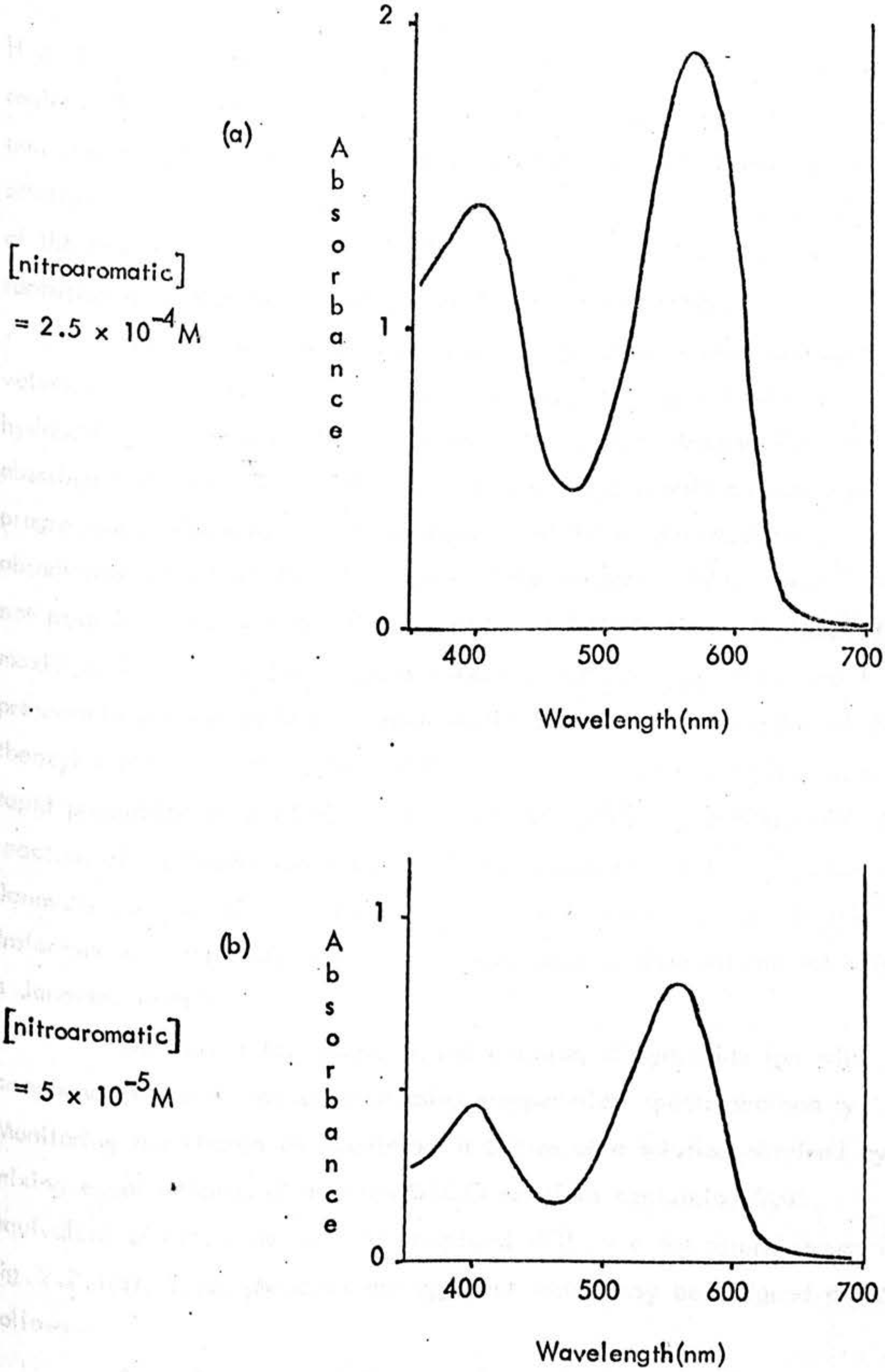


Fig.2.2.2 UV-visible spectra of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) in DMSO after:- (a) 1 equivalent of sodium hydroxide added and (b) 10 equivalents of sodium hydroxide added.

H-3 of compound (94) is absent and is replaced by a singlet in the mid-field region. The midlfield methylene resonances are apparently broadened due to non-zero coupling. The UV-visible absorbtion maximum of the diluted PMR solution is at approximately 556nm. The above PMR evidence suggests that H-3 of the product is bonded to an sp^3 carbon atom and this is consistent with formation of proton abstracted C-3 addition product (119).

The UV-visible spectrum obtained 50 seconds after mixing equal volumes of aqueous DMSO solutions containing 0.1 equivalent sodium hydroxide and compound (93) is shown in fig.2.2.3. A peak maximum absorbtion at 525nm is initially observed, but this absorbtion maximum progressively moves to higher wavelength, whilst at the same time the absorbance increases. The absorbance of the products was so great that it is not possible to measure the final spectrum at infinite time. The absorbtion maximum shifts to ~550nm before becoming immeasurably large and is presumably shifting to 560nm which would correspond to formation of the 'benzyl-type' anion of structure (94). The peak at 525nm possibly arises from rapid production of the C-3 addition complex (120), by analogy with the reaction of methoxide ion with 2,4,6-trinitroanisole(TNA),[144-5] rather than a Janovsky complex of the type produced by 2,4,6-trinitrotoluene(TNT).[18] The instantaneous nature of the reaction would seem to discount the formation of a Janovsky complex.

The initial fast stages in the reaction of hydroxide ion with compound (93) were investigated using stopped-flow spectrophotometry. Monitoring the change in absorbtion at 525nm of a solution obtained by mixing equal volumes of aqueous DMSO solutions containing 0.05 equivalent of hydroxide ion and compound (93) gave the results shown in fig.2.2.4(a). Three processes are apparent which may be assigned as follows:-

A. A mixing effect due only to the instrument(Similar jumps are obtained using solutions containing compound (93) and solvent without the presence of base).

B. This step is probably due to formation of the C-3 addition

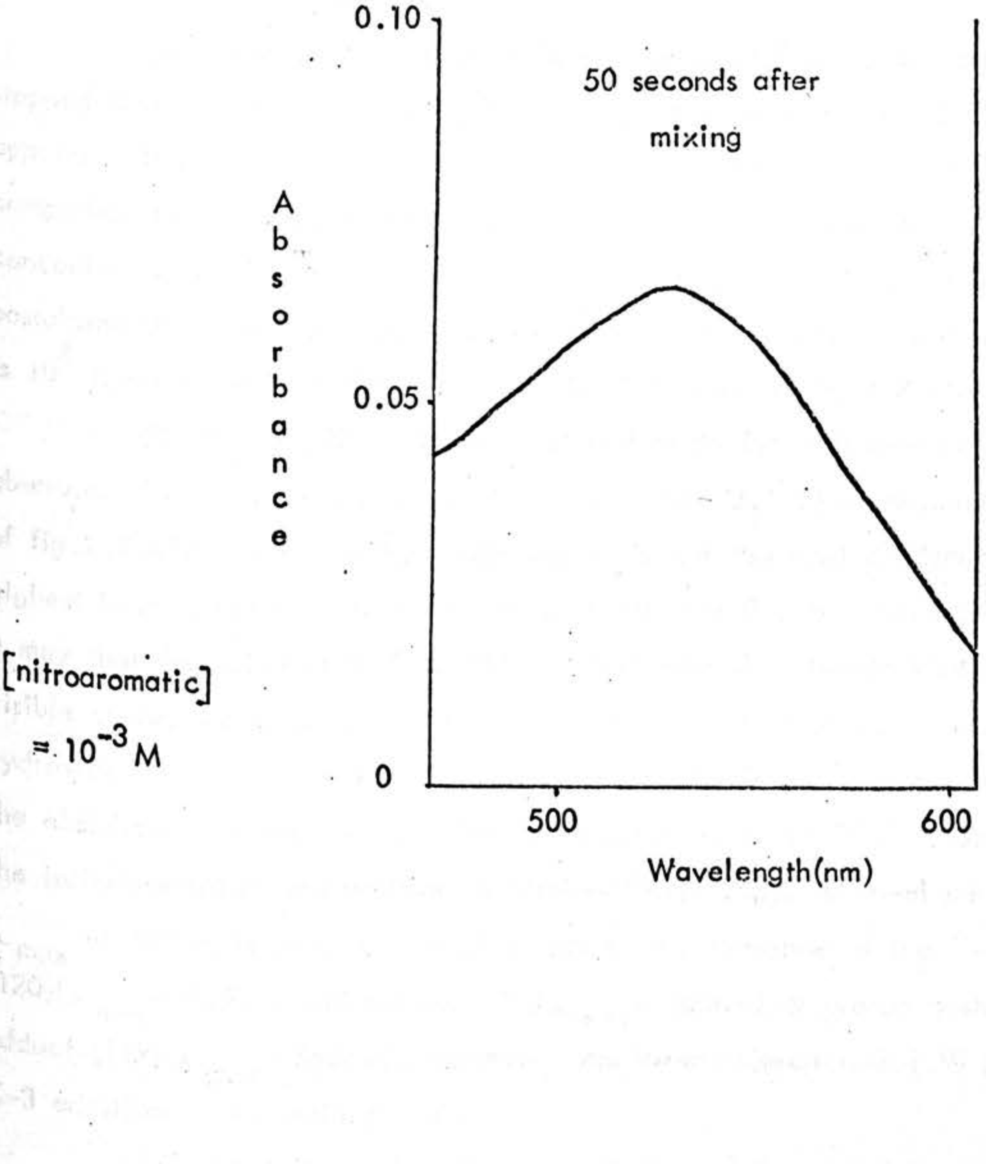


Fig.2.2.3 Visible spectrum obtained 50 seconds after mixing equal volumes of solutions containing 0.1 equivalents of sodium hydroxide and 2,4,8-trinitro-1,5-dimethylnaphthalene in aqueous DMSO.

complex (120) by analogy with the reaction of 2,4,6-trinitroanisole with methoxide ion.[144-5]

C. The slowest process is very probably due to proton abstraction. The analogous abstraction process for TNT is much slower than the addition step.[18]

On increasing the hydroxide ion concentration to 40 equivalents the stopped-flow traces shown in fig.2.2.4(b)-(d) are obtained and 2 processes are apparent. It has been noted that for the reaction of base with polynitroaromatic compounds the fastest reactions tend to become predominant as the base concentration or solvent DMSO content is increased,[102] consequently it may be postulated that the 2 processes observed correspond to the steps A and B(Step B is 10^4 times faster than the proton abstraction step) of fig.2.2.4(a).

Finally at 100 equivalents of hydroxide ion one step only is observed which from the rate constant(see section 3.1.9) corresponds to step B of fig.2.2.4(a). From the fact that step A is not the most predominant at the highest base concentration it may be inferred that this is a mixing effect. Step B may then be assigned to C-3 addition and step C to proton abstraction. A visible absorbtion spectrum for the products of reaction of 244 equivalents of hydroxide ion with compound (93) in aqueous DMSO was plotted by measuring the absorbance on the stopped-flow spectrophotometer at 10nm intervals when the infinity(equilibrium) position is attained(fig.2.2.5). A broad peak with λ_{max} at 560nm is obtained which points to the presence of the C-3 adduct (120)(λ_{max} ~ 525nm) and species (94)(λ_{max} ~ 560nm) or proton abstracted C-3 adduct (119)(λ_{max} ~ 560nm). However, the kinetics(section 3.1.9) show that C-3 addition is the main process.

Scheme 1 is an overall representation of the reaction of hydroxide ion with compound (93) in aqueous DMSO solution. For the reaction of less than one equivalent of hydroxide ion rapid reaction to form the C-3 addition complex (120) would be in competition with proton abstraction to give the 'benzyl-type' anion (94), which is a more thermodynamically stable product (see section 3.1.9). The reaction of excess base with compound (93) in aqueous DMSO appears to rapidly form the C-3 addition product (120) in high yield.

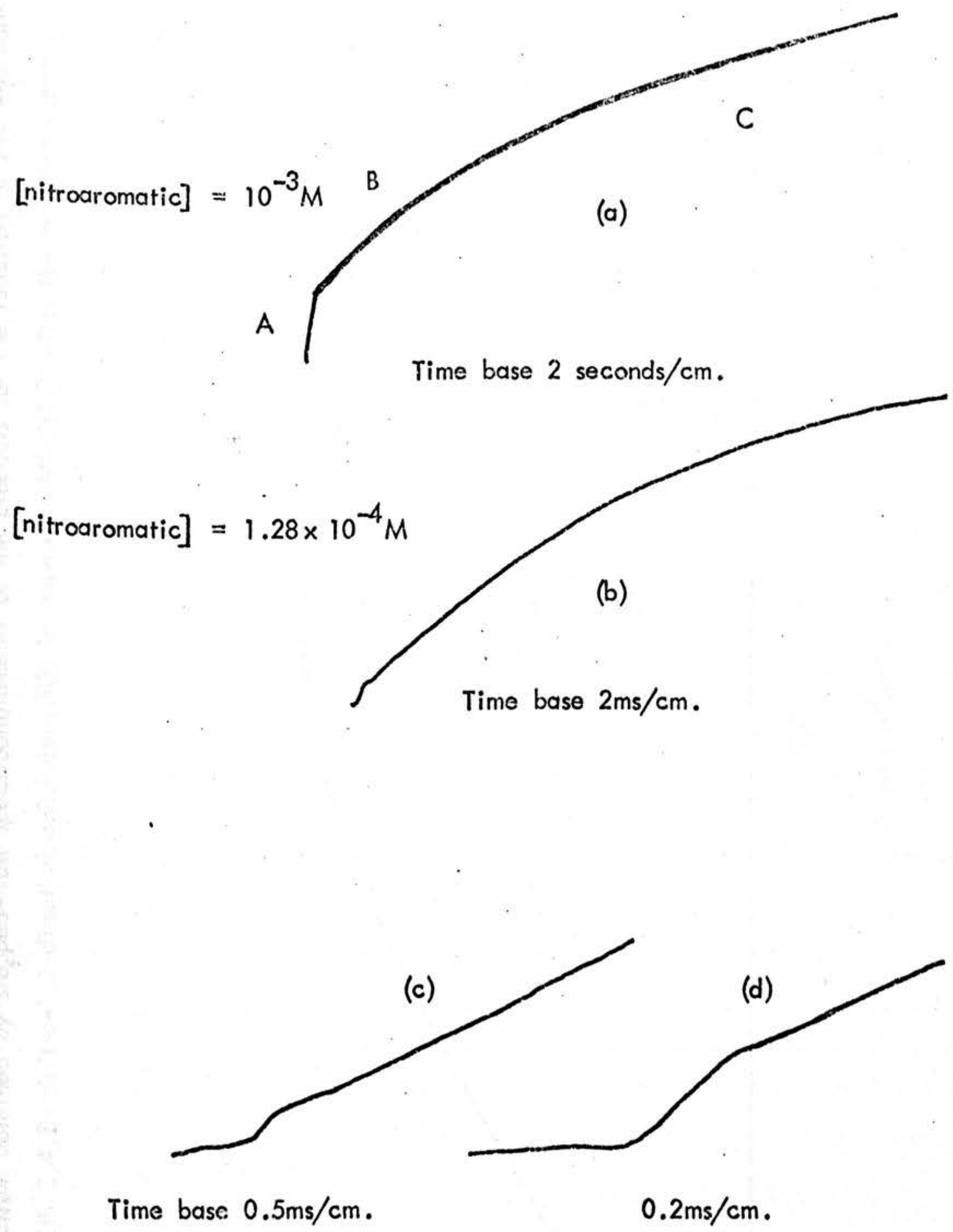
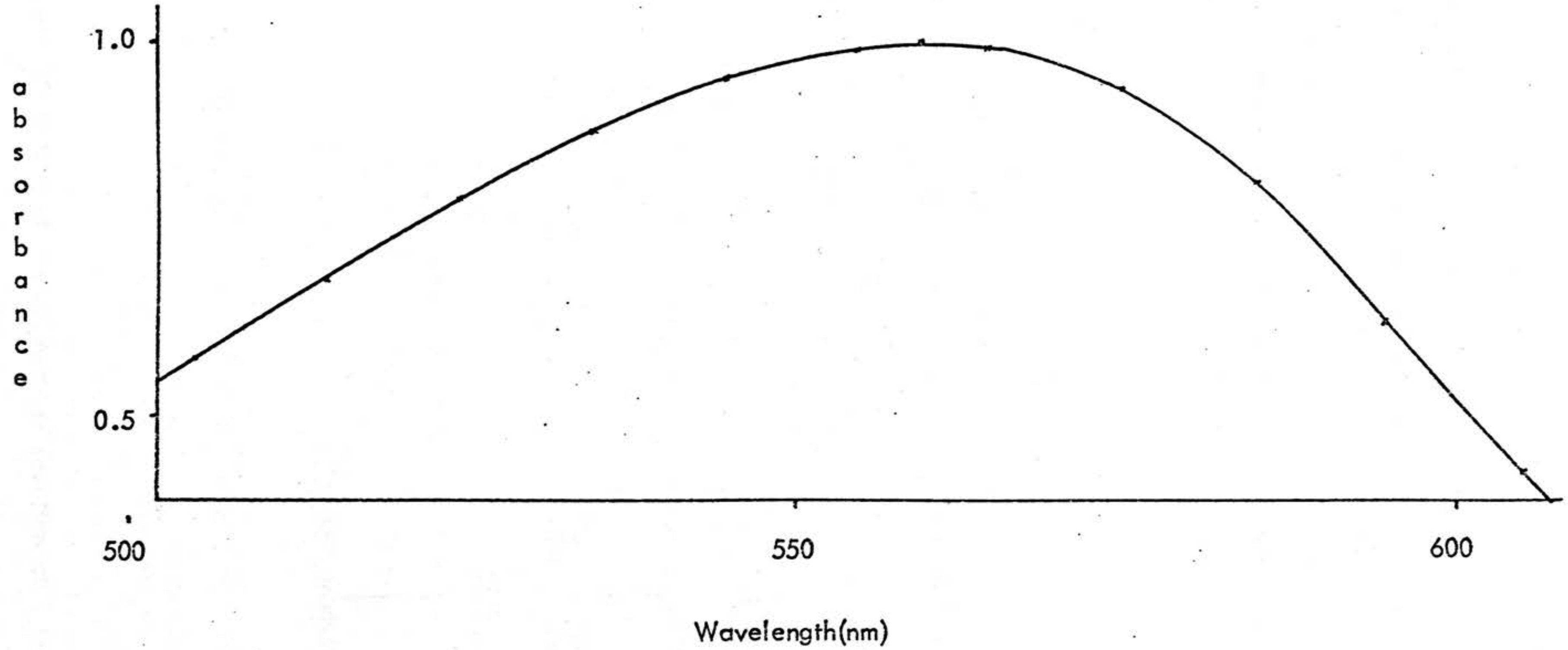
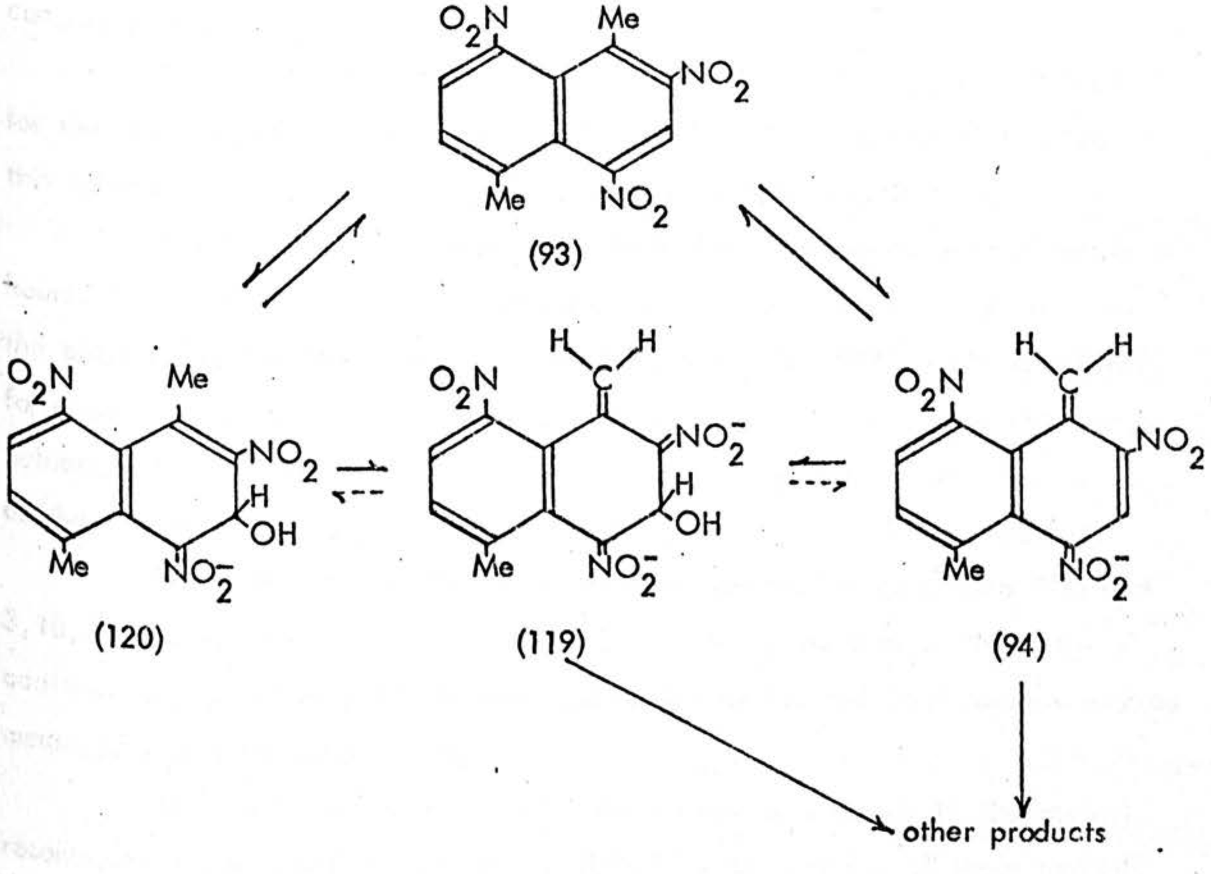


Fig.2.2.4(a) Stopped-flow trace obtained on reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) with 0.05 equivalent of sodium hydroxide in aqueous DMSO(1:9); (b),(c) and (d) Traces obtained on reaction of compound (93) with 40 equivalents of sodium hydroxide in aqueous DMSO(1:9).

Fig.2.2.5 Visible spectrum obtained by stopped-flow spectrophotometer of the products for the reaction of 244 equivalents of sodium hydroxide with 2,4,8-trinitro-1,5-dimethylnaphthalene(93) in aqueous DMSO(1:9) after the reaction reached equilibrium.



Subsequently, from the visible spectrum of the products at the infinity position compounds (94) and/or (119) seem to be formed. Compounds (94) and (119) are more thermodynamically stable than the addition complex (120) and with excess base present compound (119) would be expected to be the final product formed. It may be speculated that compound (119) forms directly from compound (120) as well as from compound (94). Finally, degradation of the complexes occurs.



Scheme 1

(B) Triethylamine

The PMR spectrum(220MHz) of the products of reaction of 1 equivalent of triethylamine with compound (93)(resonances denoted by the letter a) in d_6-DMSO(fig.2.2.6(b)) shows the formation of the 'benzyl-type' anion only (resonances denoted by letter b).

(C) Benzylamine

The PMR spectrum(220MHz) of a solution containing compound (93) and 1 equivalent of benzylamine is shown in fig.2.2.6(c).

The features of the PMR spectrum of the addition product are that the chemical shift of the singlet due to H-3 is intermediate between that of compounds (93) and (94); the 5-Me resonance is similar to compound (94) but the 1-Me which is bonded to an sp^3 carbon is upfield relative to that of compound (94).

The visible absorbtion maximum is at 560nm(minor peak ~ 395nm) for the diluted PMR solution; but on addition of a large excess of base to this solution the absorbtion maximum occurs at ~ 547nm(fig.2.2.7).

The absorbtion maximum shifts to higher wavelength over a period of hours. These changes in visible absorbtion spectra are probably explained by the presence of the 'benzyl-type' anion (94) when the PMR sample is diluted, followed by production of the addition complex on reaction with excess base. Subsequently formation of compound (94) from the addition product occurred, as the former is thermodynamically more stable than the addition complex.

The PMR spectra(60MHz) of solutions containing compound (93) and 3,10,20 and 40 equivalents of benzylamine show an increase in the ratio of addition to abstraction products from 2:3 to 1:1 to 4:3 and 16:9 respectively as measured 5 minutes after mixing.

Monitoring the spectra with time showed a decrease in the methyl resonances of the addition product paralleled by an increase of those methyl resonances due to compound (94). The rate of formation of compound (94) from the addition product(via compound (93)) increases as the base concentration decreases.

It is probable that the addition product exists mainly in the deprotonated form (123) rather than the zwitterionic form (122),[41] especially with excess amine present, although subsequent formation of the thermo-

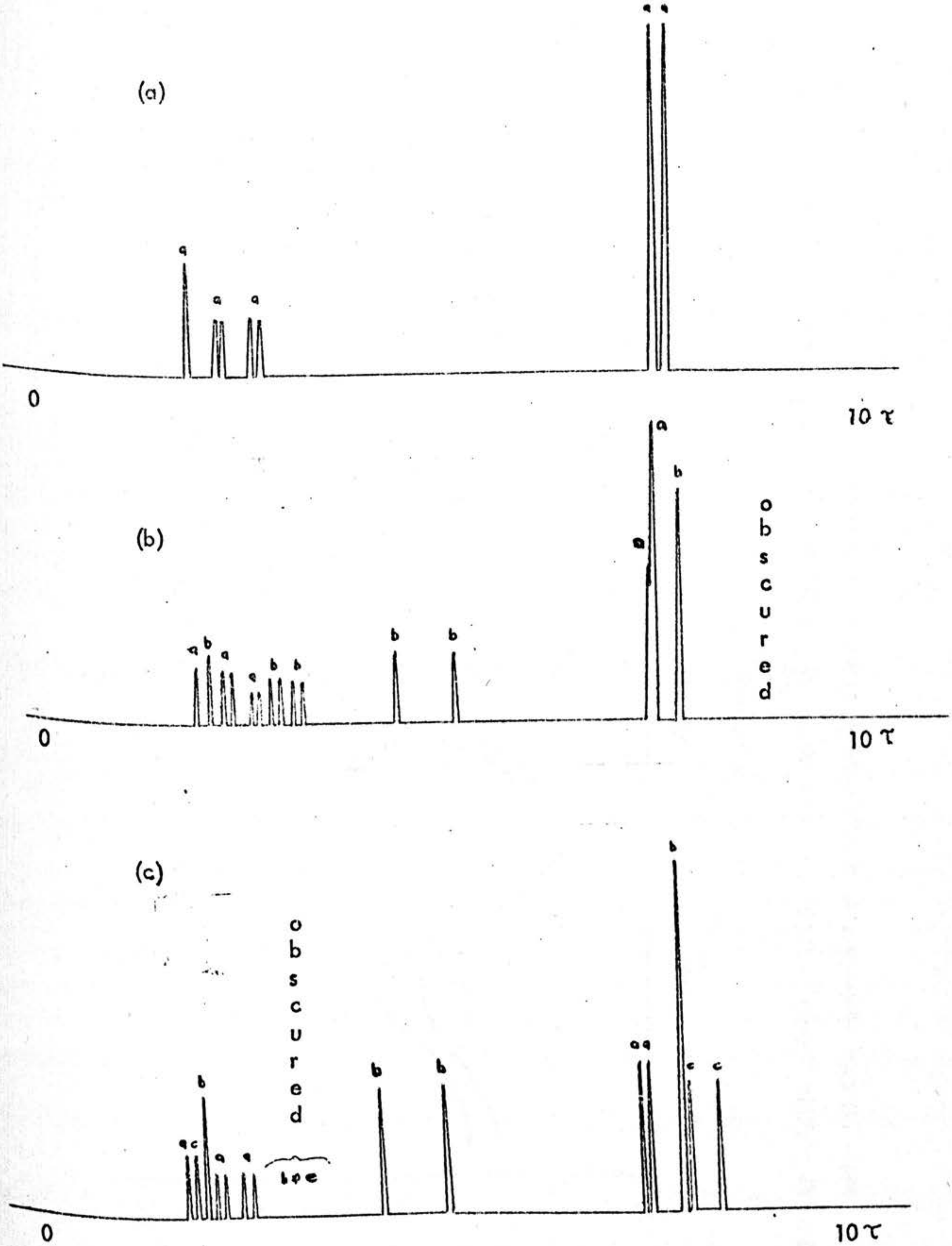


Fig.2.2.6 (a) PMR spectrum of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) in DMSO-d_6. Spectra after the addition of one equivalent of the following bases:- (b) Triethylamine (c) Benzylamine.

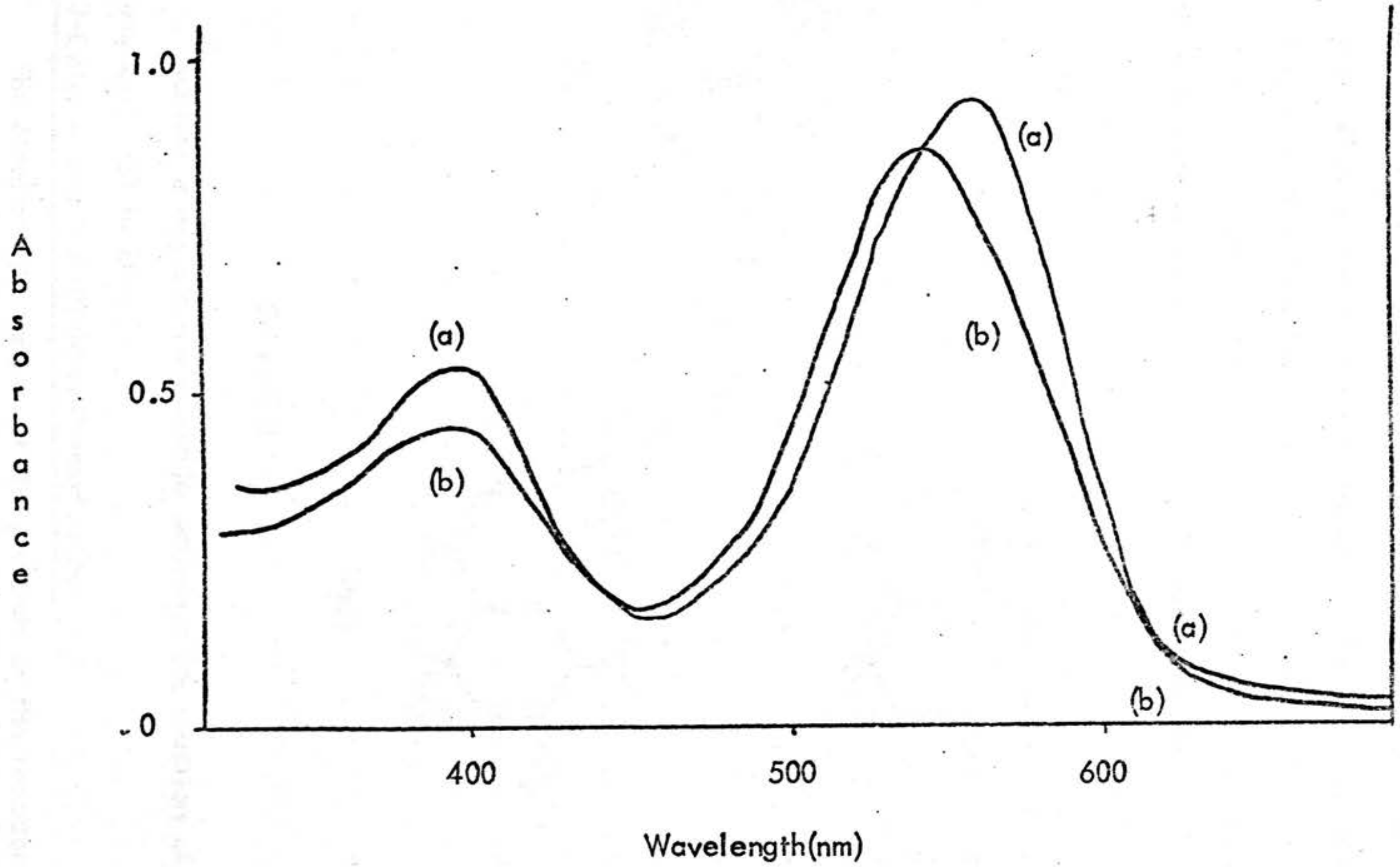
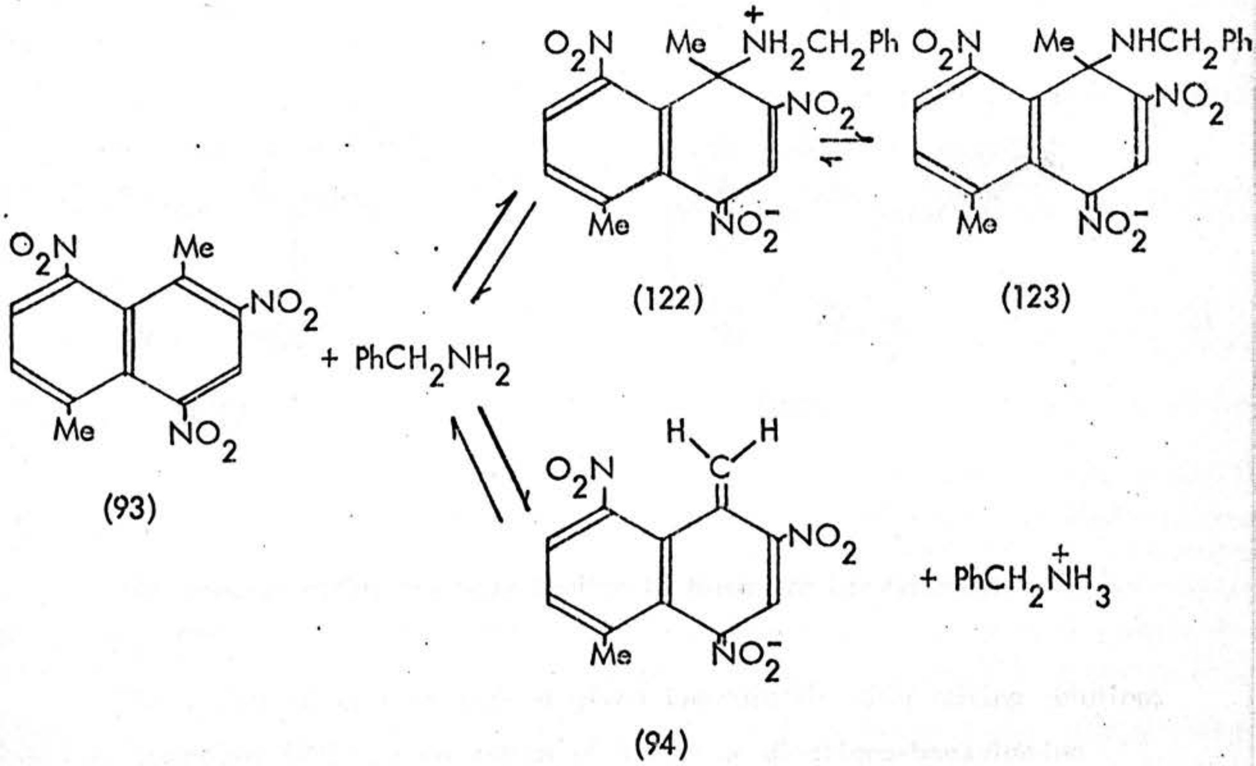


Fig.2.2.7 UV-visible spectra of DMSO solutions containing 2,4,8-trinitro-1,5-dimethylnaphthalene(93)(~ 5 × 10^{-5}M) and:- (a) One equivalent of benzylamine (b) Excess benzylamine.

dynamically more stable product (94) would be expected to occur via compounds (122) and (93). It is difficult to ascertain whether compound (122) is formed since the amino protons of all products present give a common resonance. The compounds that may give rise to this resonance by rapid proton exchange are benzylamine, $PhCH_2\overset{+}{N}H_3$, complex (122), complex (123) and trace water in the d_6-DMSO. Conductivity measurements have been made on other base nitroaromatic systems to ascertain whether or not that the zwitterion is formed,[41] but for the case of benzylamine and compound (93) in DMSO this is not easily done due to the number of charged products present.

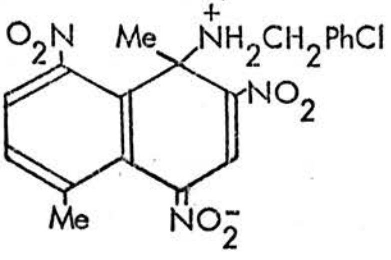


Scheme 2

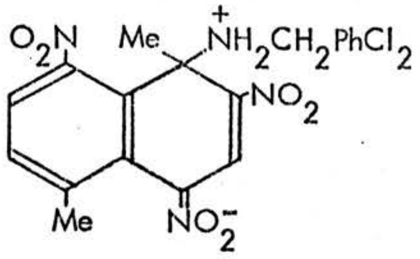
Scheme 2 depicts the probable pathways for reaction of benzylamine with compound (93) in DMSO.

(D) <u>3-Chloro- and 3,4-Dichloro-benzylamines</u>

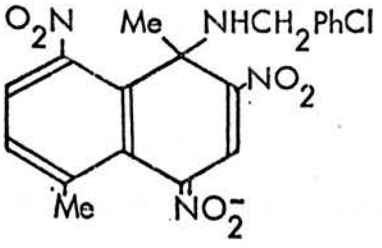
The 60MHz PMR spectra of the products of the reaction of 3-chloro- or 3,4-dichloro-benzylamine with compound (93) in d_6-DMSO show in each case the presence of a C-1 addition product and the 'benzyl-type' anion (94). The addition products may possibly exist in the zwitterionic forms, (124) and (125), or anionic forms (126) and (127).



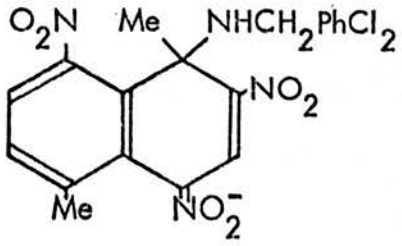
(124)



(125)



(126)



(127)

The product ratios are very similar to those for benzylamine (See reaction (C)).

The visible absorbtion maxima given immediately after mixing solutions containing compound (93) and an excess of mono- or di-chloro-benzylamine occur at 540 and 533nm respectively. The maxima are observed to shift to longer wavelength(i.e. towards 560nm) with time and this is consistent with formation of species (94) from the addition complex via compound (93), analogous to the reaction of benzylamine(cf. Scheme 2).

(E) Hexamethyldisilazane

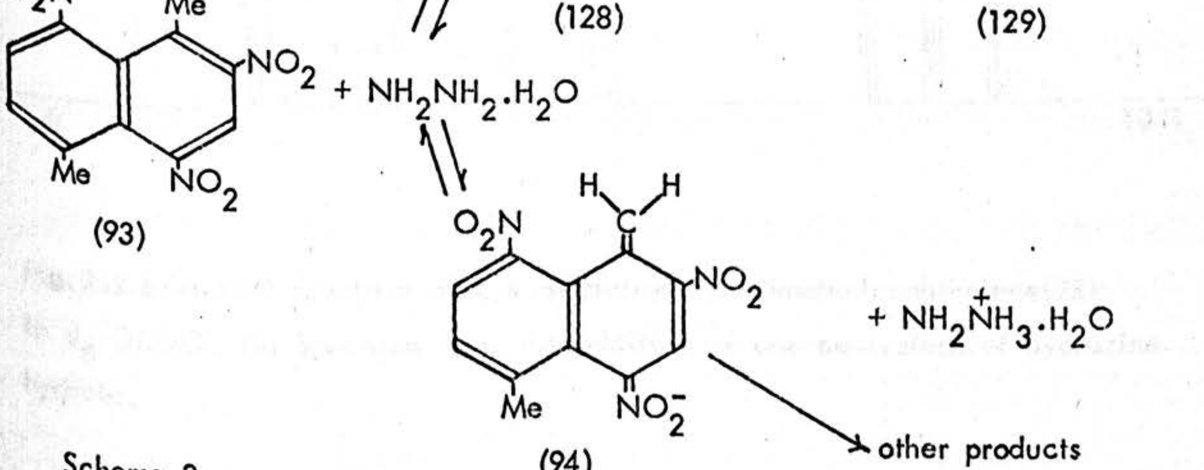
PMR shows that hexamethyldisilazane reacts with compound (93) in d_6-DMSO solution to yield species (94) only.

(F) Hydrazine hydrate

The PMR spectrum of the reaction obtained on mixing 1 equivalent of hydrazine hydrate with compound (93) in d_6-DMSO is shown in fig.2.2.8(b). The spectrum shows the presence of three species which may be assigned to compound (93)(resonances denoted by letter a); 'benzyl-type' anion(resonances denoted by letter b) and C-1 addition product (128) or (129) (resonances denoted by letter c).

The lines due to the addition product (128) or (129) decrease and those due to the 'benzyl-type' anion (94) increase with time. The visible absorbtion maximum of the diluted PMR solution is at 557nm and this may be explained as being due to a mixture of compound (94) and addition product (128) or (129). As the absorbtion maximum is close to 560nm it would seem that the solution contains mainly compound (94).

Scheme 3 shows the probable reaction pathways for the reaction of hydrazine hydrate with compound (93) in DMSO. The competitive steps for proton abstraction(slow) and addition(faster) finally result in the formation of the thermodynamically more stable product (94).



Scheme 3

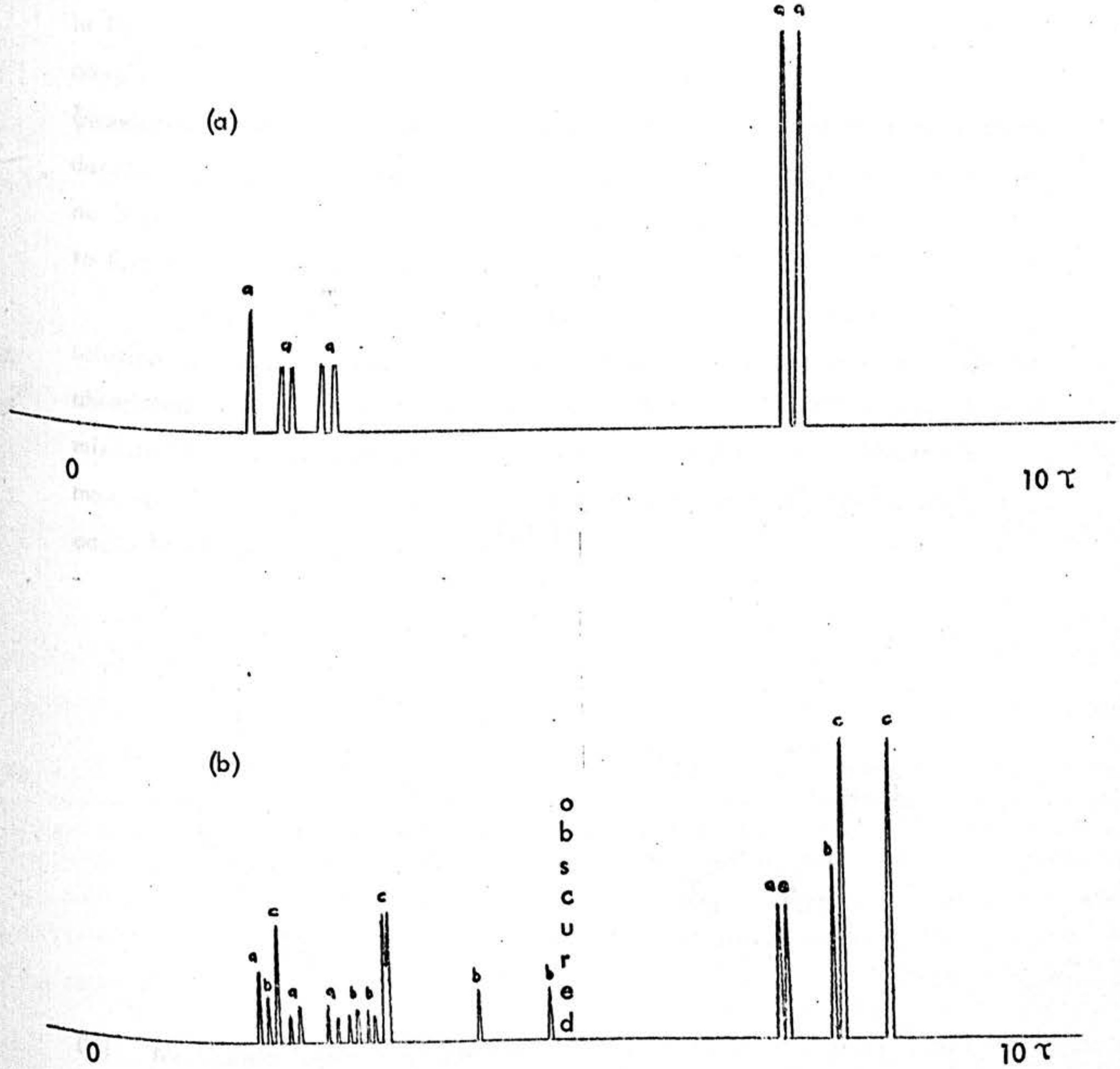
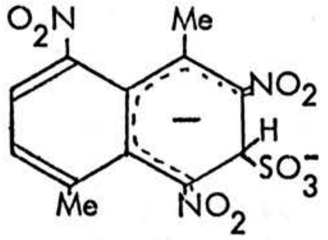


Fig.2.2.8 (a) PMR spectrum of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) in d_6-DMSO. (b) Spectrum after the addition of one equivalent of hydrazine hydrate.

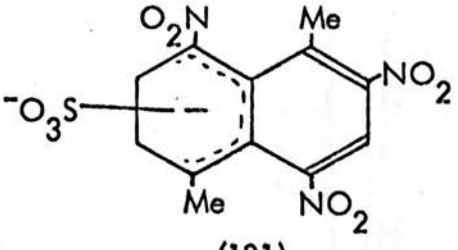
(G) Sulphite ion

The PMR spectrum of the products of reaction of 1-3 equivalents of aqueous sodium sulphite solution with compound (93) in d_6-DMSO is shown in fig.2.2.9(b). The spectrum possibly indicates the formation of 2 addition complexes which may be due to addition of sulphite ion at C-3 (130) (resonances denoted by letter b) and addition at C-6 or C-7 (131)(resonances denoted by letter c). These assignments are somewhat uncertain however, as no case of addition of sulphite ion to a ring containing only one nitro group to form an addition complex has been noted.

The addition of 100 equivalents of solid sodium sulphite to a solution of compound (93) in DMSO results in a solution exhibiting a visible absorbtion maximum at 547nm. It is possible that the absorbtion arises from a mixture of addition products, such as those mentioned above. Absorbtion maxima of sulphite Meisenheimer complexes have previously been noted to occur in the region around 500nm.[100,174]



(130)



(131)

(H) Methoxide ion(in methanol)

The reaction of methoxide ion with compound (93) in DMSO has been studied previously.[132] Reaction of compound (93) with one equivalent of methoxide ion gives the 'benzyl-type' anion (94), but on addition of a further 2 equivalents of methoxide ion to the reaction mixture formation of the dianion complex (95) was observed.[132]

The PMR spectrum of a methanolic solution of compound (93) to

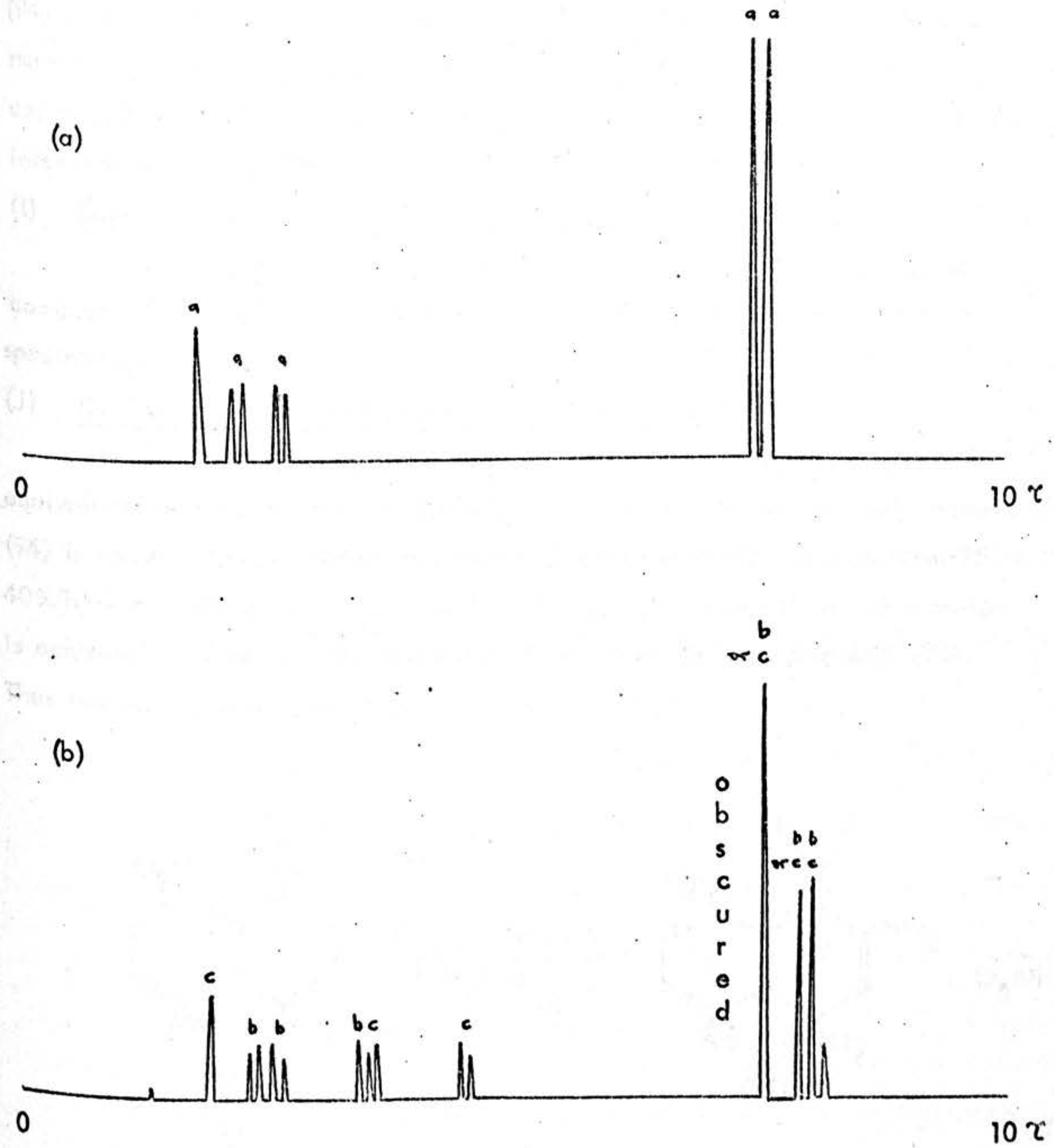


Fig.2.2.9 (a) PMR spectrum of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) in DMSO-d_6. (b) Spectrum after the addition of one, two or three equivalents of sodium sulphite in D_2O.

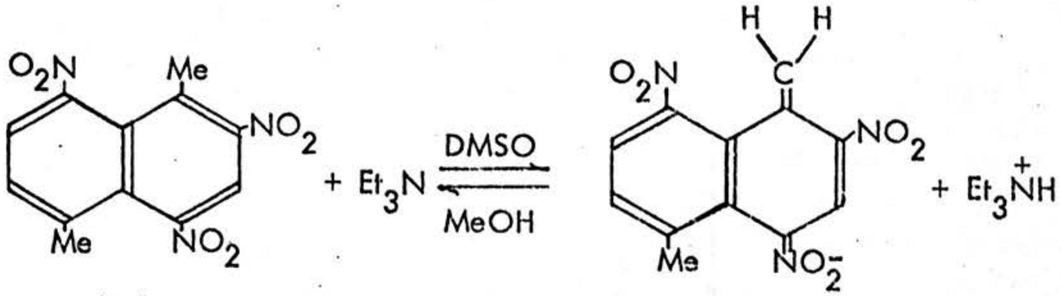
which one equivalent of sodium methoxide-d_3 is added shows that only compound (94) is formed(fig.2.2.10(b)). Addition of 3 equivalents of the base to a methanolic solution of compound (93) gives a PMR spectrum which shows that compound (95) is formed(fig.2.2.10(c)), presumably by addition to C-3 of the intermediate product (94).

(I) Diethylamine(in methanol)

The addition of excess diethylamine to a methanolic solution of compound (93) results in the formation of compound (94) as shown by PMR spectroscopy.

(J) Diethylamine and triethylamine(in DMSO/methanol)

The PMR spectrum of a solution containing compound (93) and 3 equivalents of triethylamine in d_6-DMSO/CD_3OD(3:1) shows that only compound (94) is formed. On increasing the methanol content of this solution from 25 to 40%(by the addition of CD_3OD to the PMR solution) reversal of the reaction is achieved as shown by the reappearence of peaks due to compound (93). Thus the equilibrium shown below can be postulated:-



(93) (94)

The effect of added methanol is in agreement with kinetic measurements which show that the equilibrium constant for the reaction of triethylamine with compound (93) in mixed solvent decreases with increase in methanol content (See section 3.5). The visible absorbtion maxima of solutions containing compound (93) and up to 1600 equivalents of diethylamine or triethylamine in DMSO/methanol(1:1,2:1,4:1 and 9:1) occur at 560nm(fig.2.2.11). The peak with λ_{max} at 560nm can be assigned to the compound (94).

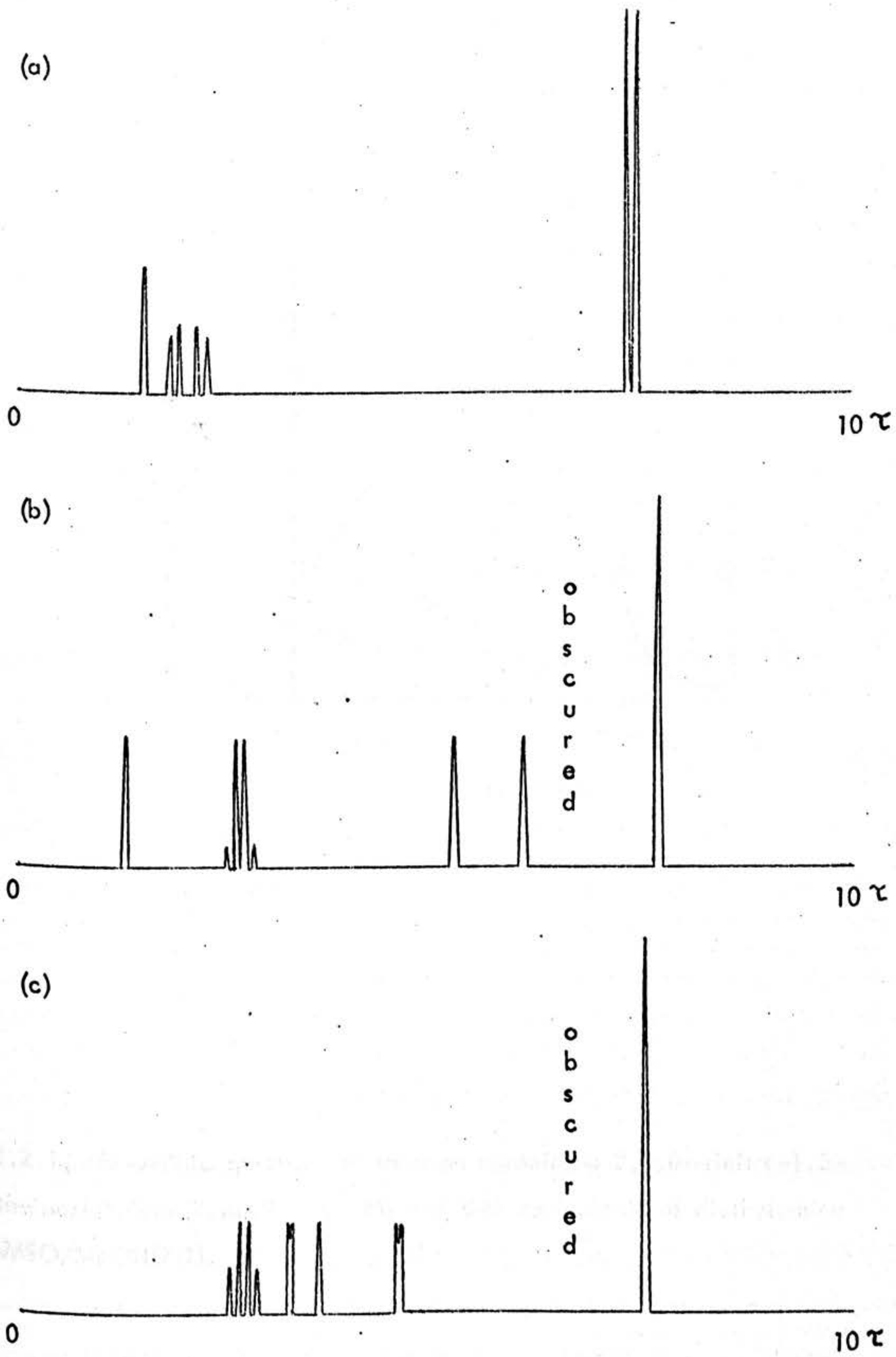


Fig.2.2.10 (a) PMR spectrum of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) in CD_3OD. Spectra after the addition of:- (b) One equivalent of sodium methoxide-d_3 and (c) Three equivalents of sodium methoxide-d_3 in CD_3OD.

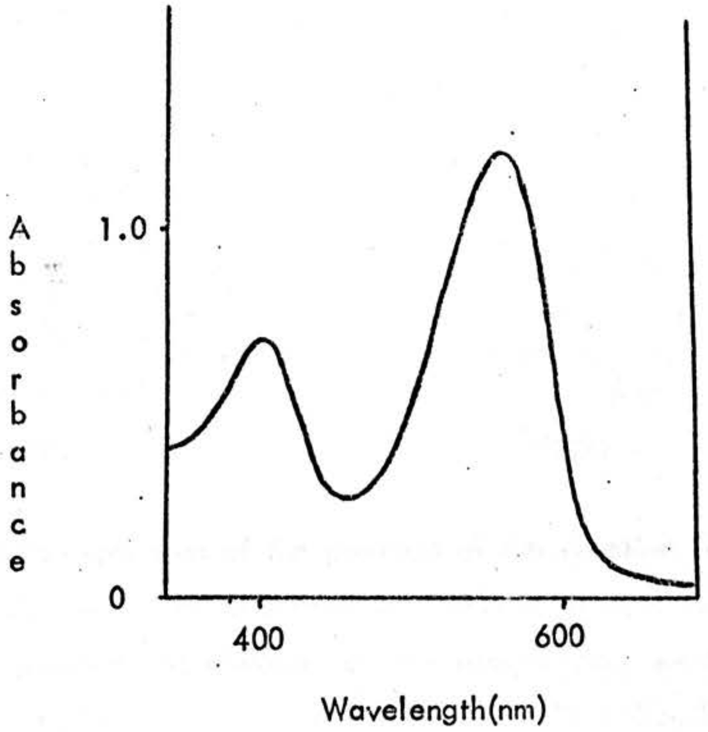
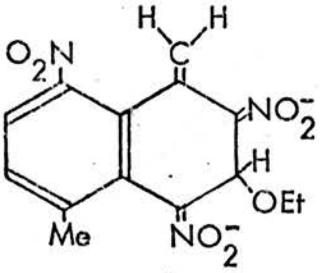


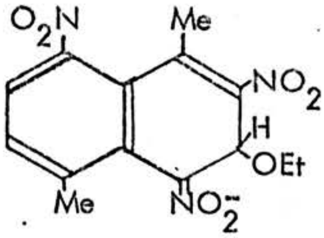
Fig.2.2.11 UV-visible spectrum of solution containing 2,4,8-trinitro-1,5-dimethylnaphthalene(93)(6.8×10^{-5}M) and 800 equivalents of diethylamine in DMSO/MeOH(2:1).

(K) Ethoxide ion(in DMSO and ethanol)

The PMR spectrum of a d_6-DMSO solution containing compound (93) to which 1-3 equivalents of sodium ethoxide in ethanol has been added shows that only compound (94) is formed. The PMR spectrum showed that after addition of a total of 6 equivalents of base the proton abstracted C-3 adduct (132) was formed.



(132)



(133)

The visible absorbtion spectrum of the products of the reaction of 200 equivalents of sodium ethoxide with compound (93) in ethanol is shown in fig.2.2.12. The spectrum was obtained on the stopped-flow spectrophotometer at 10nm intervals of the reactant solution once the infinity(equilibrium) position was attained. A broad peak with a maximum at 560nm and shoulder at ~520nm may be taken to indicate the formation of compound (94)(λ_{max} = 560nm) and possibly the proton abstracted C-3 adduct (132), whilst the shoulder at ~520nm could be due to the C-3 adduct (133). Formation of the C-3 adduct (133) should be rapid compared with the process of proton abstraction as noted with the reaction of ethoxide ion with 2,4,6-trinitrotoluene in ethanol.[124]

(L) Tert-Butoxide ion(in DMSO/t-butanol and butanol)

The PMR spectrum of a d_6-DMSO solution containing compound (93) to which 1 equivalent of sodium tert-butoxide in t-butanol has been added shows that only compound (94) is formed. The PMR spectrum failed to show the formation of an addition compound even after the addition of 4 equivalents of base. Steric hindrance to close approach of the t-butoxide ion to position C-3 of compound (93) probably accounts for the inability to form an addition complex under the conditions employed. A spectrum of the products for the

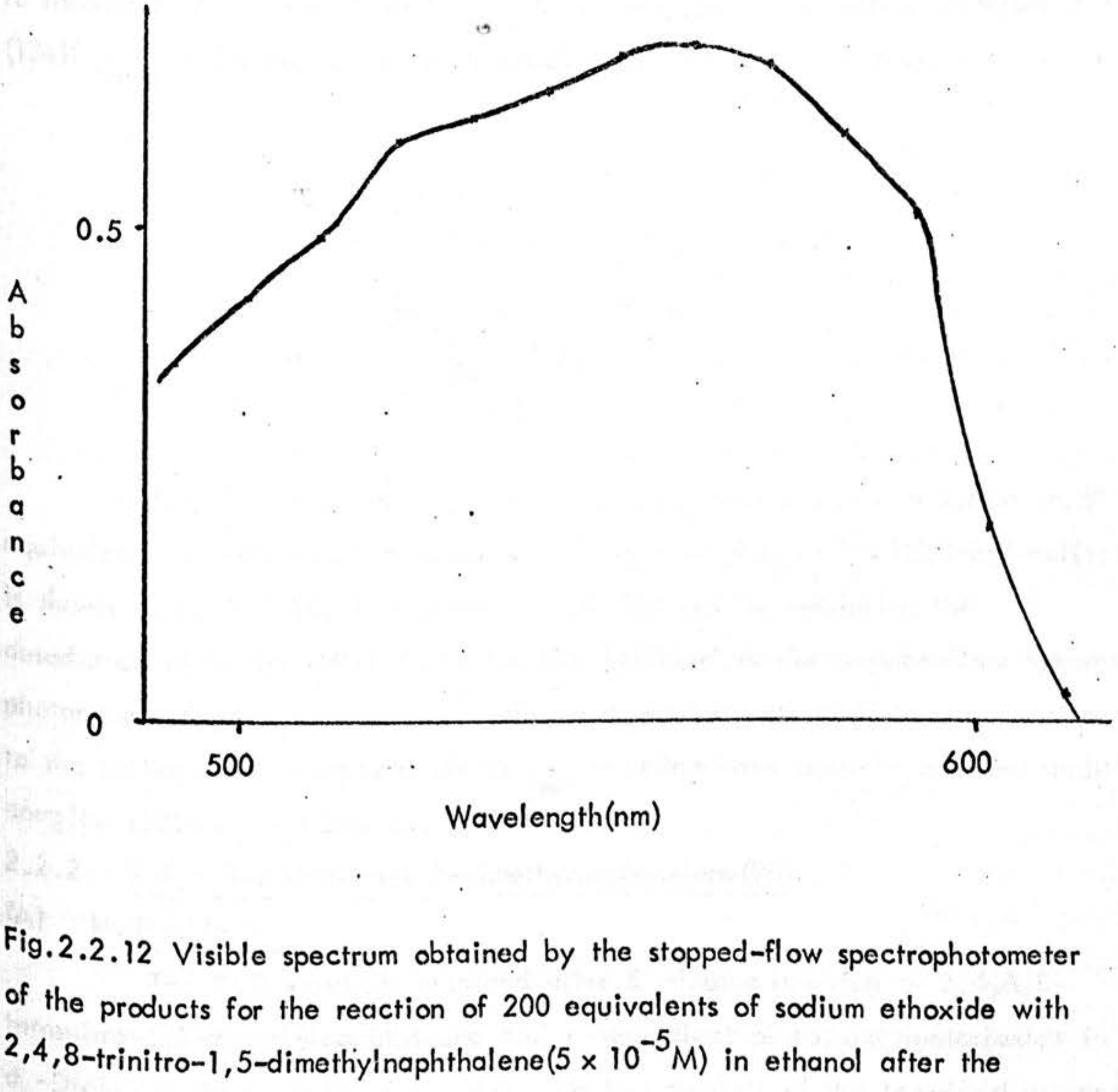
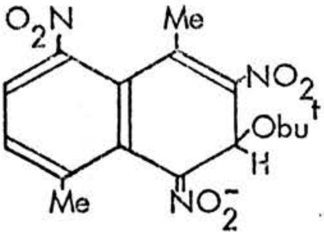


Fig.2.2.12 Visible spectrum obtained by the stopped-flow spectrophotometer of the products for the reaction of 200 equivalents of sodium ethoxide with 2,4,8-trinitro-1,5-dimethylnaphthalene(5×10^{-5}M) in ethanol after the reaction reached equilibrium.

reaction of 200 equivalents of sodium tert-butoxide with compound (93) in tert-butanol is shown in fig.2.2.13. This spectrum was obtained using the stopped-flow spectrophotometer by measuring the absorbance at 10nm intervals when the infinity position was attained after 8 seconds reaction time. Three overlapping maxima are observed at 500,530 and ~550nm which may be due to formation of compound (94)(λ_{max} = 560nm), the C-3 addition complex (134)(λ_{max} = 530nm) and another product with (λ_{max} = 500nm).



(134)

A visible absorbtion spectrum for the products of the reaction of 20 equivalents of sodium tert-butoxide with compound (93) in DMSO/t-butanol(1:1) is shown in fig.2.2.14. The spectrum was obtained by measuring the absorbance when the infinity position was attained on the stopped-flow spectrophotometer. A peak maximum at 560nm and shoulder at ~540nm may be due to the formation of compound (94)(λ_{max} = 560nm) and possibly the C-3 addition complex (134)(λ_{max} ~ 540nm).

2.2.2 2,4,6,8-Tetranitro-1,5-dimethylnaphthalene(98)

(A) Hydroxide ion

The PMR spectrum obtained after 5 minutes reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene and 1 equivalent of sodium deuterioxide in d_6-DMSO is shown in fig.2.2.15(b). The two singlets in the low-field region; the two singlets in the mid-field region and the single methyl resonance observed in the spectrum may be assigned to the 'benzyl-type' anion (100). This anion has been observed previously in the reaction of 1 equivalent of methoxide ion with compound (98) in DMSO.[132] The PMR spectrum of the reaction mixture containing 1 equivalent of deuterioxide ion and compound (98)

Fig.2.2.13 Visible spectrum obtained by the stopped-flow. spectrophotometer of the products for the reaction of 200 equivalents of sodium tert-butoxide with 2,4,8-trinitro-1,5-dimethylnaphthalene(5×10^{-5}M) in tert-butanol after the reaction reached equilibrium.

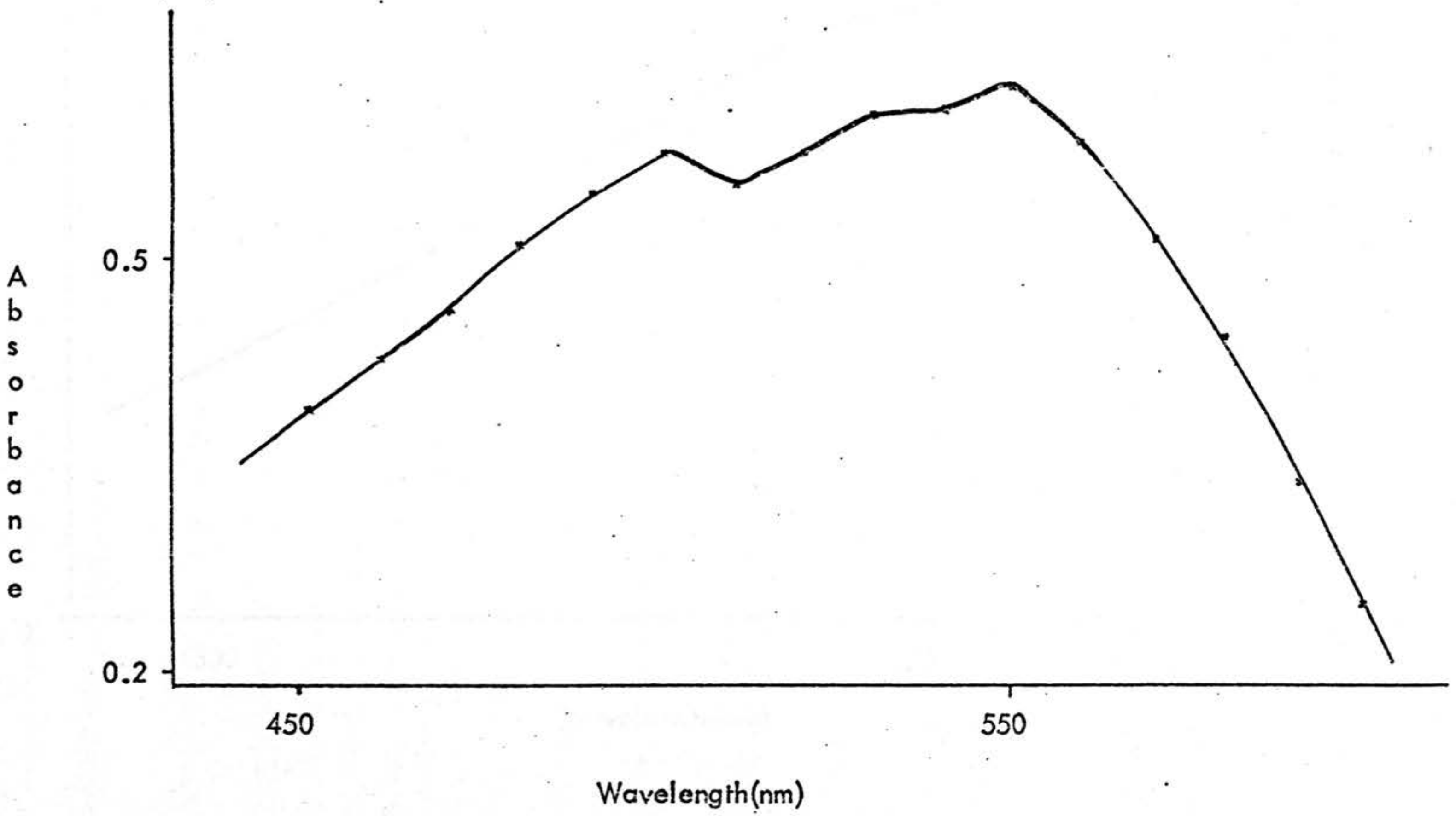
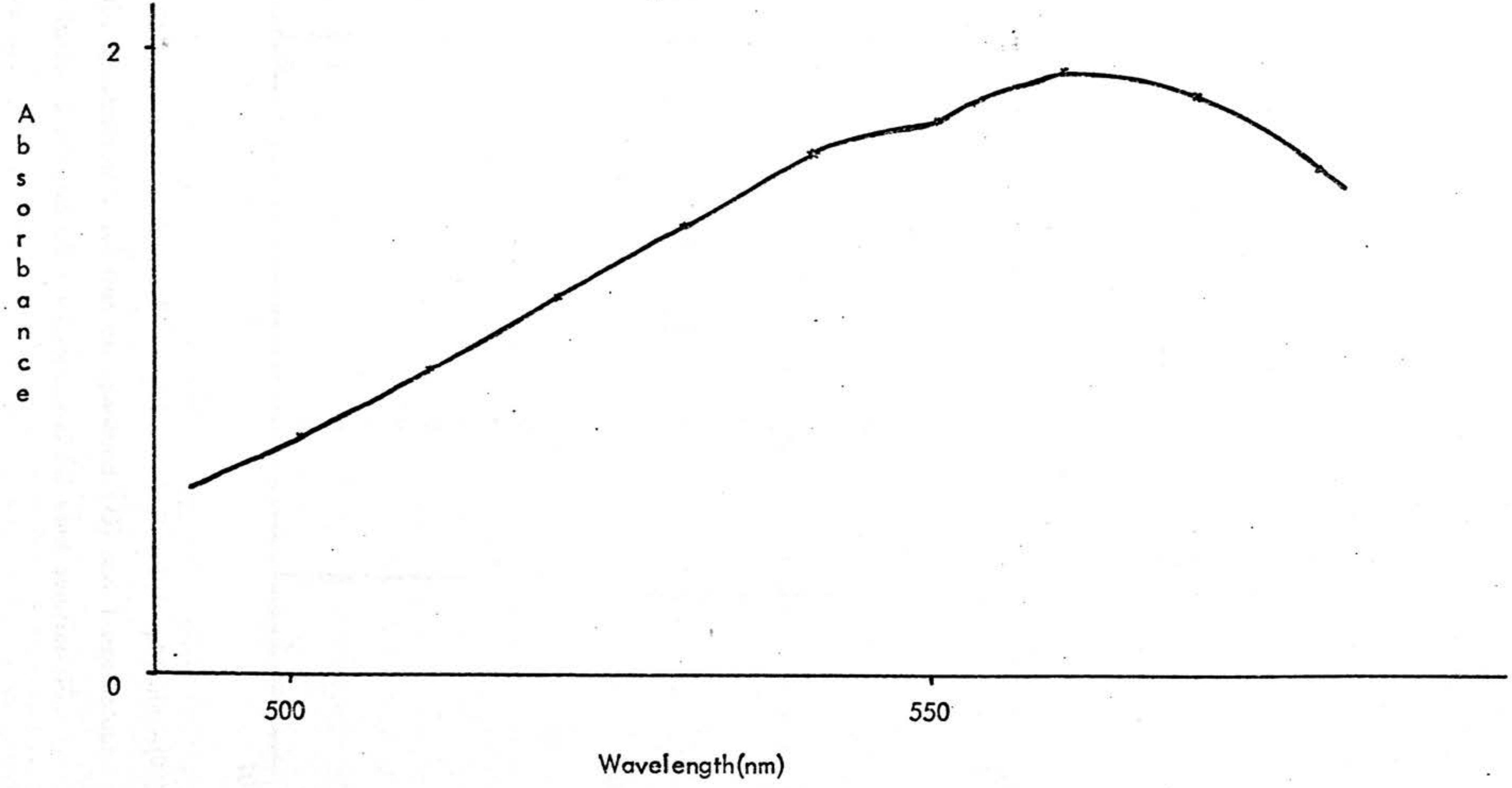


Fig.2.2.14 Visible spectrum obtained by the stopped-flow spectrophotometer of the products for the reaction of 20 equivalents of sodium tert-butoxide with 2,4,8-trinitro-1,5-dimethylnaphthalene(5×10^{-5}M) in tert-butanol/DMSO(1:1).



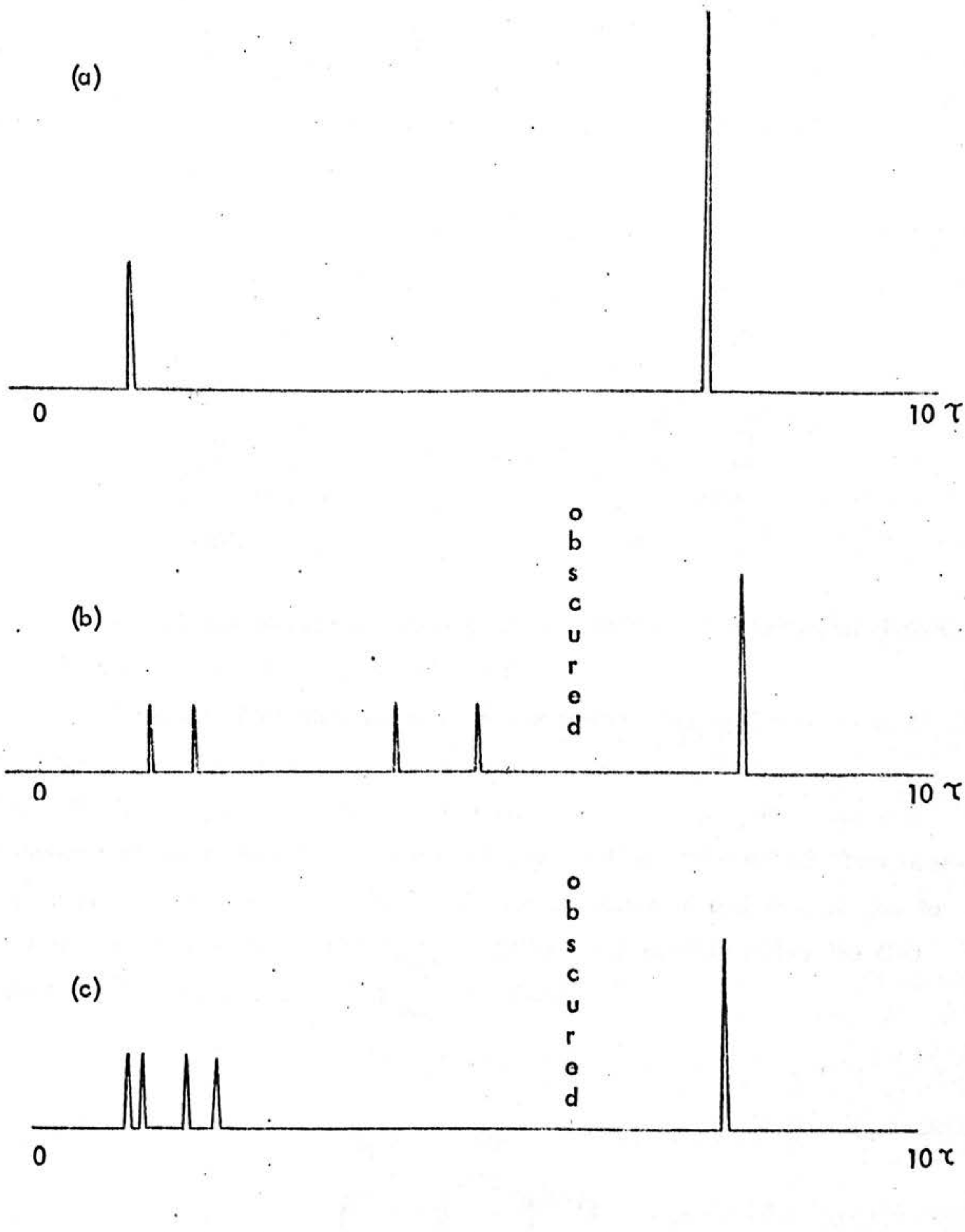
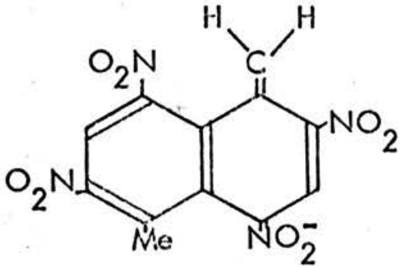
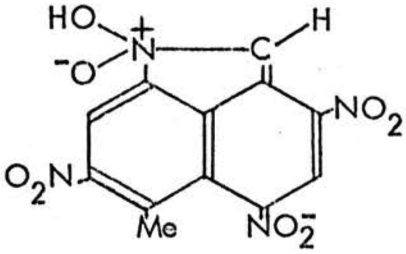


Fig.2.2.15 (a) PMR spectrum of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene(98) in DMSO-d_6. (b) Spectrum of a solution of compound (98) and 1 equivalent of sodium deuterioxide 5 minutes after mixing, and (c) same solution 40 minutes after mixing.

in d_6-DMSO was recorded after 40 minutes(fig.2.2.15(c)). This spectrum shows the presence of 4 singlets in the aromatic region and one methyl resonance. The spectrum may be assigned to compound (101) which is formed by intramolecular reaction of compound (100) to give a bridged structure (101). Compound (101) has also been observed to be the final product on reaction of methoxide ion with compound (98) in DMSO.[132]



(100)



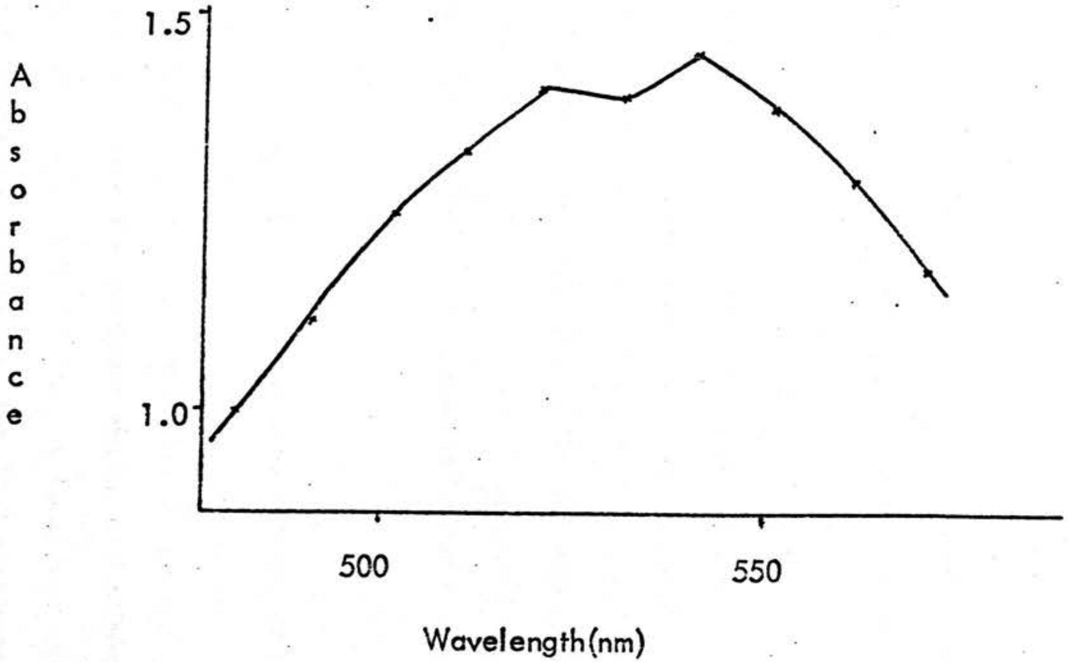
(101)

The visible absorbtion maximum of the PMR solution occurs at 540nm and this is probably due to compound (101).

A visible absorbtion spectrum of the products for the reaction of 11 equivalents of sodium hydroxide with compound (98) in DMSO/H_2O(9:1) was plotted(fig.2.2.16) by measuring the absorbance on the stopped-flow spectrophotometer at 10nm intervals when the infinity position was attained. Two overlapping peaks with maxima at 520 and 540nm are observed and may be due to the formation of compound (101)(λ_{max} = 540nm) and possibly either the C-3 adduct (135) or compound (100)(λ_{max} = 520nm).

(135)

Fig.2.2.16 Visible spectrum obtained by the stopped-flow spectrophotometer for the reaction of 11 equivalents of sodium hydroxide with 2,4,6,8-tetranitro-1,5-dimethylnaphthalene(1.83×10^{-4}M) in DMSO/H_2O(9:1).



(B) Diethylamine and triethylamine

The PMR spectrum of a solution containing 1 equivalent of diethylamine and compound (98) in d_6-DMSO is shown in fig.2.2.17(b). The spectrum is that of compound (101)(resonances denoted by letter c).

The PMR spectrum of a solution containing 0.3 equivalent of triethylamine and compound (98) in d_6-DMSO recorded after a reaction time of 5 minutes shows the formation of compound (100)(resonances denoted by letter b) and compound (101)(resonances denoted by letter c)(fig.2.2.17(c)). On increasing the base concentration for the reaction with compound (98) in DMSO it is observed that the relative proportion of compound (101) to (100) is increased(spectra recorded after 5 minutes reaction). This may be explained in terms of an increased rate of formation of compound (100) with increase in base concentration(and also on changing from triethylamine to the stronger base diethylamine), such that as intramolecular reaction removes compound (100) with more rapidity, lower concentrations remain to be detected after a given time.

(C) Benzylamine

The PMR spectrum of the product of reaction after 5 minutes of one equivalent of benzylamine with compound (98) in d_6-DMSO is shown in fig.2.2.18(b). The spectrum shows two singlets in the aromatic region and 2 singlets in the aliphatic region and although the aromatic region and aliphatic region are partly obscured by base resonances this spectrum is consistent with the formation of a C-1 addition complex (127) or (128). The PMR spectrum of the above solution was recorded after 1 day and shows the formation of a small quantity of compound (100) and compound (101). The overall process is represented by Scheme 4.

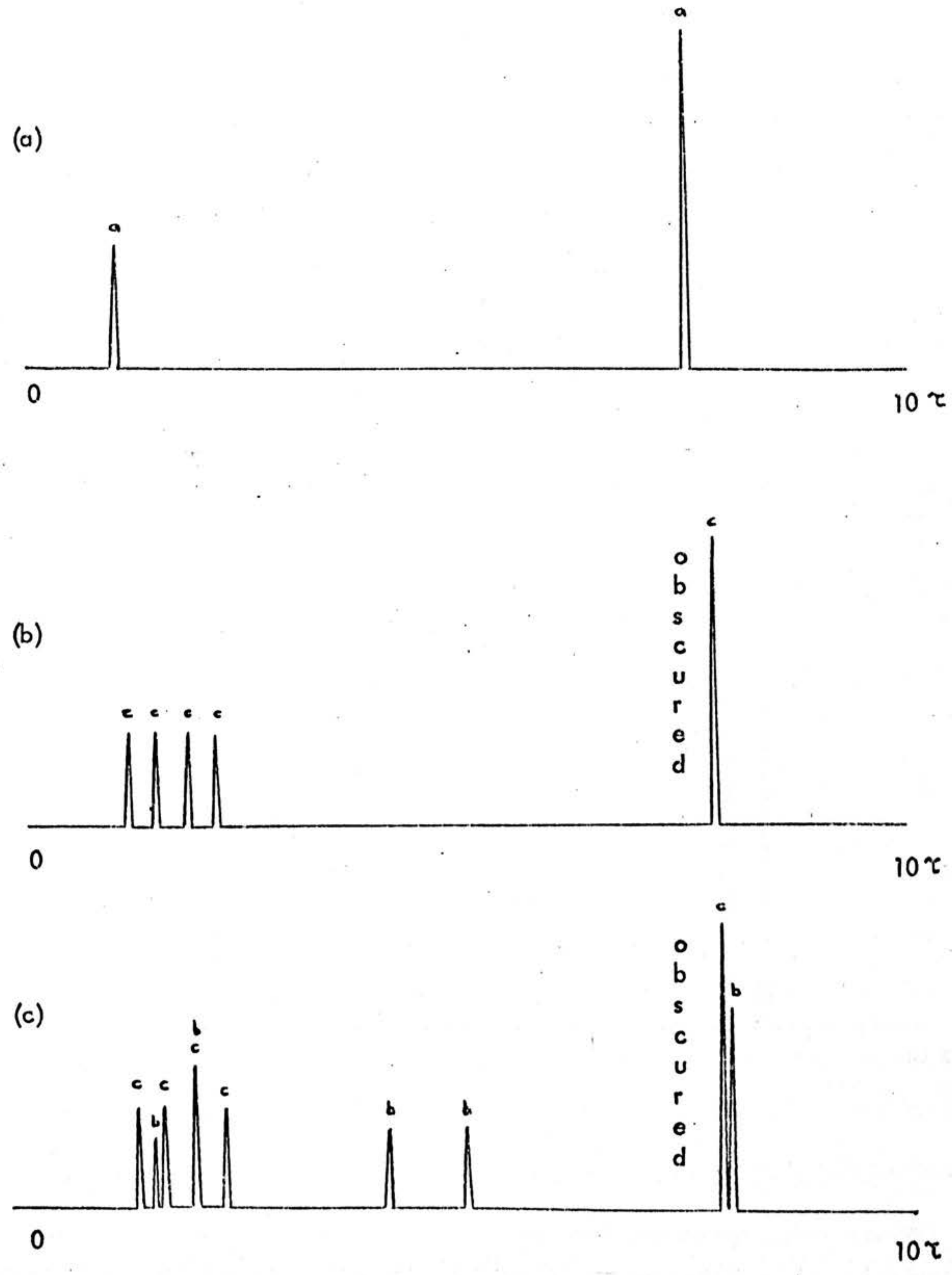


Fig.2.2.17 (a) PMR spectrum of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene(98) in DMSO-d_6. Spectra after the addition of:- (b) 1 equivalent of diethylamine and (c) 0.3 equivalent of triethylamine.

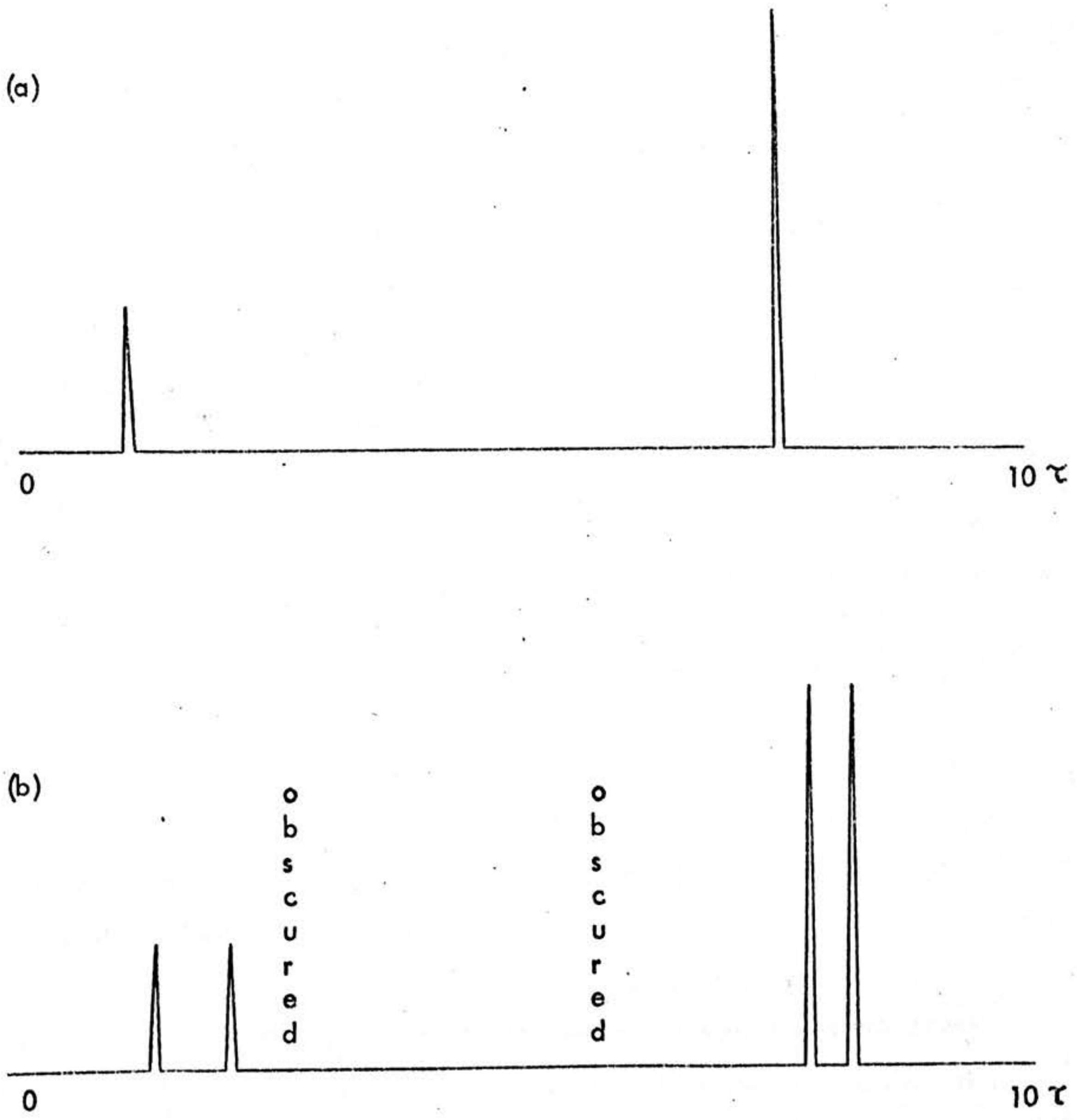
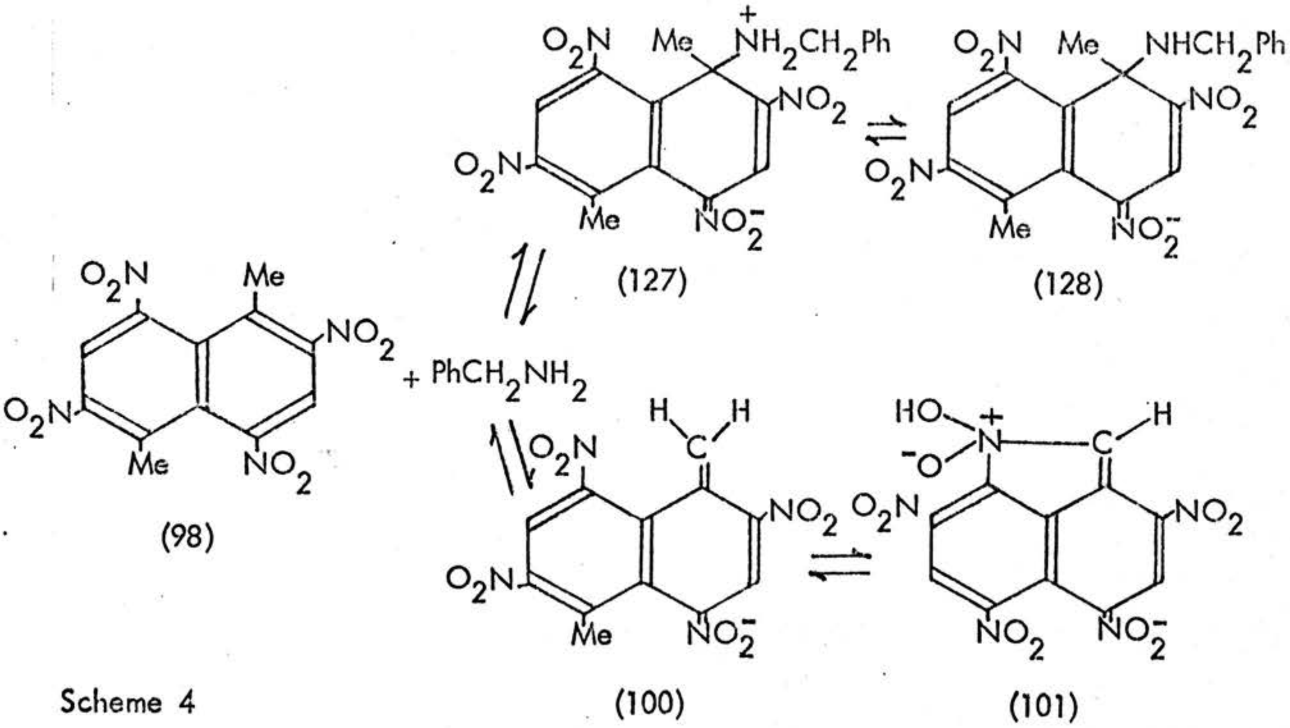


Fig.2.2.18 (a) PMR spectrum of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene(98) in DMSO-d_6. (b) Spectrum after the addition of one equivalent of benzylamine.



Scheme 4

The addition of 2 and 10 equivalents of benzylamine to a solution of compound (98) in d_6-DMSO gives similar PMR spectra to those obtained for the addition of one equivalent of base.

It might be expected that in the presence of excess base the zwitterion (127) would undergo proton abstraction to form the anion (128). However no obvious change in the PMR spectrum occurred on changing the base concentration from 1 to 10 equivalents. It is possible that compounds (127) and (128) exhibit similar PMR spectra(as far as can be measured, due to obscuration by other resonances) or even that on reaction of 1 equivalent of benzylamine with compound (98) the DMSO solvent deprotonates the zwitterion (127) to give species (128).

Stopped-flow spectrophotometry shows 2 steps for the reaction of compound (98) with 100-500 equivalents of benzylamine in DMSO(fig.2.2.19). The first rapid step which accounts for at least 60% of compound (98) is probably due to formation of an addition compound (127) or (128). The slower

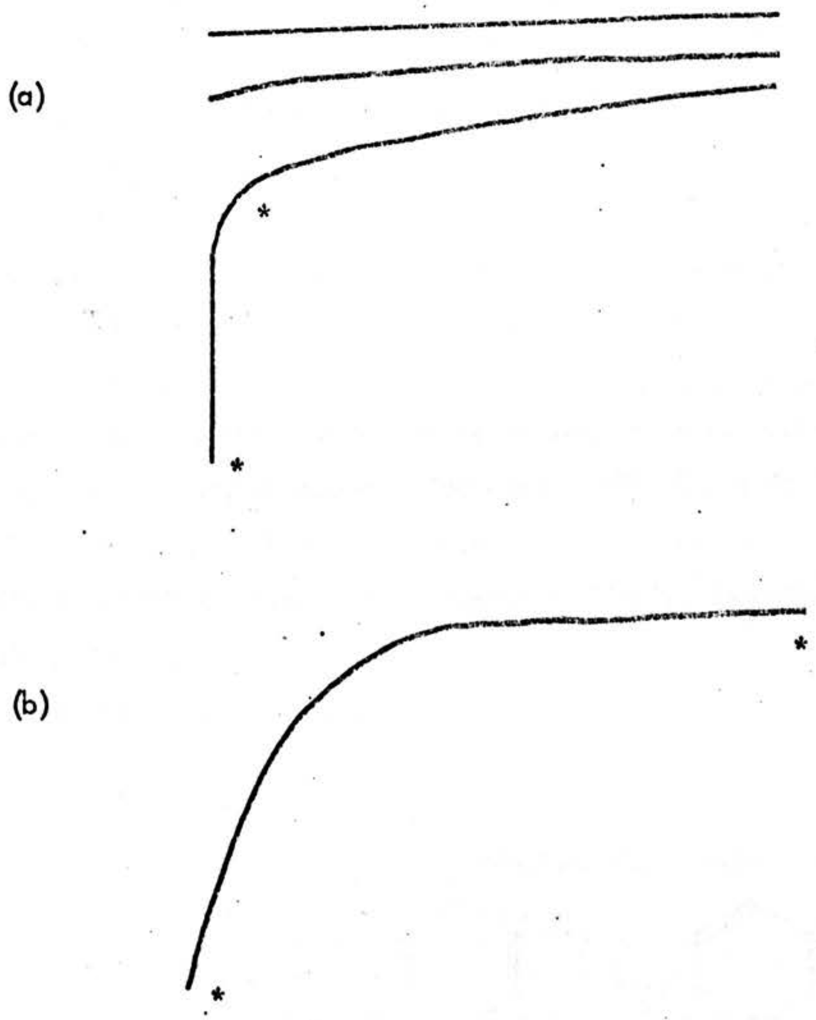


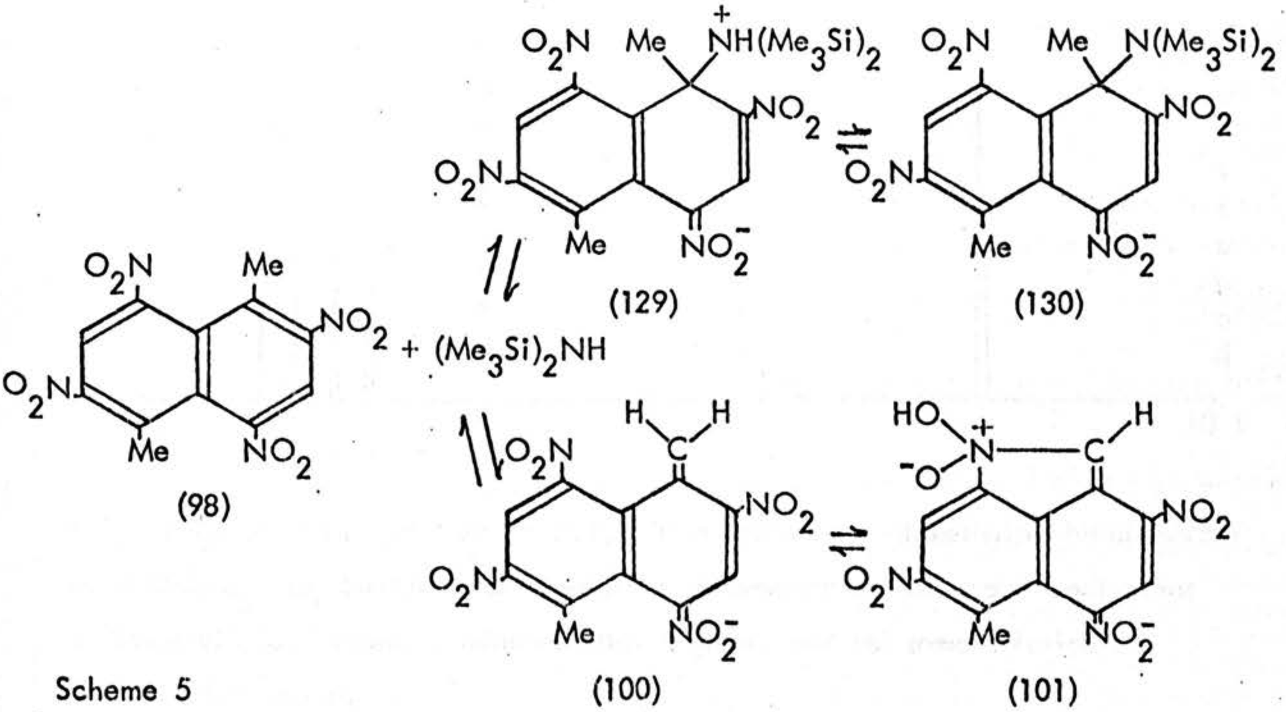
Fig.2.2.19 Stopped-flow traces obtained for the reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene(10^{-4}M) with 500 equivalents of benzylamine in DMSO:-
(a) 86 second scan and (b) 0.4 second scan.

second step is probably due to proton abstraction from compound (98) to give compound (100) which then possibly forms compound (101).

The visible absorbtion maximum of a solution containing 50 equivalents of benzylamine and compound (98) in DMSO occurs at 530nm and this is probably produced by a mixture containing mainly addition compound (127) or (128) and traces of compounds (100) and (101).

(D) Hexamethyldisilazane

The PMR spectrum obtained after reaction for 4 minutes of a solution containing one equivalent of hexamethyldisilazane and compound (98) is shown in fig.2.2.20(b). The presence of a C-1 addition complex (129) or (130) (resonances denoted by letter d) and compound (100)(resonances denoted by letter b) is indicated. Uncertainty exists as to whether the complex occurs in the zwitterionic form (129) or deprotonated form (130). The PMR lines due to compounds (129) or (130) and (100) decrease with time and those due to compound (101), which is more thermodynamically stable, increase with time (fig.2.2.20(c). The competitive reaction pathways accounting for these observations are shown in Scheme 5.



Scheme 5

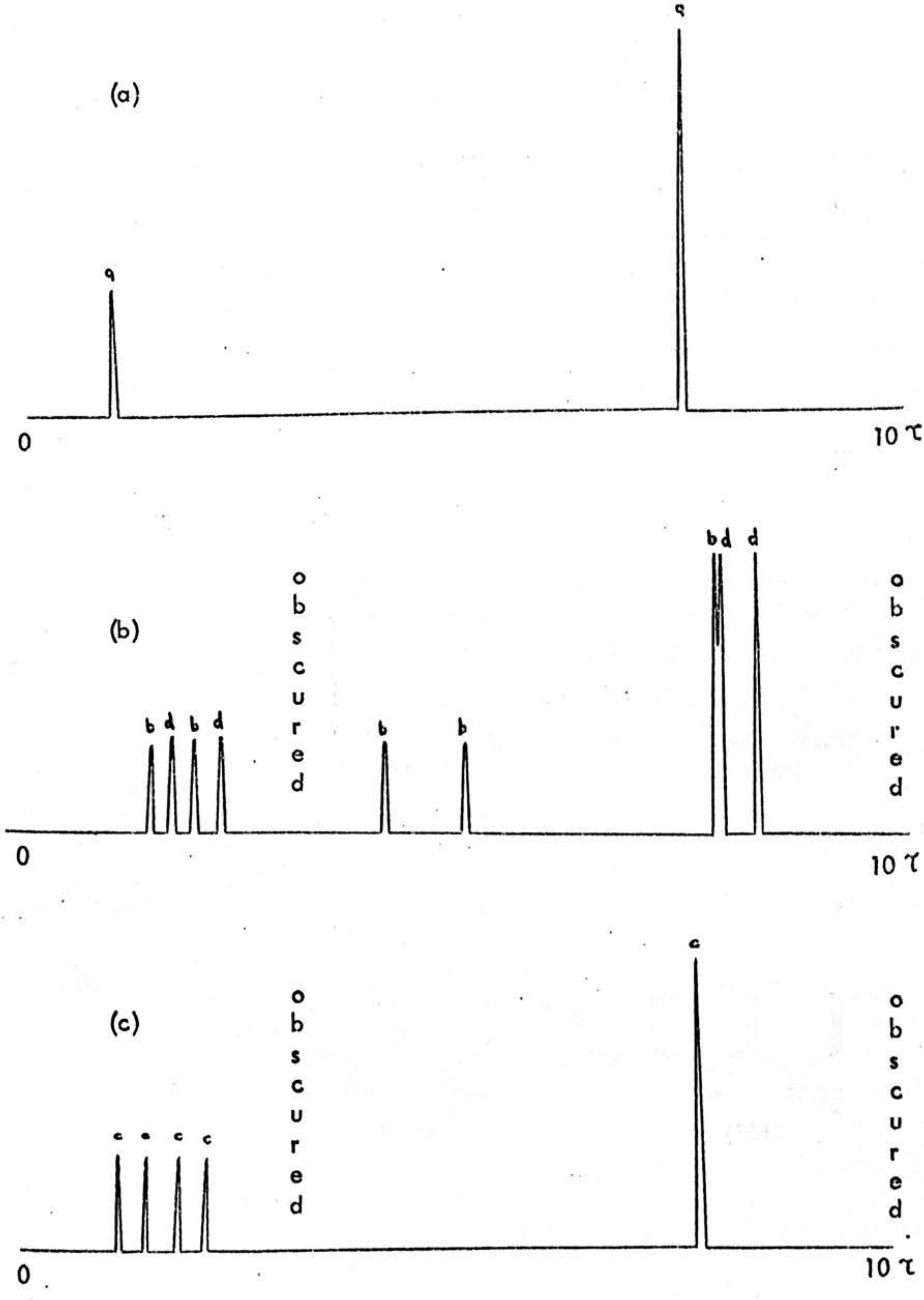
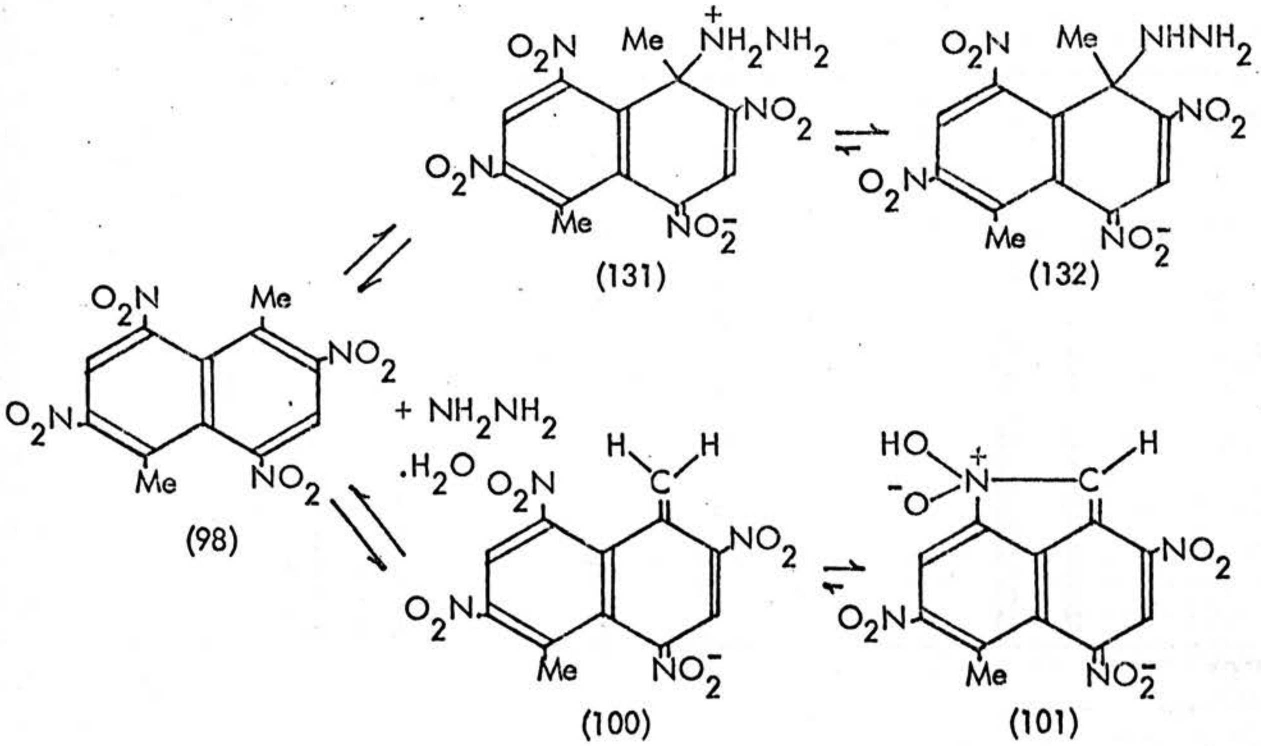


Fig.2.2.20 (a) PMR spectrum of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene(98) in DMSO-d_6. (b) Spectrum of a solution of compound (98) and 1 equivalent of hexamethyldisilazane 5 minutes after mixing, and (c) same solution 50 minutes after mixing.

(E) Hydrazine hydrate

The PMR spectrum of the product of reaction after 5 minutes of one equivalent of hydrazine hydrate with compound (98) in d_6-DMSO is shown in fig.2.2.21(b). The spectrum indicates the formation of a C-1 addition complex (131) or (132)(resonances denoted by letter d) and compound (100)(resonances denoted by letter b). After 30 minutes reaction time the spectrum shows only compound (101) which is probably formed from compounds (100) and (131) or (132) by the reaction pathways shown in Scheme 6.



Scheme 6

The visible absorbtion maximum of the PMR sample diluted, after 20 minutes reaction, with DMSO occurs at 524nm and is probably due to compound (101).

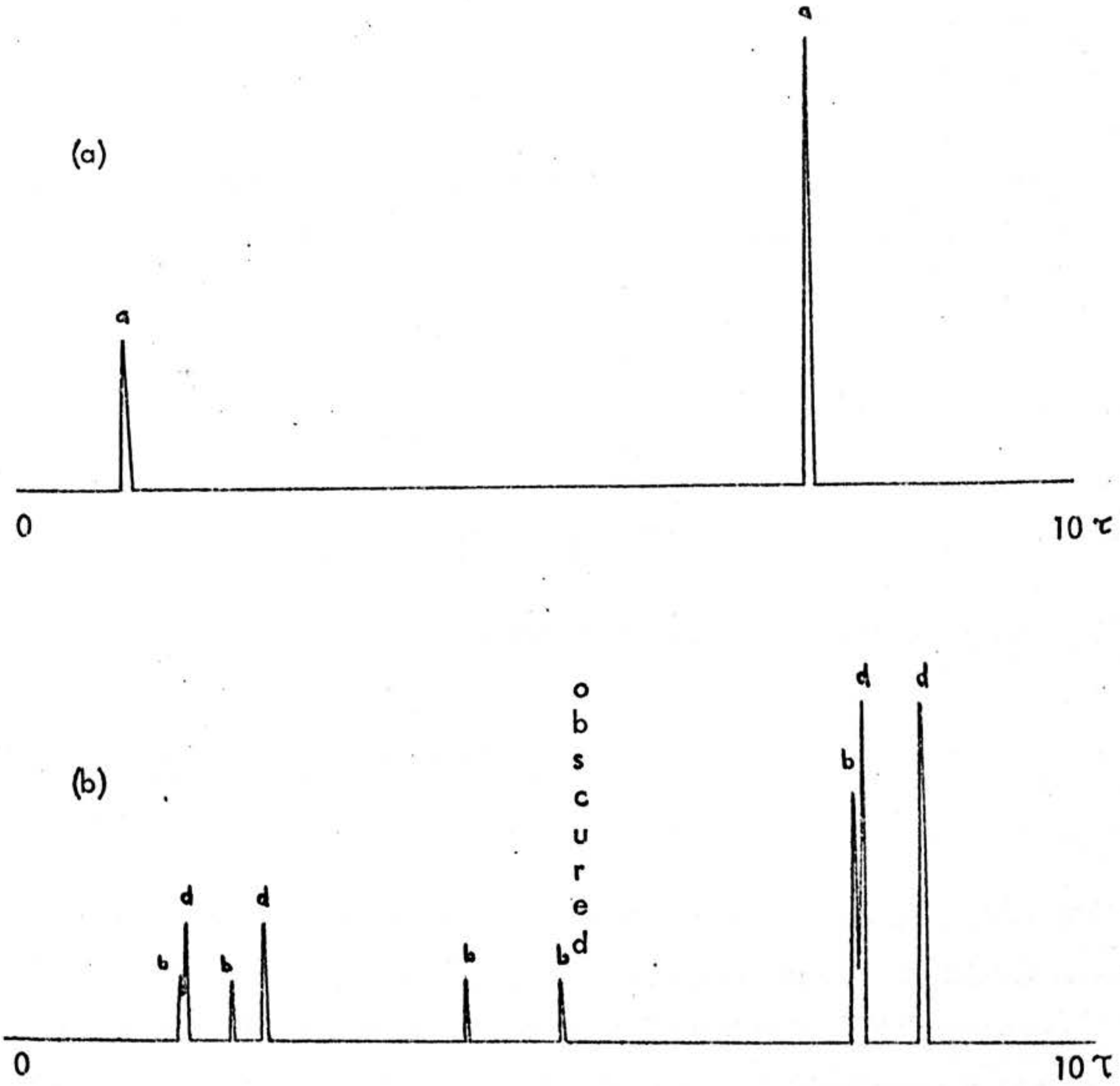
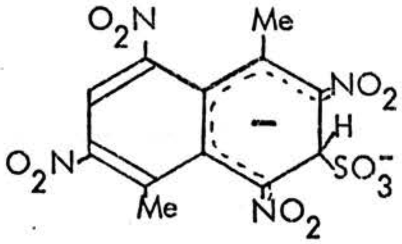


Fig.2.2.21 (a) PMR spectrum of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene(98) in DMSO-d_6. (b) Spectrum obtained 5 minutes after the addition of one equivalent of hydrazine hydrate.

(F) Sulphite ion

The PMR spectrum of the product of the reaction of 3 equivalents of sodium sulphite with compound (98) in aqueous DMSO(1:2) is shown in fig.2.2.22(b). The spectrum indicates that only the C-3 mono-addition complex (105) is formed in agreement with previous work.[109] The visible absorbtion maximum of an aqueous DMSO solution containing excess sulphite ion and compound (98) occurs at 505nm and is probably due to compound (105).



(105)

2.3 Polynitro-1,8-dimethylnaphthalenes

2.3.1 2,4,5-Trinitro-1,8-dimethylnaphthalene(106)

(A) Hydroxide ion

The PMR spectrum of the products of reaction of one equivalent of deuterioxide ion with 2,4,5-trinitro-1,8-dimethylnaphthalene in d_6-DMSO is shown in fig.2.3.1(b). Formation of the 'benzyl-type' anion (142)(resonances denoted by letter b) and of the C-1 addition complex (143)(resonances denoted by letter c) is indicated. The peaks due to compound (143) gradually decrease with time, possibly due to conversion via the reaction pathways shown in Scheme 7 into compound (142) which is more thermodynamically stable.

PMR shows that the reaction of deuterioxide ion with compound (142)(formed from reaction of diethylamine with compound (106)) in d_6-DMSO is consistent with formation of the dianion (144) as indicated by the H-3 resonance at τ 4.1.

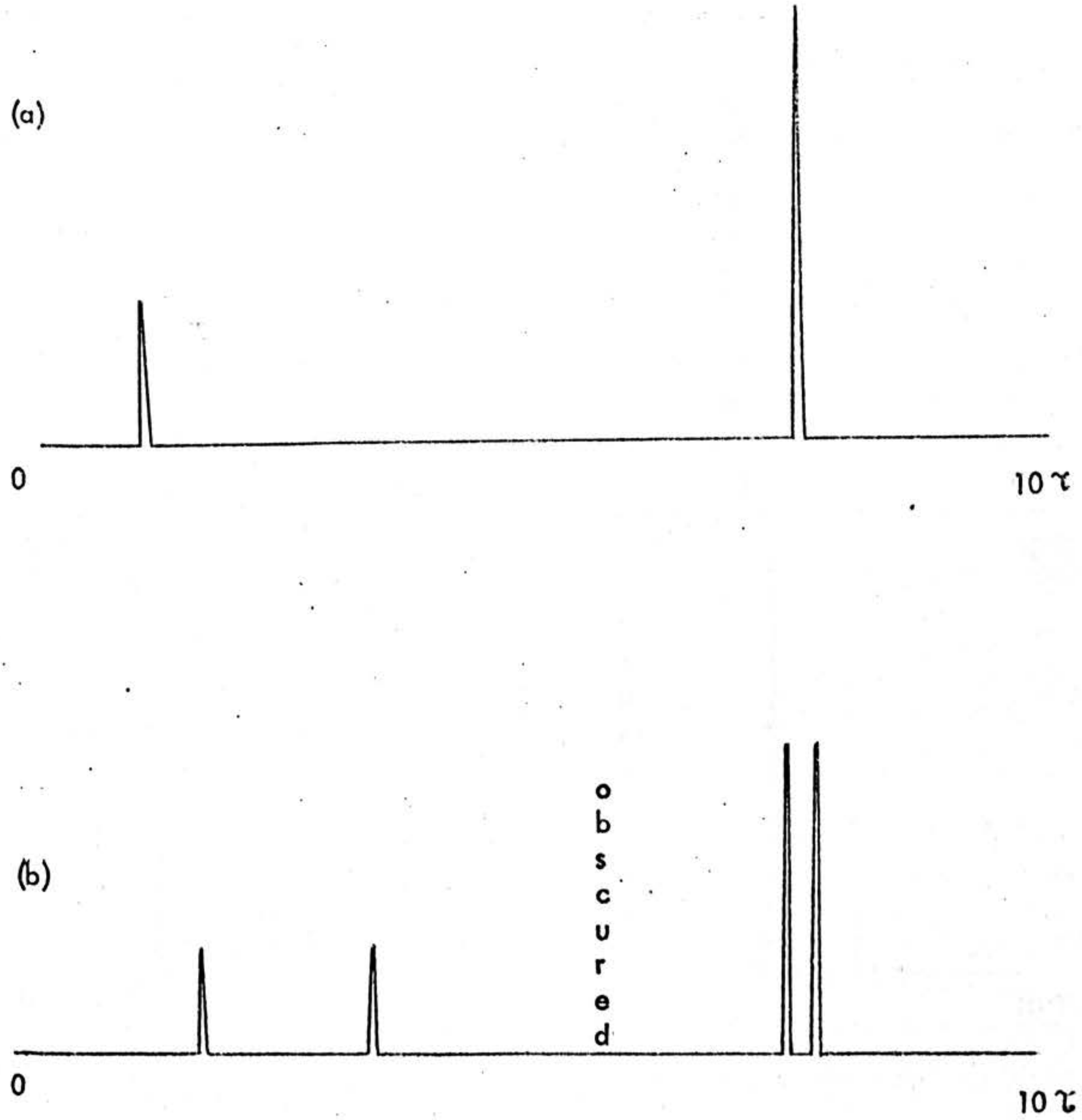


Fig.2.2.22 (a) PMR spectrum of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene(98) in DMSO-d_6. (b) Spectrum after the addition of three equivalents of sulphite ion.

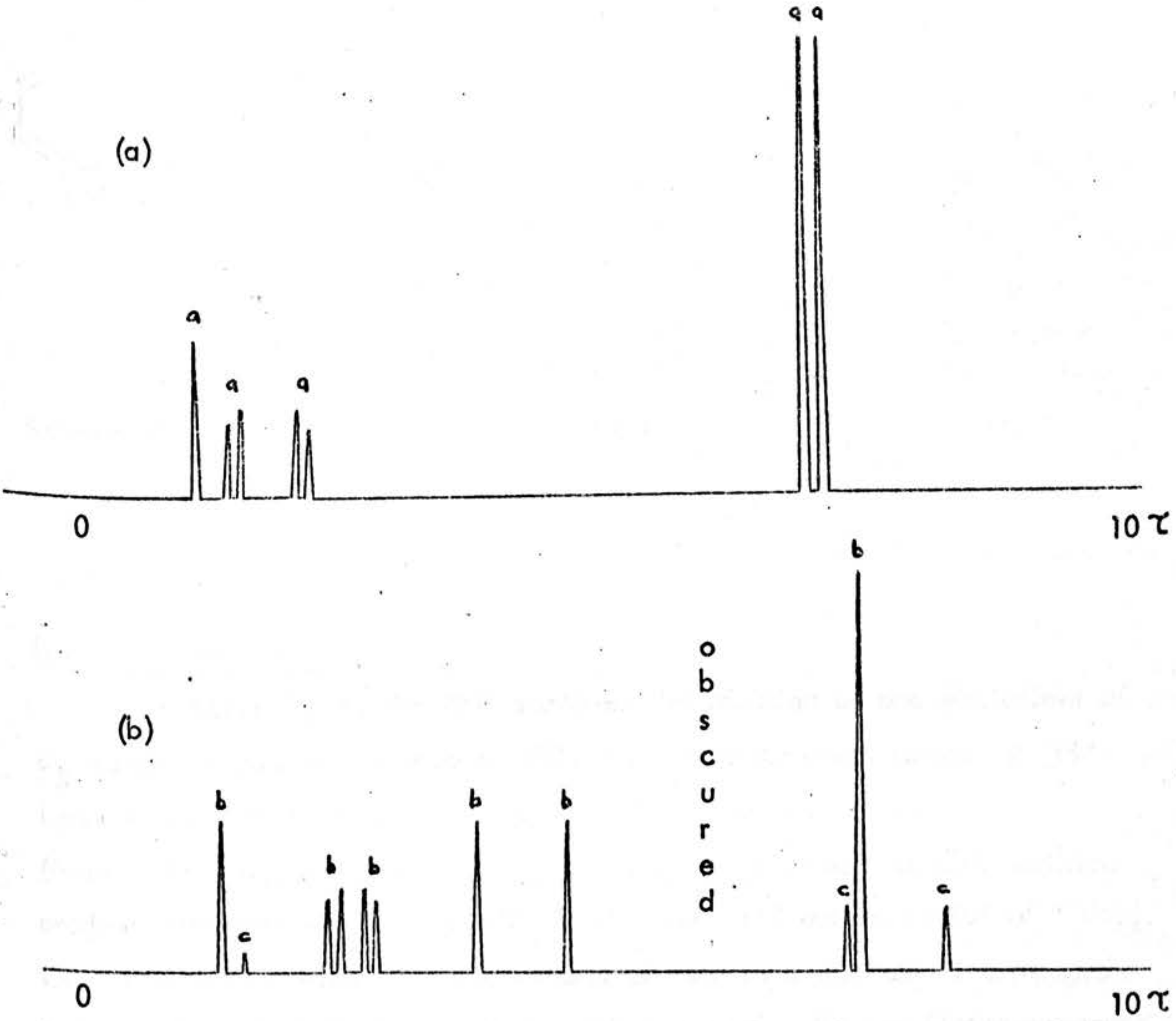
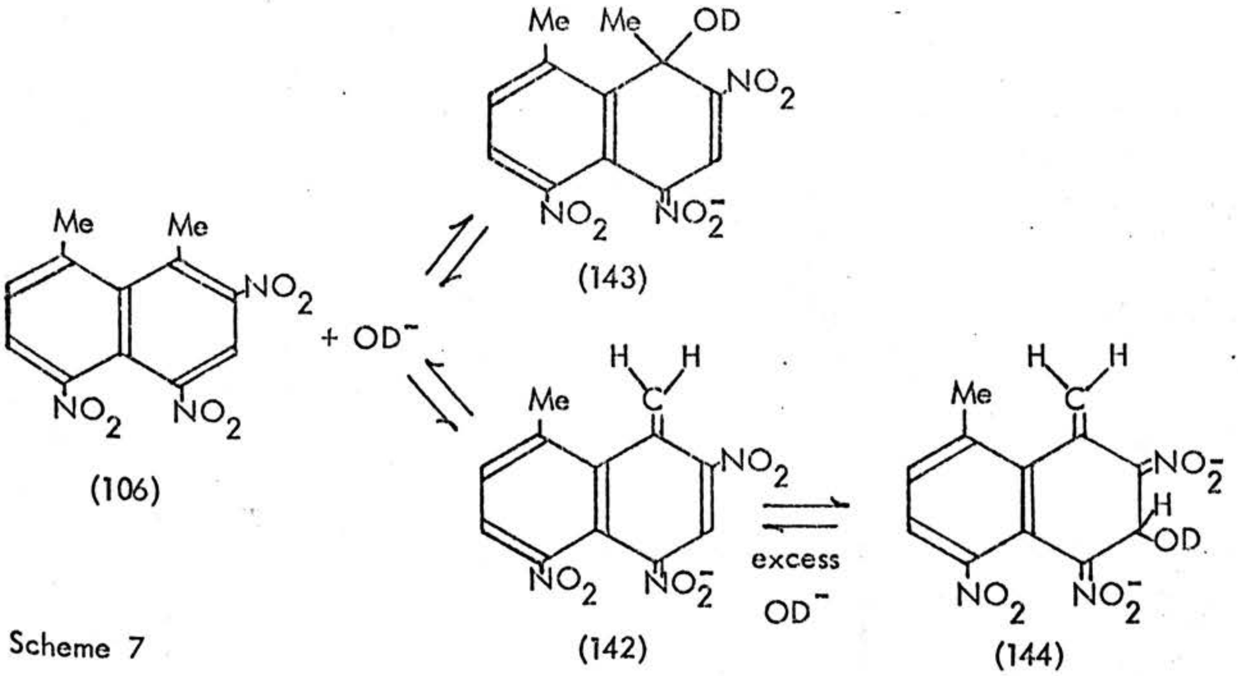


Fig.2.3.1 (a) PMR spectrum of 2,4,5-trinitro-1,8-dimethylnaphthalene(106) in DMSO-d_6. (b) Spectrum after the addition of one equivalent of sodium deuterioxide.



Scheme 7

(B) Methoxide ion

According to the PMR spectrum the reaction of one equivalent of d_3-methoxide ion with compound (106) in d_6-DMSO gives compound (142) (resonances denoted by letter b) and the C-1 addition complex (145) (resonances denoted by letter c)(fig.2.3.2(b)). The amount of C-1 addition product decreases very slowly with time(as measured over a period of 1 day). On addition of a total of 3 equivalents of base to a solution of compound (106) in d_6-DMSO PMR shows that a mixture of the dianion (146)(resonances denoted by letter d) and compound (145)(resonances denoted by letter c) is produced(fig.2.3.2(c)). The olefinic protons of the dianion (145) show a non-zero coupling whereas those of the 'benzyl-type' anion (142) do not show this, in common with itaconic anhydride which possesses an exocyclic $C=CH_2$ group where there is 1,3-conjugation between the olefinic group and another π-bonded group. Scheme 8 shows the probable reaction pathways for the reaction of compound (106) with d_3-methoxide ion in d_6-DMSO.

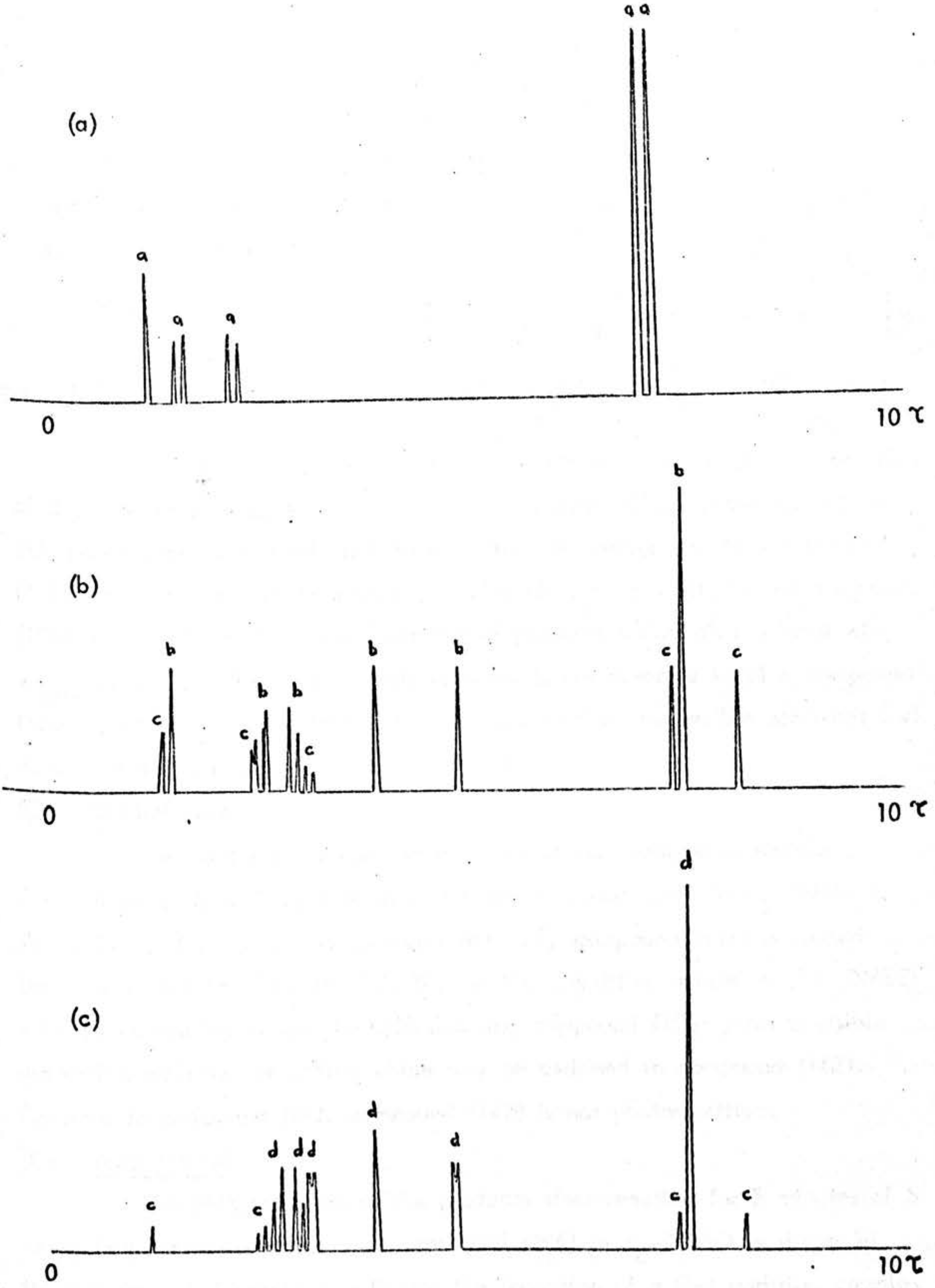
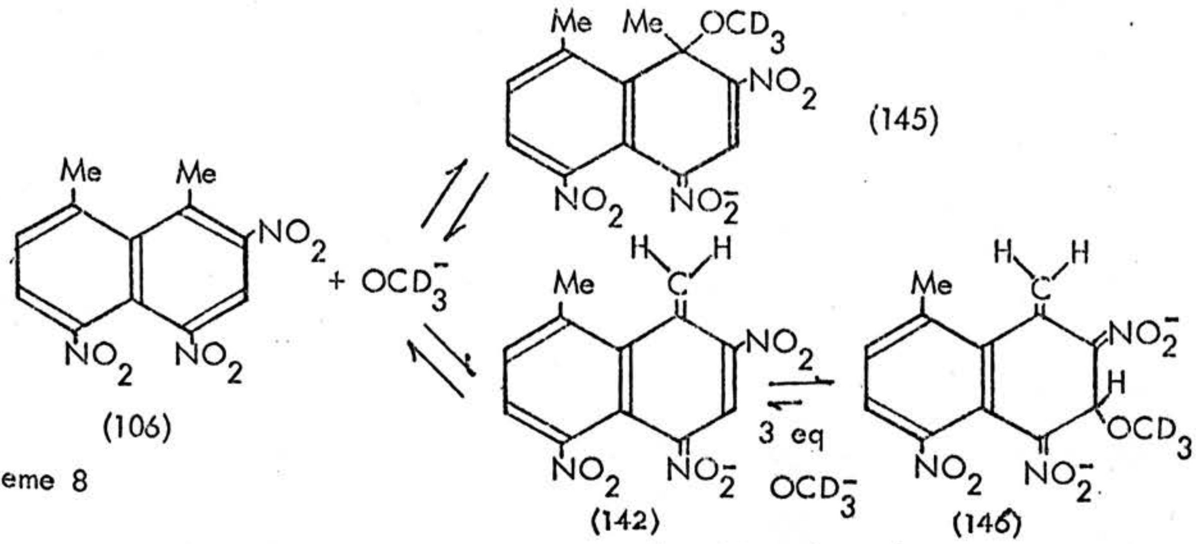


Fig.2.3.2 (a) PMR spectrum of 2,4,5-trinitro-1,8-dimethylnaphthalene(106) in DMSO-d_6. Spectra after the addition of:- (b) 1 equivalent and (c) 3 equivalents of sodium methoxide-d_3.



Scheme 8

The visible absorbtion maximum of the PMR solution(for the reaction of 3 equivalents of d_3-methoxide ion) diluted with DMSO occurs at 549nm. This broad band is probably due to a mixture of compounds (142),(145) and (146). Addition of a large excess of methoxide ion to a solution of compound (106) in DMSO results in the formation of products which give a band with λ_{max} at 510nm. However, as this reaction is not reversed to give compound (106) by neutralising the base, it would appear that irreversible processes such as substitution are occurring.

(C) Diethylamine

The PMR spectrum of the products of the reaction of excess diethylamine(3.5 or 10.5 equivalents) with compound (106) in d_6-DMSO is shown in fig.2.3.3(b). This indicates that only compound (142) is formed (resonances denoted by letter b). The visible absorbtion maximum of a DMSO solution containing excess diethylamine and compound (106) gives a visible absorbtion maximum at 558nm which may be assigned to compound (142). Contrary to compound (94), compound (142) is not photosensitive.

(D) Benzylamine

The PMR spectrum of the products after reaction for 5 minutes of 5 equivalents of benzylamine with compound (106) in d_6-DMSO is shown in fig.2.3.4(b). The spectrum indicates the formation of a C-1 addition complex (147) or (148)(resonances denoted by letter c) and proton abstraction product (142)(resonances denoted by letter b). The lines due to the addition complex decrease as those due to compound (133) increase with time and this process is complete within 1 hour. The overall reaction pathways are shown in Scheme 9.

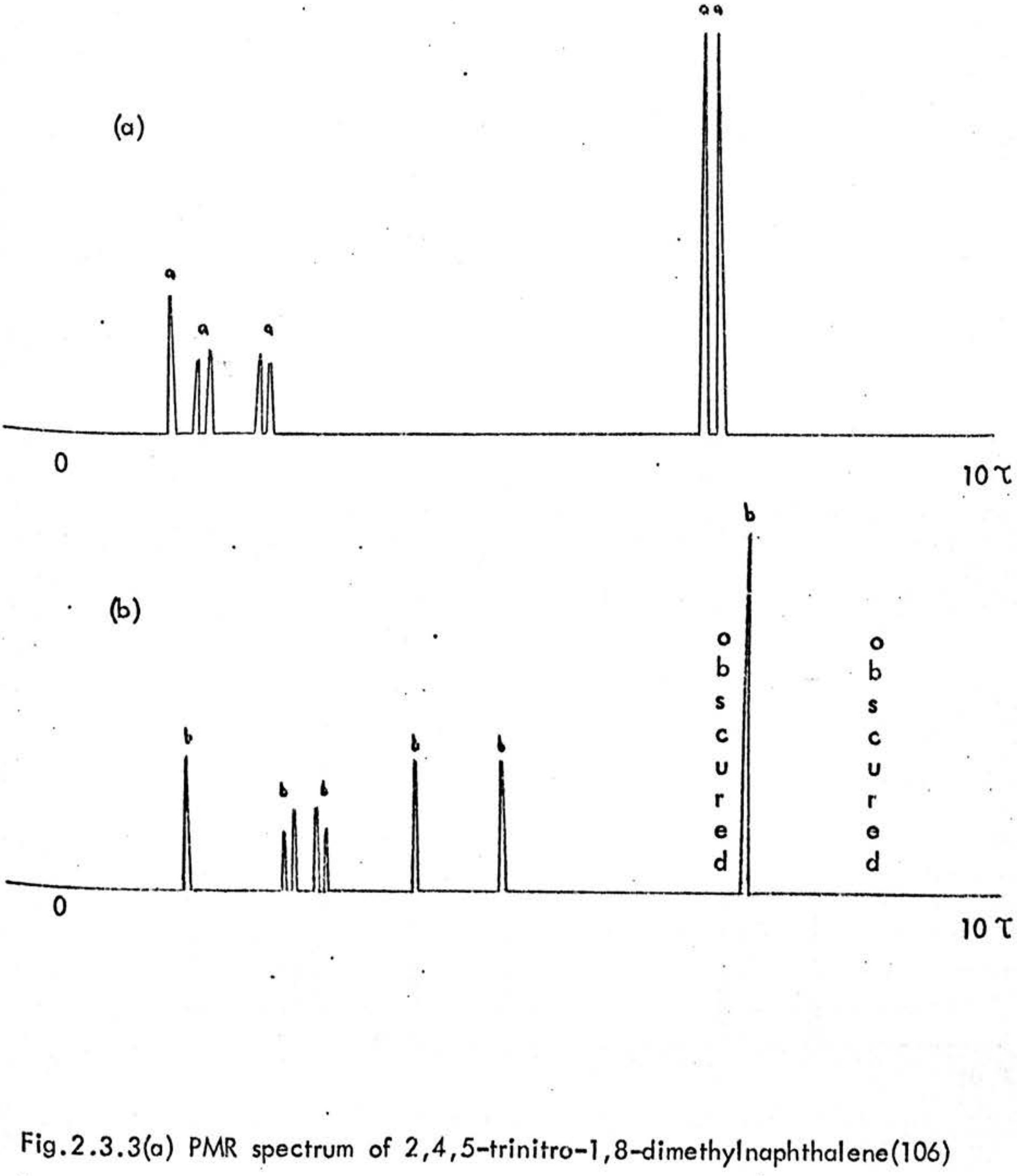


Fig.2.3.3(a) PMR spectrum of 2,4,5-trinitro-1,8-dimethylnaphthalene(106) in DMSO-d_6. (b) Spectrum after the addition of 3.5 or 10.5 equivalents of diethylamine.

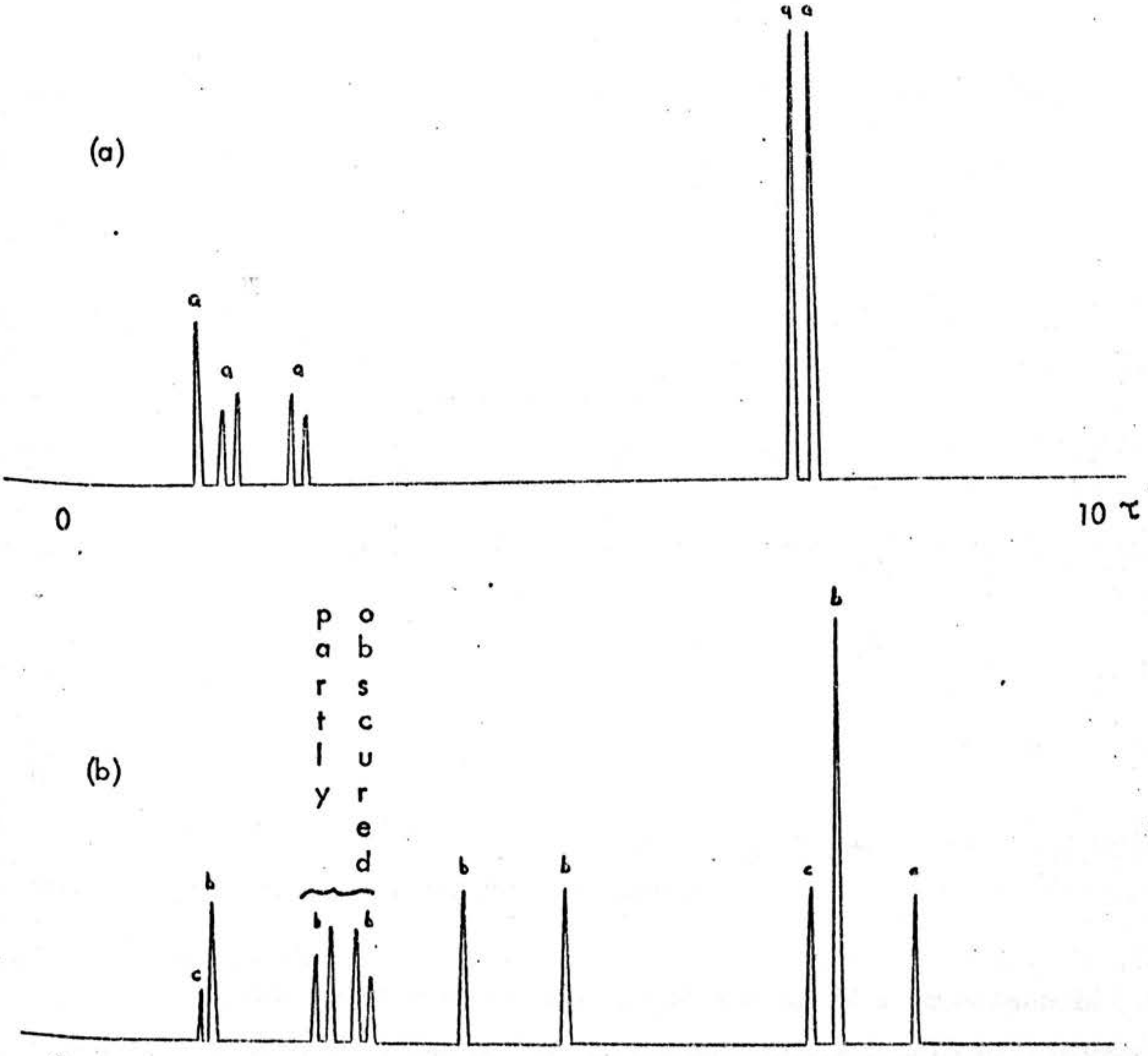
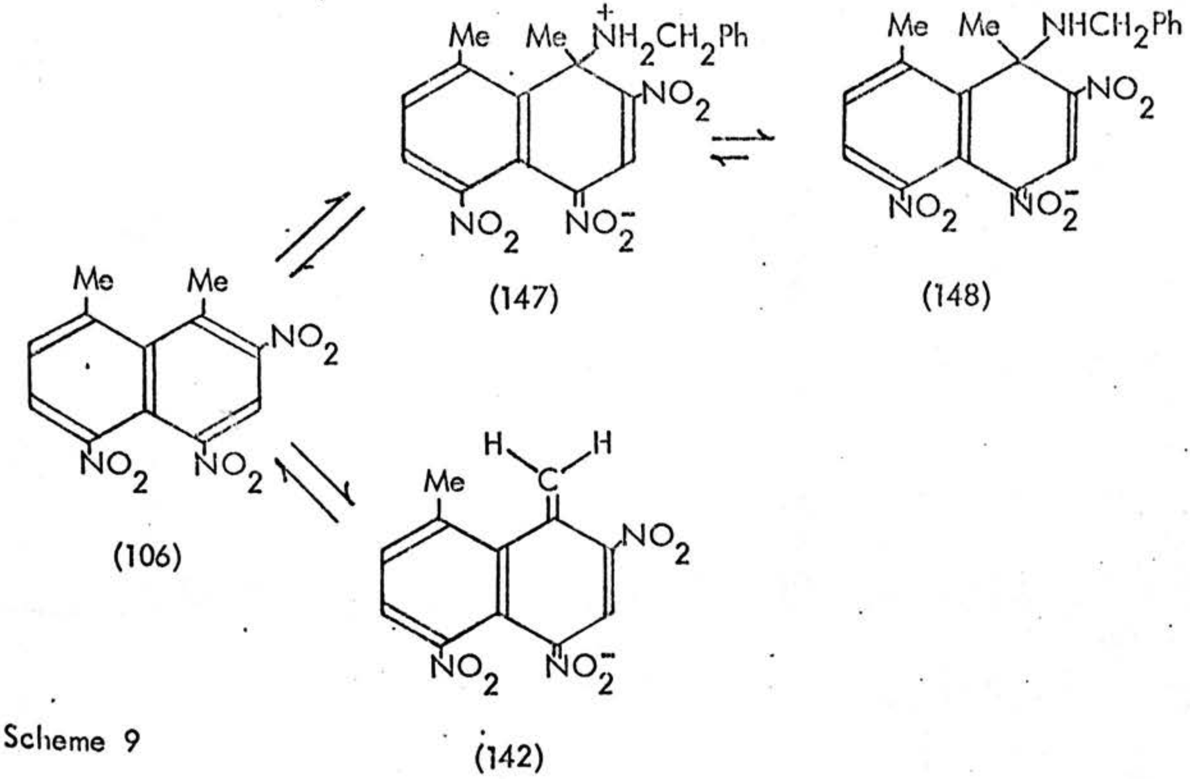


Fig.2.3.4 (a) PMR spectrum of 2,4,5-trinitro-1,8-dimethylnaphthalene(106) in DMSO-d_6. (b) Spectrum obtained 5 minutes after the addition of 5 equivalents of benzylamine.



Scheme 9

(E) Hexamethyldisilazane

PMR shows that the reaction of hexamethyldisilazane with compound (106) in d_6-DMSO gives compound (142) only.

(F) Hydrazine hydrate

The PMR spectrum of the products of reaction of 2 equivalents of hydrazine hydrate with compound (106) in d_6-DMSO(fig.2.3.5(b)) is consistent with the formation of a C-1 addition complex (149) or (150)(resonances denoted by letter c). Subsequently, what appear to be decomposition products and not compound (142) are produced. Scheme 10 indicates the probable products of the reaction of hydrazine hydrate with compound (106) in DMSO although it is not possible to distinguish whether the zwitterion (149) or anion (150) is the stable form of the addition complex.

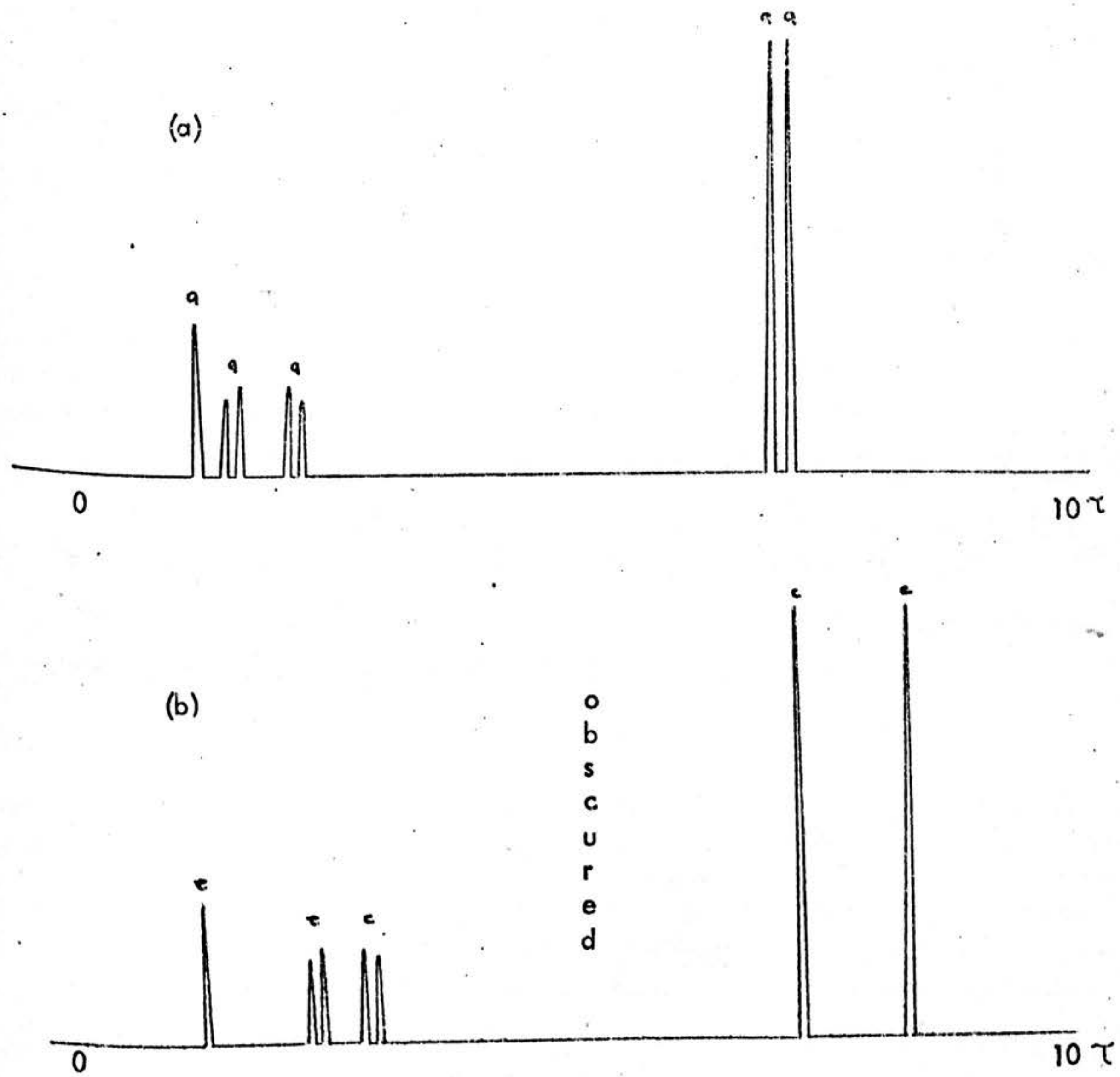
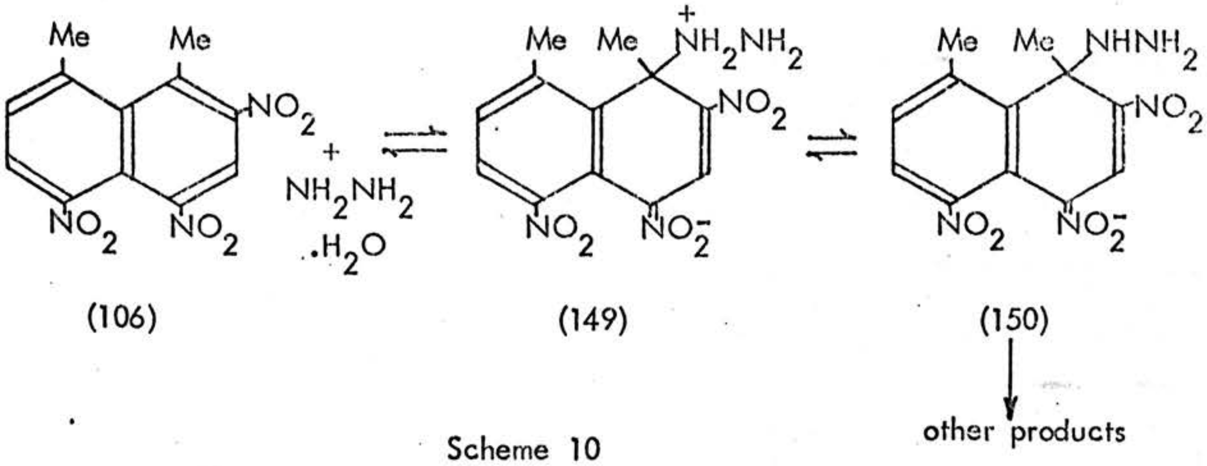


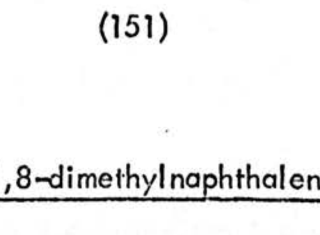
Fig.2.3.5 (a) PMR spectrum of 2,4,5-trinitro-1,8-dimethylnaphthalene(106) in DMSO-d_6. (b) Spectrum after the addition of 2 equivalents of hydrazine hydrate.



Scheme 10

(G) Sulphite ion

The PMR spectrum for the product of reaction of sodium sulphite with compound (106) in aqueous DMSO(1:2) is shown in fig.2.3.6(b). This indicates the formation of a C-3 addition complex (151). The visible absorbtion maximum of the PMR sample diluted with DMSO occurs at 534nm and may be assigned to compound (151).



(151)

2.3.2 2,4,5,7-Tetranitro-1,8-dimethylnaphthalene(107)

(A) Deuterioxide ion

PMR shows that the only product formed in the reaction of 1 equivalent of deuterioxide ion with 2,4,5,7-tetranitro-1,8-dimethylnaphthalene (107) is the 'benzyl-type' anion (109)(resonances denoted by letter b)(fig.2.3.7(b)).

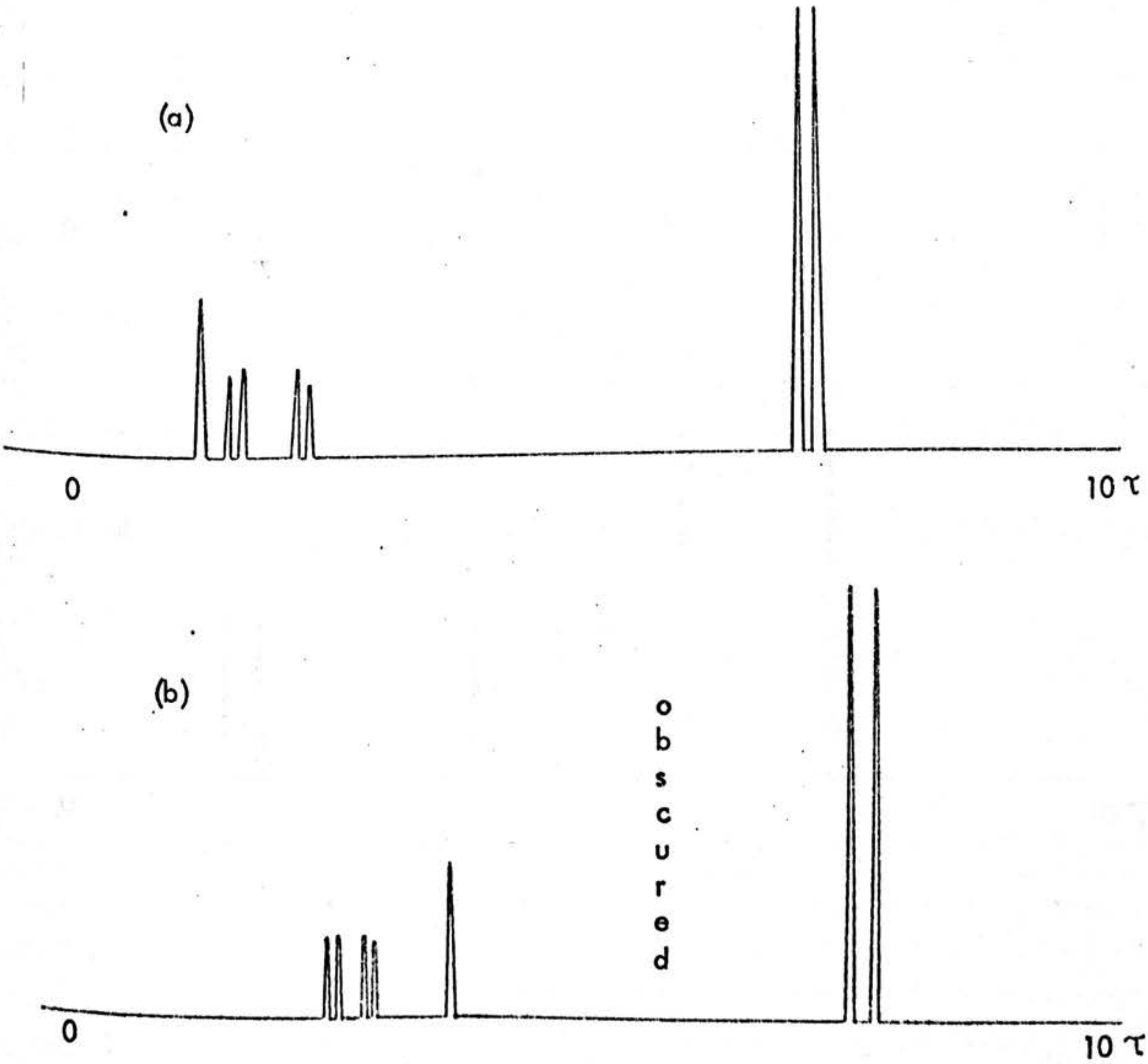


Fig.2.3.6 (a) PMR spectrum of 2,4,5-trinitro-1,8-dimethylnaphthalene(106) in DMSO-d_6. (b) Spectrum after the addition of 2 equivalents of sodium sulphite.

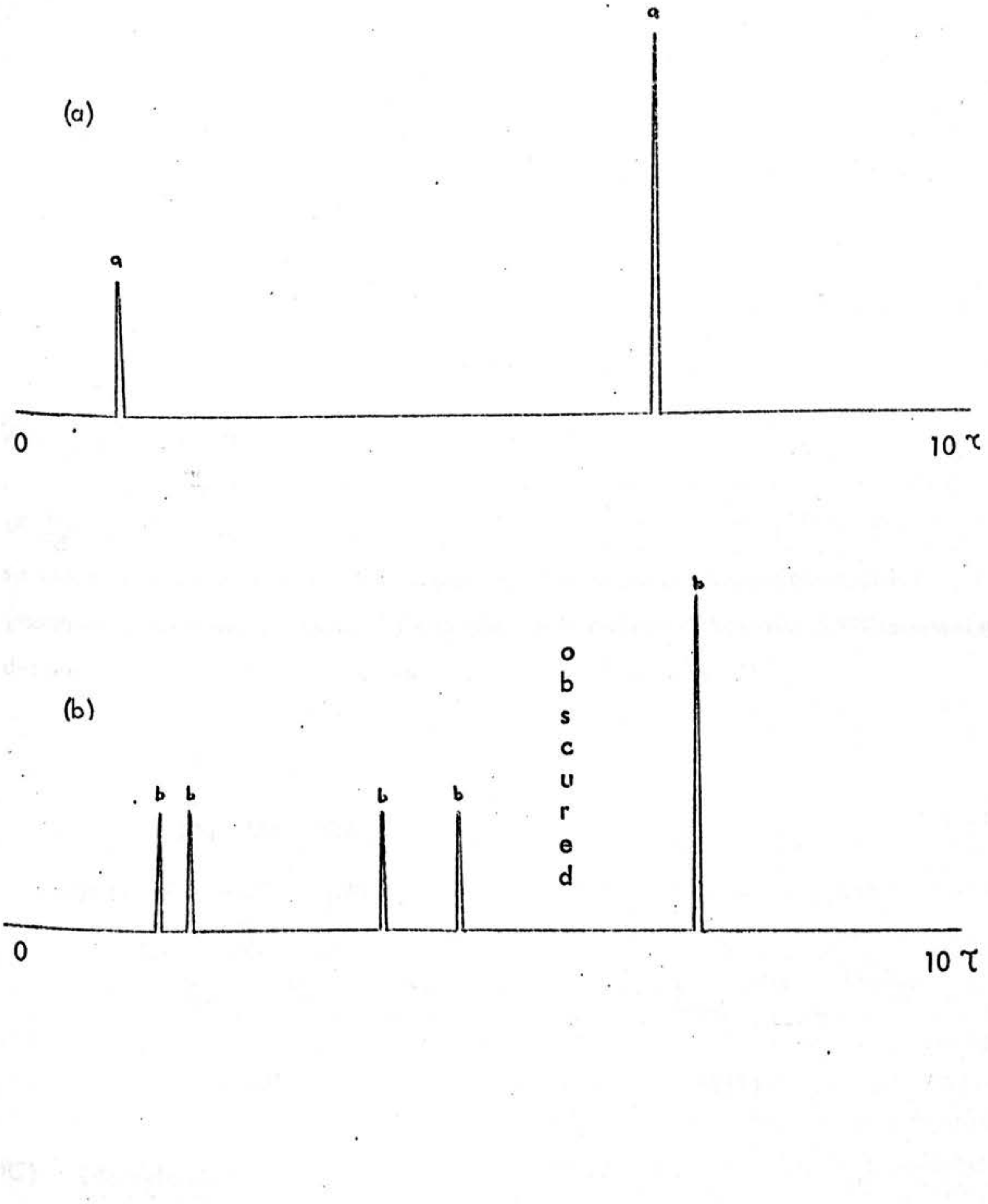
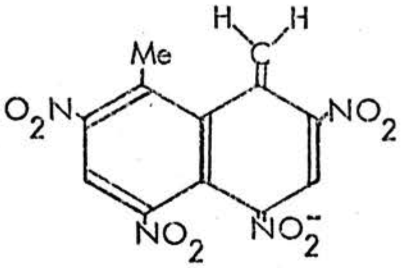


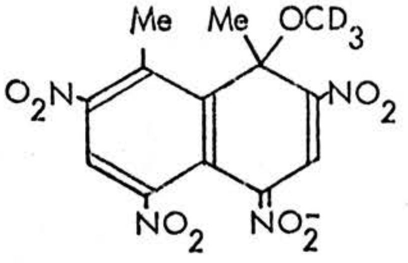
Fig.2.3.7 (a) PMR spectrum of 2,4,5,7-tetranitro-1,8-dimethylnaphthalene(107) in DMSO-d_6. (b) Spectrum after the addition of 1 equivalent of sodium deuterioxide.



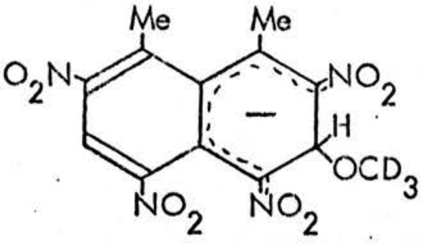
(109)

(B) Methoxide ion

The PMR spectrum of the products of the reaction of 1 equivalent of d_3-methoxide ion with compound (107) is shown in fig.2.3.8(b). The spectrum is consistent with the formation of a mixture of compound (109) (resonances denoted by letter b) and the C-1 addition complex (110)(resonances denoted by letter c), but not the C-3 addition compound (111).



(110)



(111)

(C) Diethylamine

The PMR spectrum of the product of reaction of 2 equivalents of diethylamine with compound (107) indicates the formation of compound (109) (resonances denoted by letter b) only(fig.2.3.9(b)). The visible absorbtion maximum of the PMR sample diluted with DMSO occurs at 535nm and is probably due to compound (109).

(D) Benzylamine

The PMR spectrum of the products of reaction of 2 equivalents of

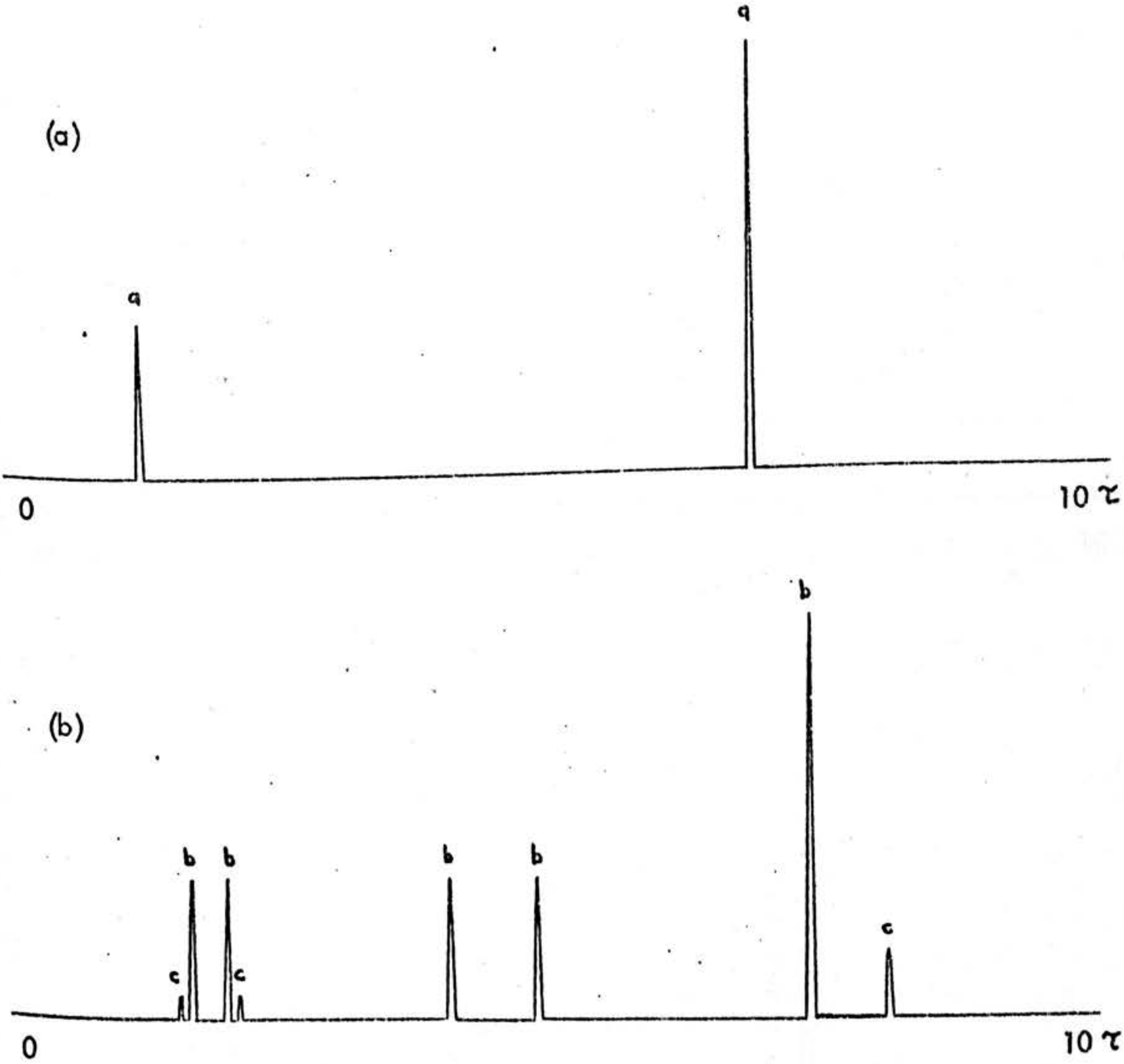


Fig.2.3.8 (a) PMR spectrum of 2,4,5,7-tetranitro-1,8-dimethylnaphthalene(107) in DMSO-d_6. (b) Spectrum after the addition of one equivalent of sodium methoxide-d_3.

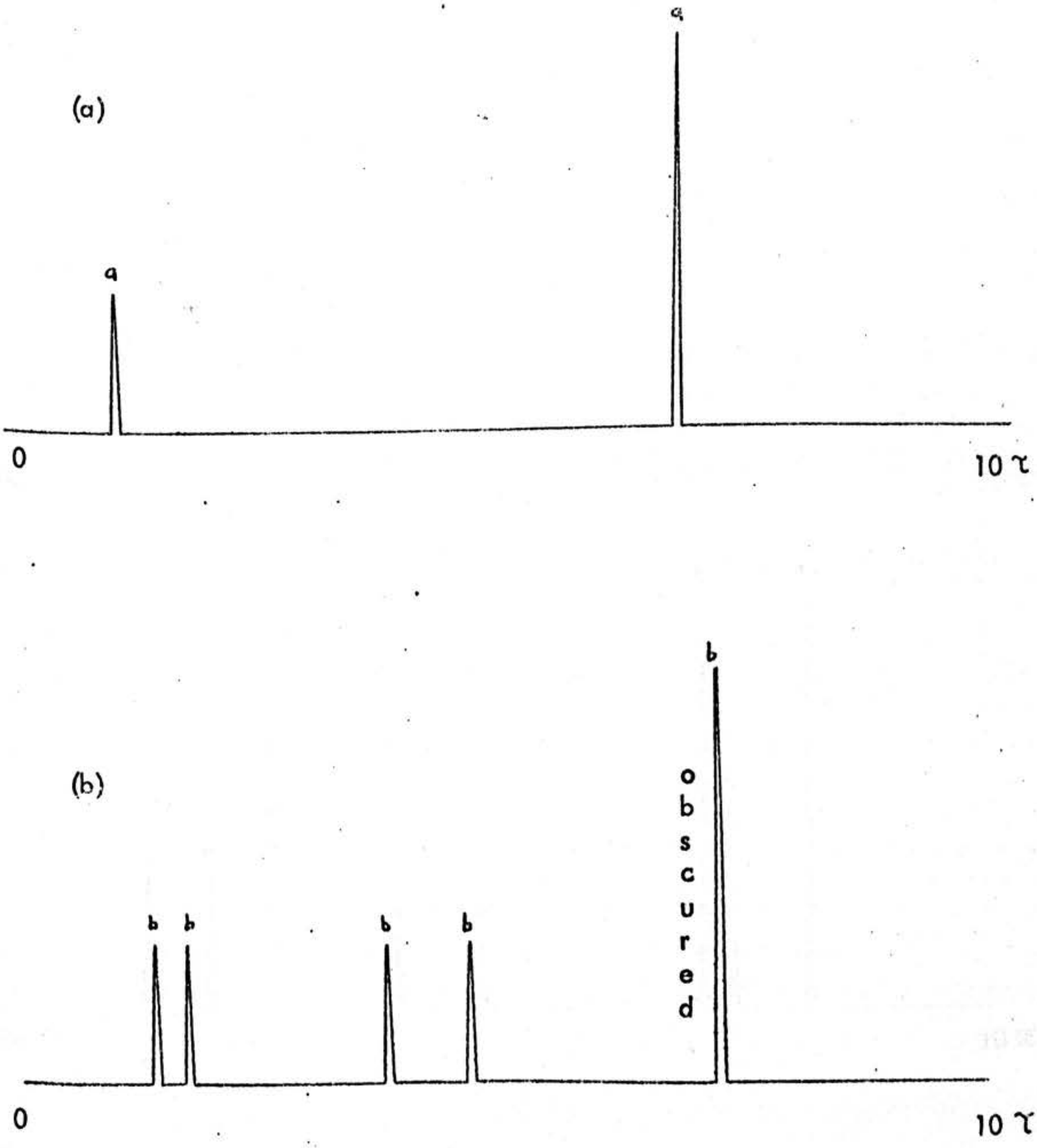


Fig.2.3.9 (a) PMR spectrum of 2,4,5,7-tetranitro-1,8-dimethylnaphthalene(107) in DMSO-d_6. (b) Spectrum after the addition of 2 equivalents of diethylamine.

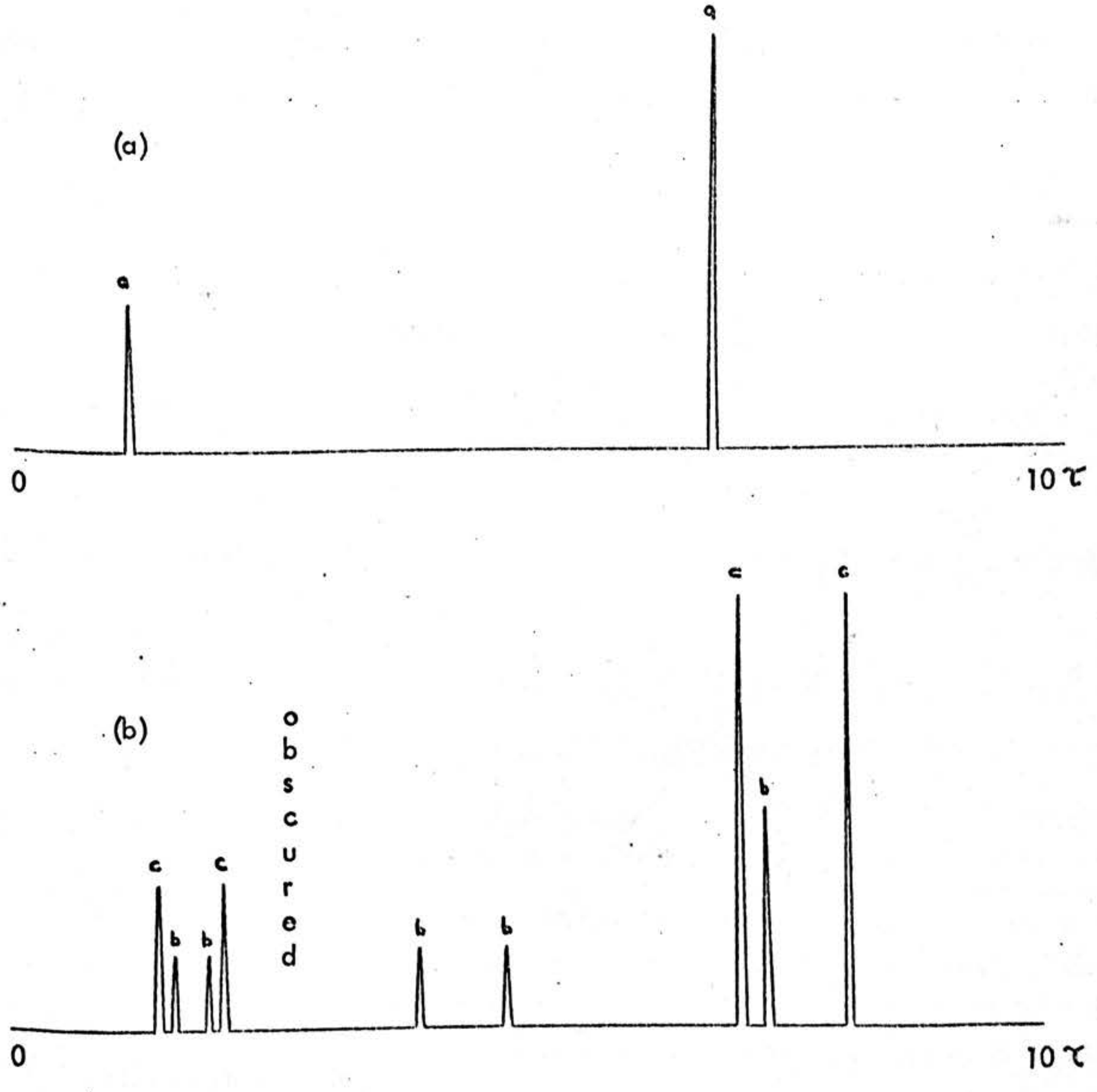
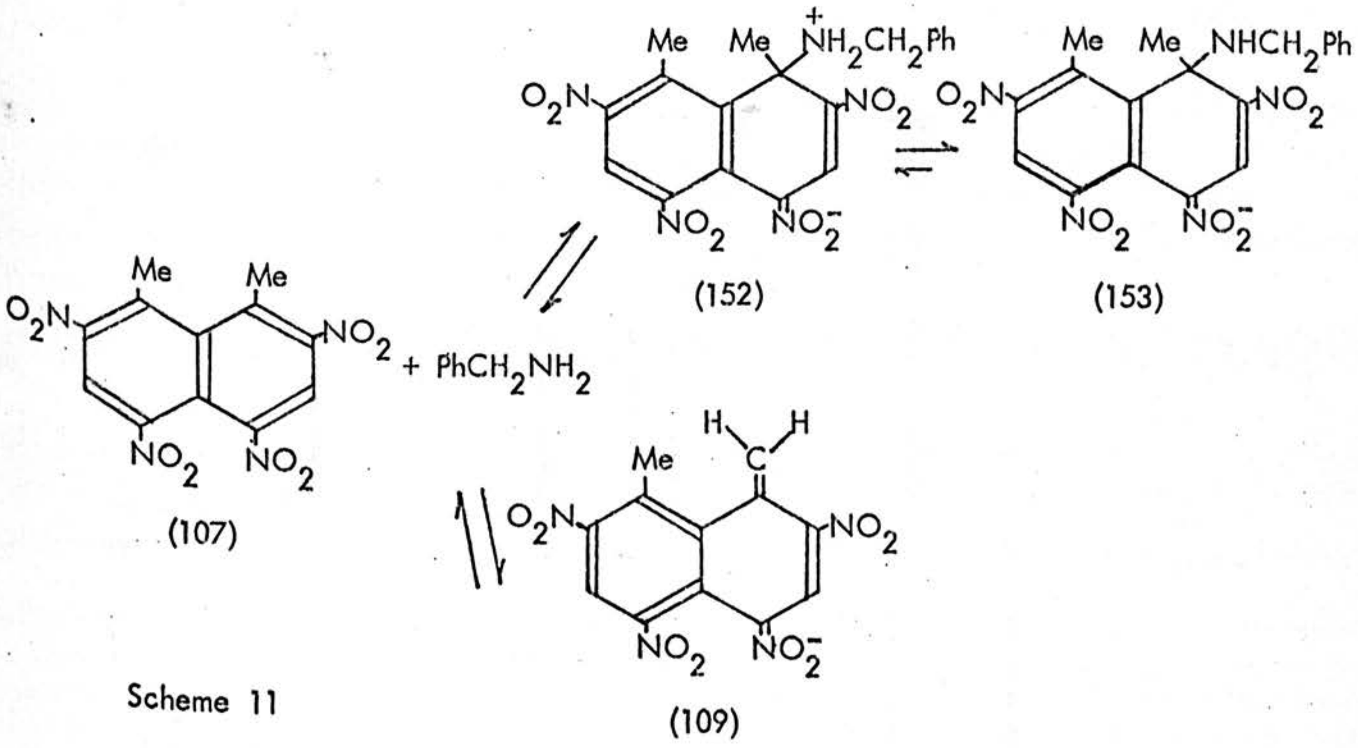


Fig.2.3.10 (a) PMR spectrum of 2,4,5,7-tetranitro-1,8-dimethylnaphthalene(107) in DMSO-d_6. (b) Spectrum 5 minutes after the addition of 2 equivalents of benzylamine.

benzylamine with compound (107) in d_6-DMSO is shown in fig.2.3.10(b). Formation of a C-1 addition complex (152) or (153)(resonances denoted by letter c) and compound (109)(resonances denoted by letter b) is indicated. The lines due to the addition complex decrease and those of compound (107) increase with time. The conversion of compound (152) or (153) to compound (109) probably occurs via the reaction pathways shown in Scheme 11.



Scheme 11

(E) Hexamethyldisilazane

PMR shows that the product of reaction of 1.5 equivalents of hexamethyldisilazane with compound (107) in d_6-DMSO is compound (109).

(F) Hydrazine hydrate

The PMR spectrum of the products formed in reaction of one equivalent of hydrazine hydrate and compound (107) in d_6-DMSO is shown in fig.2.3.11(b). The formation of compound (109)(resonances denoted by letter b)

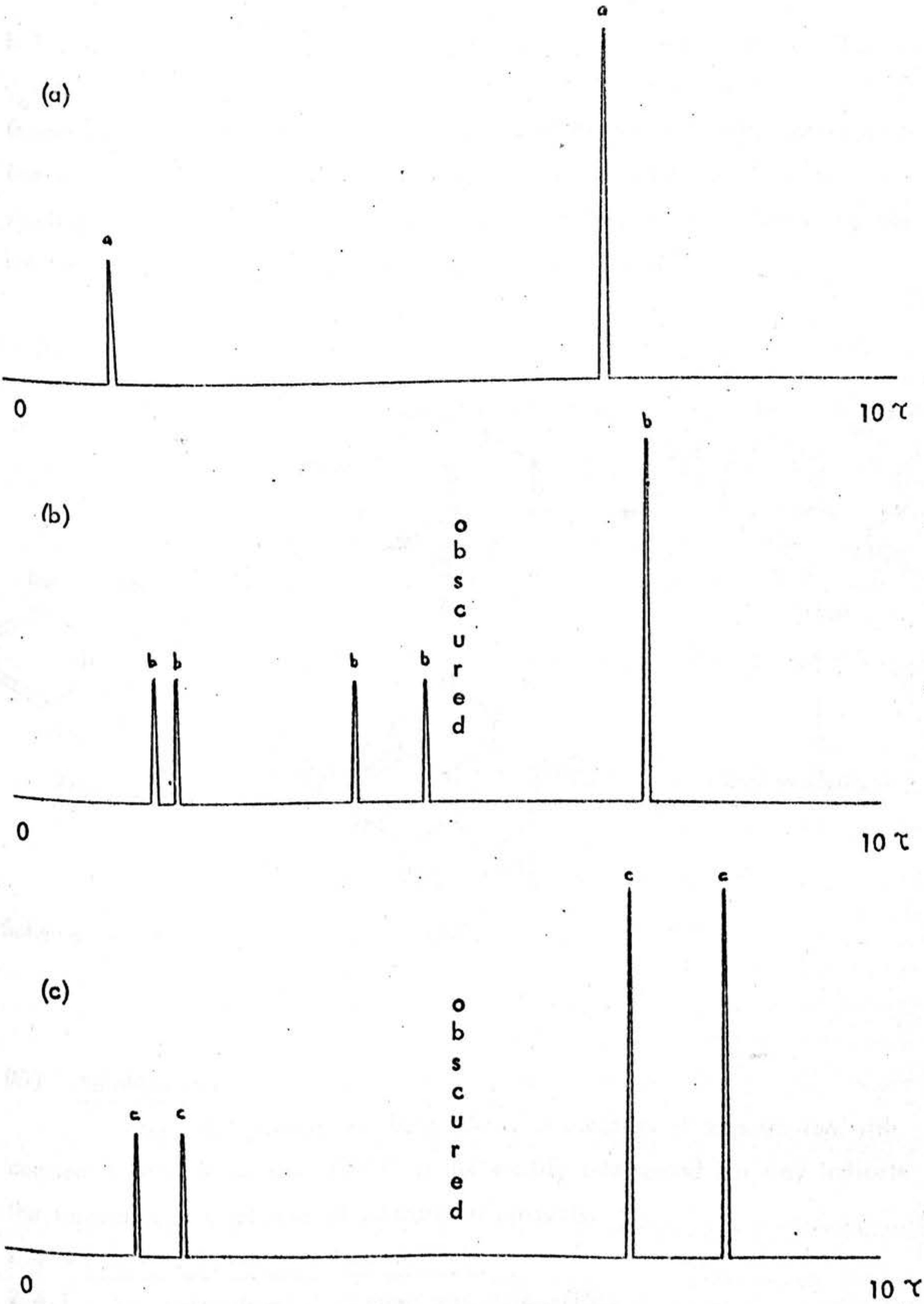
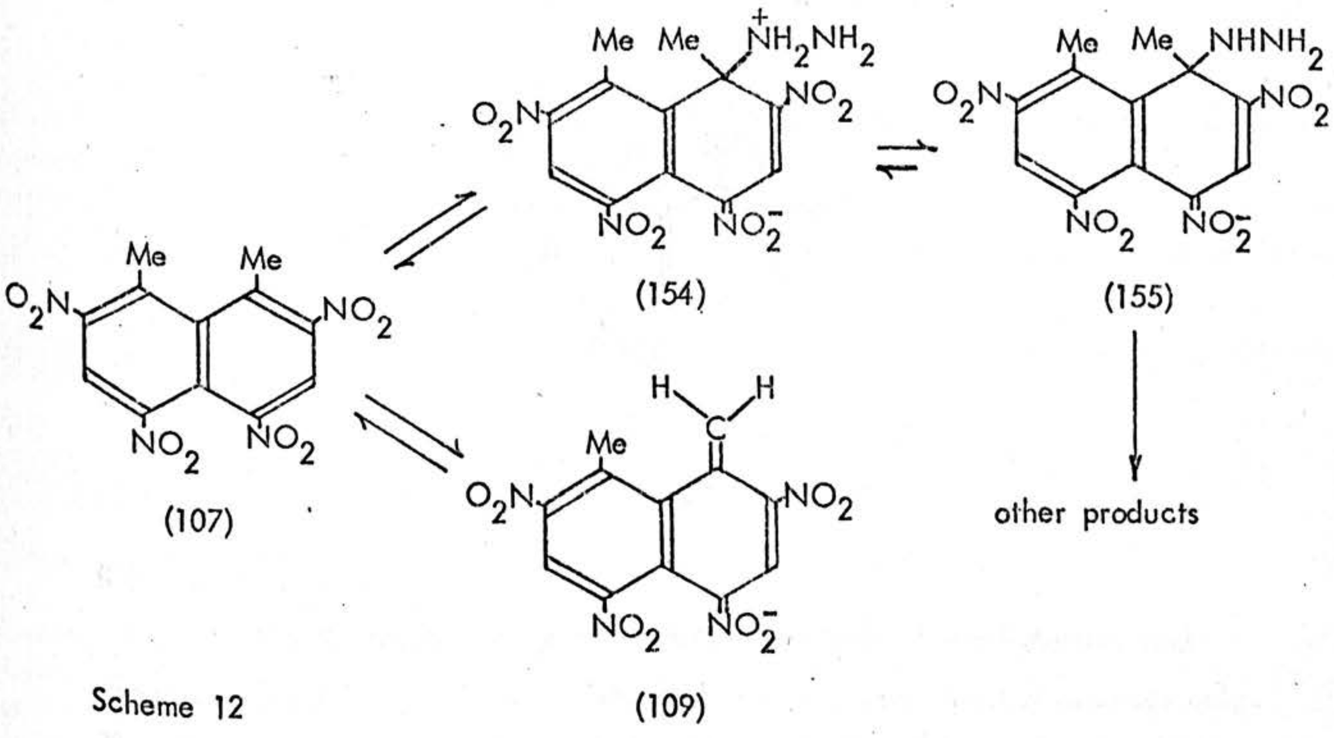


Fig.2.3.11 (a) PMR spectrum of 2,4,5,7-tetranitro-1,5-dimethylnaphthalene(107) in DMSO-d_6. Spectra after the addition of:- (b) 1 equivalent and (c) 3 equivalents of hydrazine hydrate.

is indicated. However 3 equivalents of this base react with compound (107) in d_6-DMSO to give almost exclusively the C-1 addition complex (154) or (155) (resonances denoted by letter c) as shown by PMR(fig.2.3.11(c)). Subsequently, irreversible reactions occur to give other compounds which may include substitution products. Scheme 12 shows the probable reaction pathways for the reaction of hydrazine hydrate with compound (107) in DMSO.



Scheme 12

(G) Sulphite ion

The PMR spectrum of the products of reaction of sulphite ion with compound (107) in aqueous DMSO is not readily interpreted but may indicate the formation of a mixture of substitution products.

2.4 Polynitro-2,3-dimethylnaphthalenes

2.4.1 1,5,7-Trinitro-2,3-dimethylnaphthalene(156)

(A) Hydroxide ion

PMR indicates the formation of products with unknown composition for the reaction of deuterioxide ion with compound (156) in d_6-DMSO.

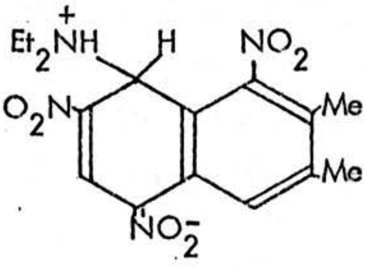
(B) Methoxide ion

The PMR spectrum of the products for the reaction of d_3-methoxide ion with compound (156) in d_6-DMSO shows the formation of a complex mixture of compounds. Although uncertainty exists, there is a resonance at τ 4.0 which is suggestive as being due to an addition complex (157)(probably C-8 by analogy with the reaction of methoxide ion and 1,4,5,7-tetranitro-2,3-dimethylnaphthalene[109]).

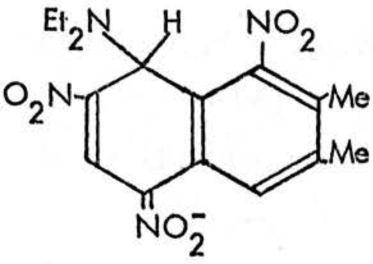
(157)

(C) Diethylamine

The PMR spectrum of the reaction products of diethylamine and compound (156) in d_6-DMSO showed low intensity broadened resonances only. The visible absorbtion maximum of the diluted PMR sample occurred at 531nm, but whether this is due to the C-8 zwitterionic (158) or anionic (159) adducts is open to doubt.



(158)

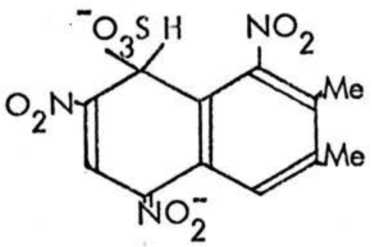


(159)

(D) Sulphite ion

The PMR spectrum of the product of reaction of sodium sulphite with compound (156) in aqueous DMSO is shown in fig.2.4.1(b). Previous results indicate that this is consistent with formation of the C-8 rather than C-6 adduct.[109]

The visible absorbtion maximum of the PMR sample diluted with aqueous DMSO occurs at 543nm and is probably due to compound (160).



(160)

2.4.2 1,4,5,7-Tetranitro-2,3-dimethylnaphthalene(161)

(A) Hydroxide, diethylamine and benzylamine

Reaction of hydroxide ion, diethylamine or benzylamine with compound (161) in d_6-DMSO gives rise to products which exhibit broadened PMR spectra. This may be indicative of the formation of insoluble solids or free radicals.

(B) Sulphite ion

The PMR spectrum of the product of the reaction of 1-3 equivalents of sodium sulphite with compound (161) in aqueous d_6-DMSO is shown in fig.2.4.2(b). The spectrum is consistent with the formation of a C-8 mono-adduct (60), which has previously been postulated(See section 1.2.9).

The stopped-flow trace for the reaction of 10 equivalents of sulphite ion with compound (161) in aqueous DMSO(1:4) shows one rapid step (fig.2.4.3) which probably corresponds to the formation of compound (60).

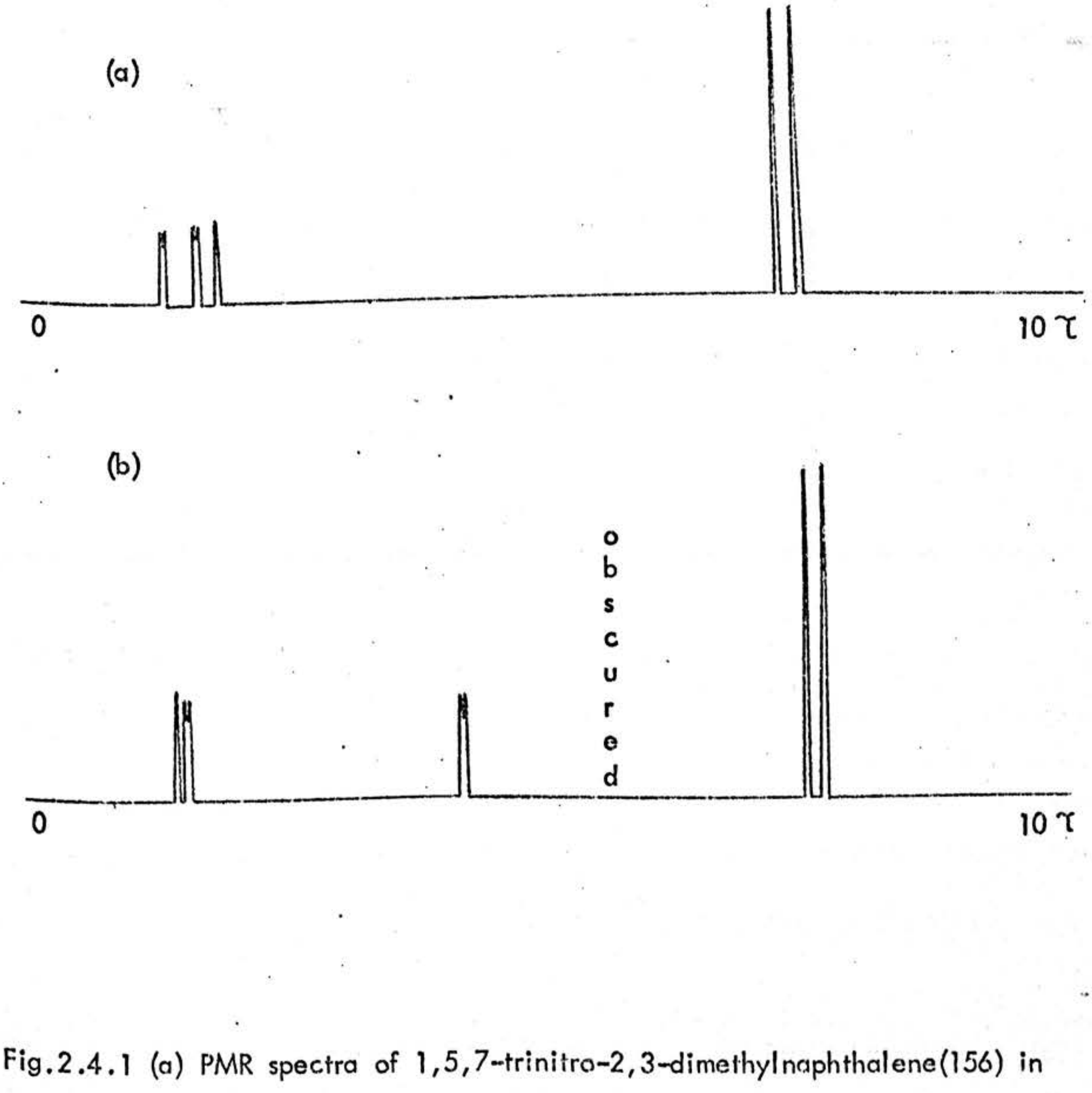


Fig.2.4.1 (a) PMR spectra of 1,5,7-trinitro-2,3-dimethylnaphthalene(156) in DMSO-d_6 and (b) after addition of one equivalent of sodium sulphite.

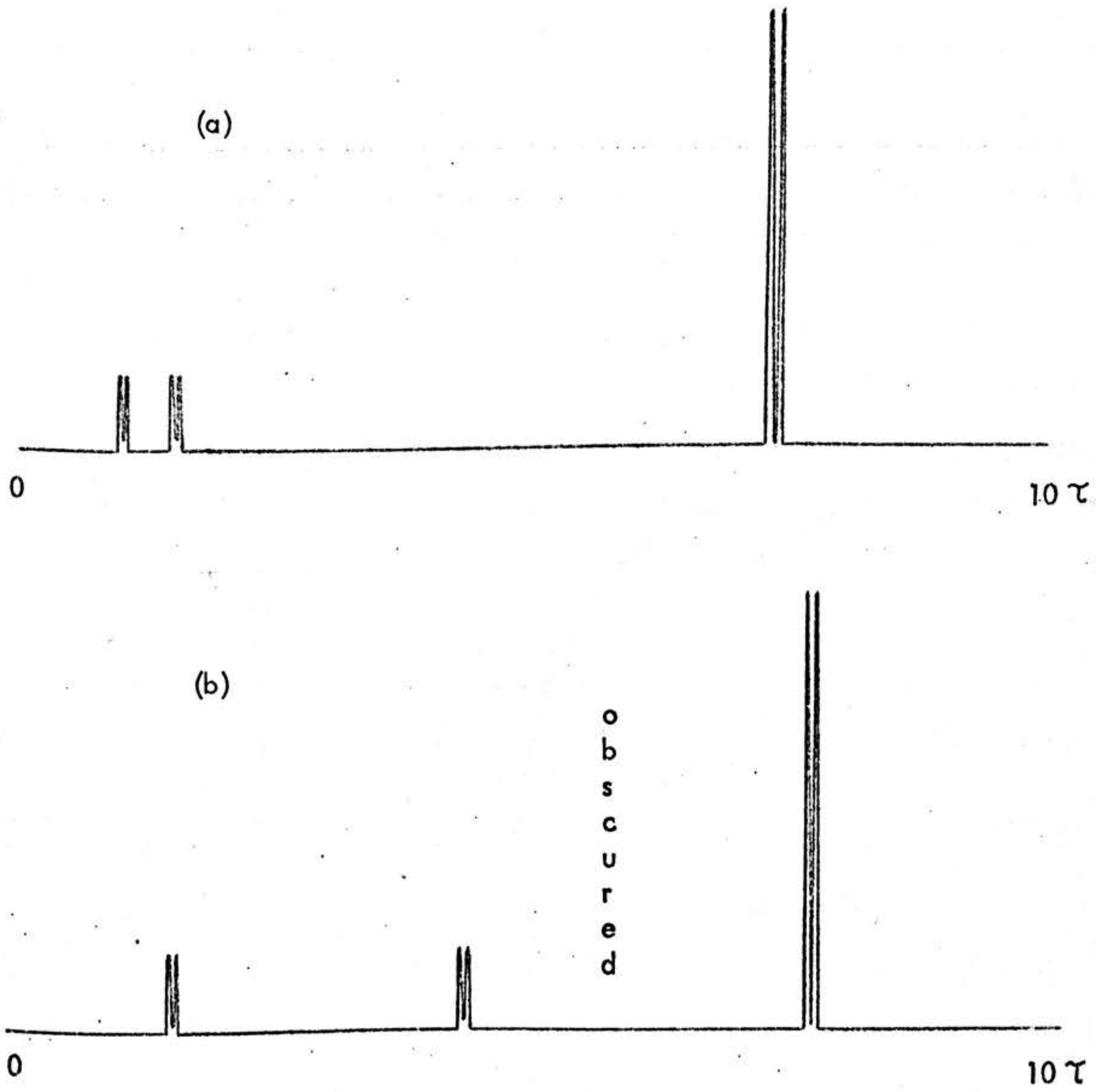


Fig.2.4.2 (a) PMR spectrum of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene(161) in DMSO-d_6 and (b) after addition of 3 equivalents of aqueous sodium sulphite.

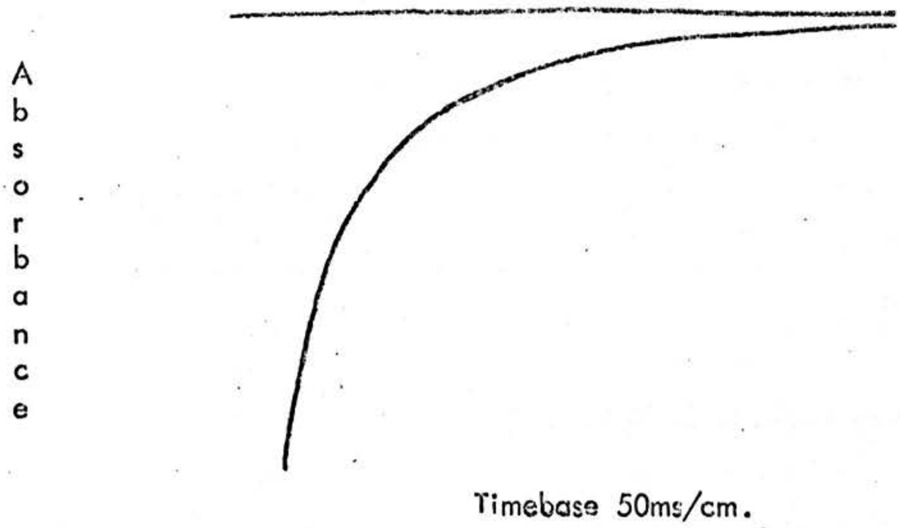
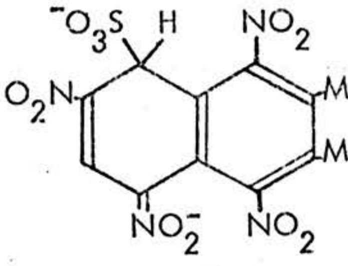


Fig.2.4.3 Stopped-flow trace for the reaction of 10 equivalents of sulphite ion with 1,4,5,7-tetranitro-2,3-dimethylnaphthalene(161) in aqueous DMSO(1:4).



(60)

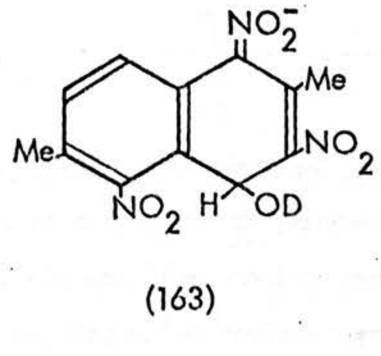
The visible absorbtion maximum of an aqueous DMSO(2:3) solution containing compound (161) and an excess of sulphite ion occurs at 527nm.

2.5 Polynitro-2,6-dimethylnaphthalenes

2.5.1 1,3,5-Trinitro-2,6-dimethylnaphthalene(162)

(A) Hydroxide ion

The PMR spectrum of the products of reaction of up to one equivalent of deuterioxide ion with compound (162) in d_6-DMSO is shown in fig.2.5.1(b). The aromatic resonances are complex, but the appearance of what look to be doublets(from AB quartets) suggest the presence of at least 2 major products. The spectrum possesses mid-field multiplets which change with time and seem to consist of 2 overlapping components. The methyl resonances are overlapped by the solvent absorbtion lines. One of the compounds formed may be the C-4 addition complex (163). The C-4 position is the most likely position of addition as the other ring contains only one nitro group.



(163)

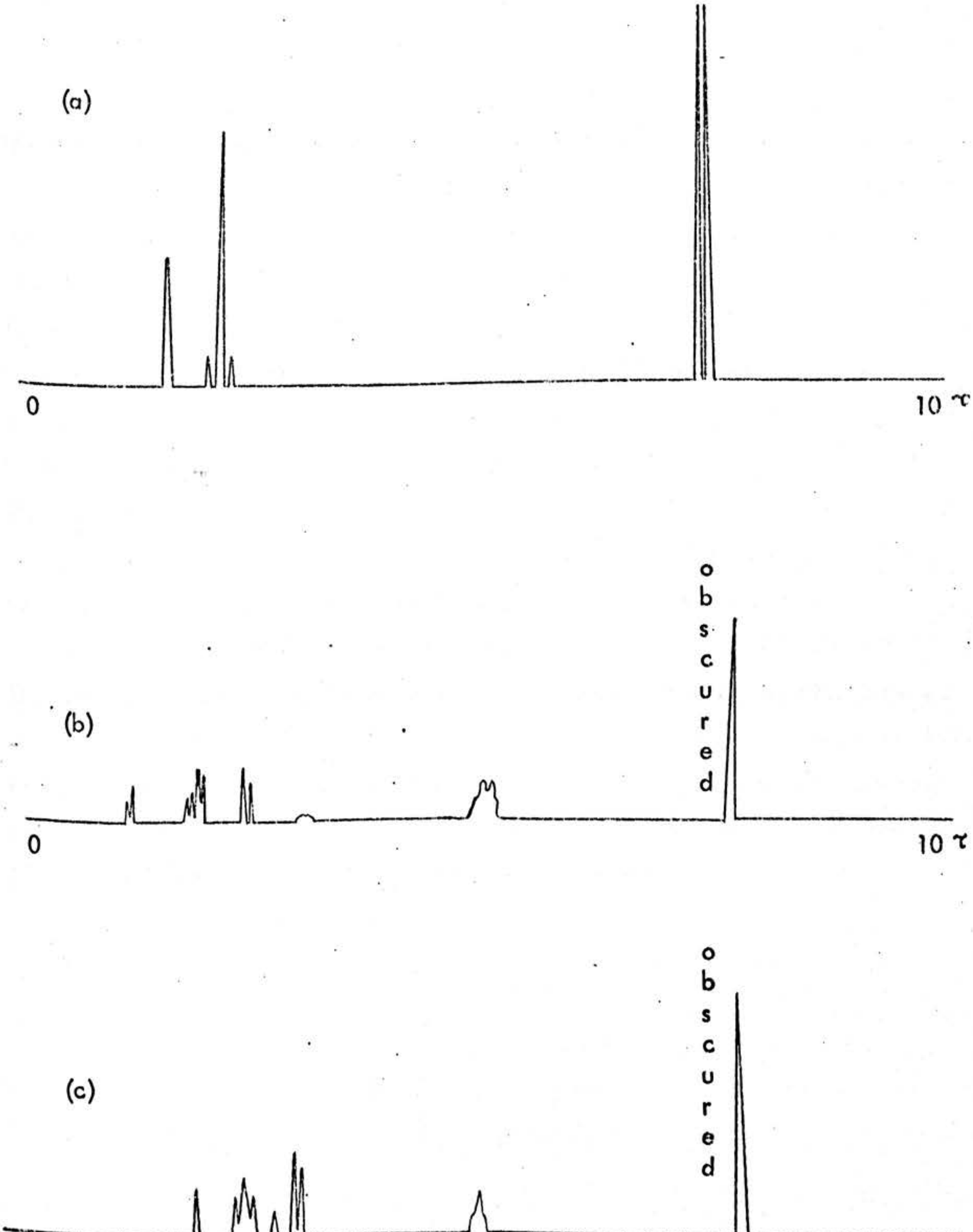


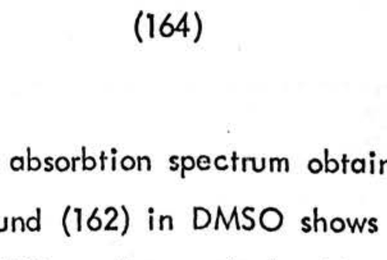
Fig. 2.5.1 (a) PMR spectrum of 1,3,5-trinitro-2,6-dimethylnaphthalene (162) in DMSO-d_6 (b) Spectrum of a solution of compound (162) and 1 equivalent of sodium deuterioxide 10 minutes after mixing and (c) Spectrum of a solution of compound (162) and 1 equivalent of sodium methoxide-d_3 7 minutes after mixing.

The visible absorbtion maximum of a solution containing 100 equivalents of hydroxide ion and compound (162) in aqueous DMSO(3:7) shifts from 508 to 515nm over a period of 20 minutes.

A visible absorbtion spectrum for the reaction of 364 equivalents of hydroxide ion with compound (162) in aqueous DMSO(1:4) was plotted by measuring the absorbance on the stopped-flow spectrophotometer at 10nm intervals when the infinity position was attained(i.e. after 15 seconds reaction)(fig2.5.2). A broad peak with λ_{max} at 511nm is obtained. The above optical absorbtion data may possibly be explained by rapid formation of a C-4 addition complex (163) followed by decomposition to other products.

(B) Methoxide ion

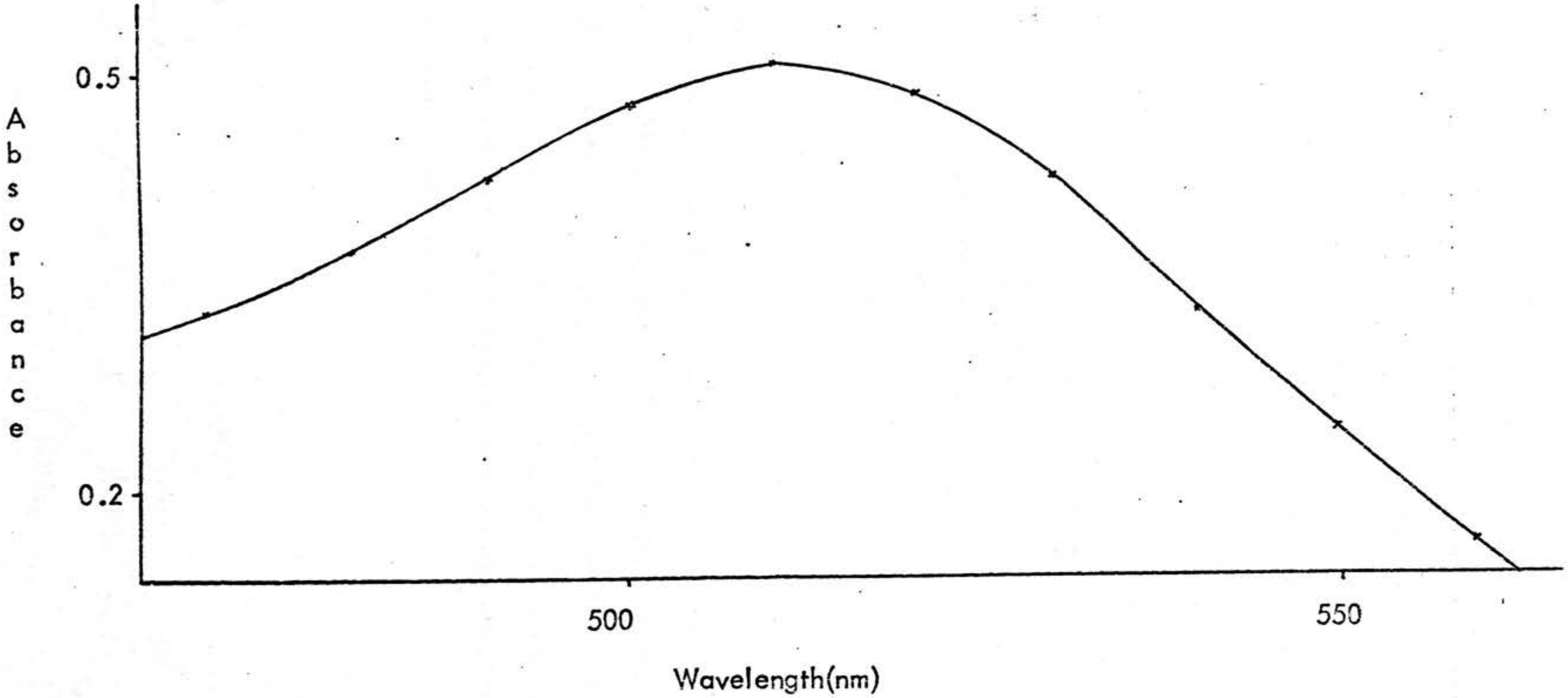
A PMR spectrum similar to that observed for the reaction products of hydroxide ion and compound (162) is obtained for the reaction of one equivalent of d_3-methoxide ion and compound (162) in d_6-DMSO(fig.2.5.1(c)). The visible absorbtion maximum of a short lived red coloured species obtained on reaction of from 0.5 to 1 equivalent of methoxide ion with compound (162) in DMSO occurs at 511nm. Both the above pieces of spectroscopic data may possibly be taken to indicate the formation of a short lived addition complex (164). The most likely position of addition is probably C-4.



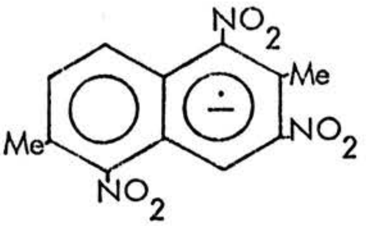
(164)

The UV-visible absorbtion spectrum obtained on reaction of excess methoxide ion and compound (162) in DMSO shows a peak with λ_{max} at 365nm and a shoulder at 500nm. Interestingly this yellow solution is para-

Fig.2.5.2 Visible absorbtion spectrum obtained by stopped-flow spectrophotometer of the products for the reaction of 364 equivalents of sodium hydroxide with 1,3,5-trinitro-2,6-dimethylnaphthalene(162) in aqueous DMSO(1:4) after the reaction reached equilibrium.



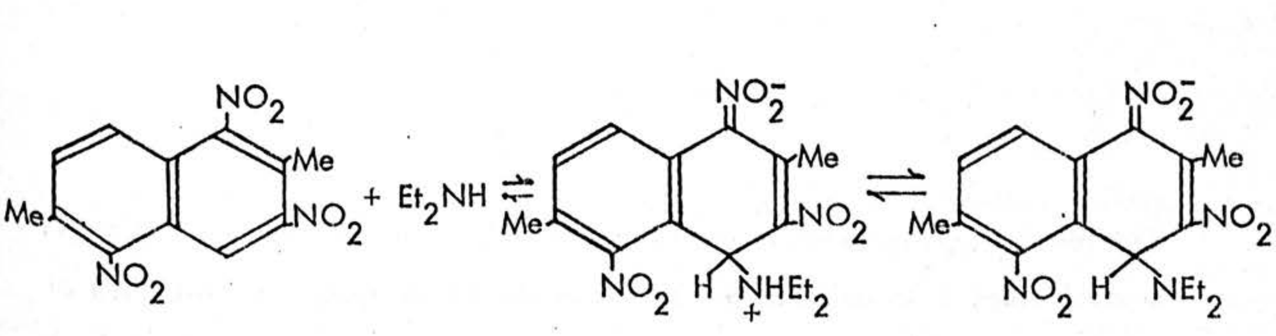
magnetic and displays an EPR spectrum(broad as solution not degassed) as does a solution containing 1 equivalent of methoxide ion and compound (164) which has been exposed to the air. The capillary tube containing the red solution turned yellow at the point of air contact, but the addition of water did not accelerate the change. It is probable that an oxygen mediated radical formation occurs, perhaps giving the radical anion (165) of (162).



(165)

(C) Diethylamine

The PMR spectrum of the products of reaction of diethylamine with compound (162) in d_6-DMSO is similar to those obtained for the reaction of hydroxide or methoxide ion with compound (162)(fig.2.5.3(b)). This may indicate that formation of a C-4 addition complex occurs along with other products. The addition complex could exist in the zwitterionic form (166) or anionic form (167)(See Scheme 13).



Scheme 13

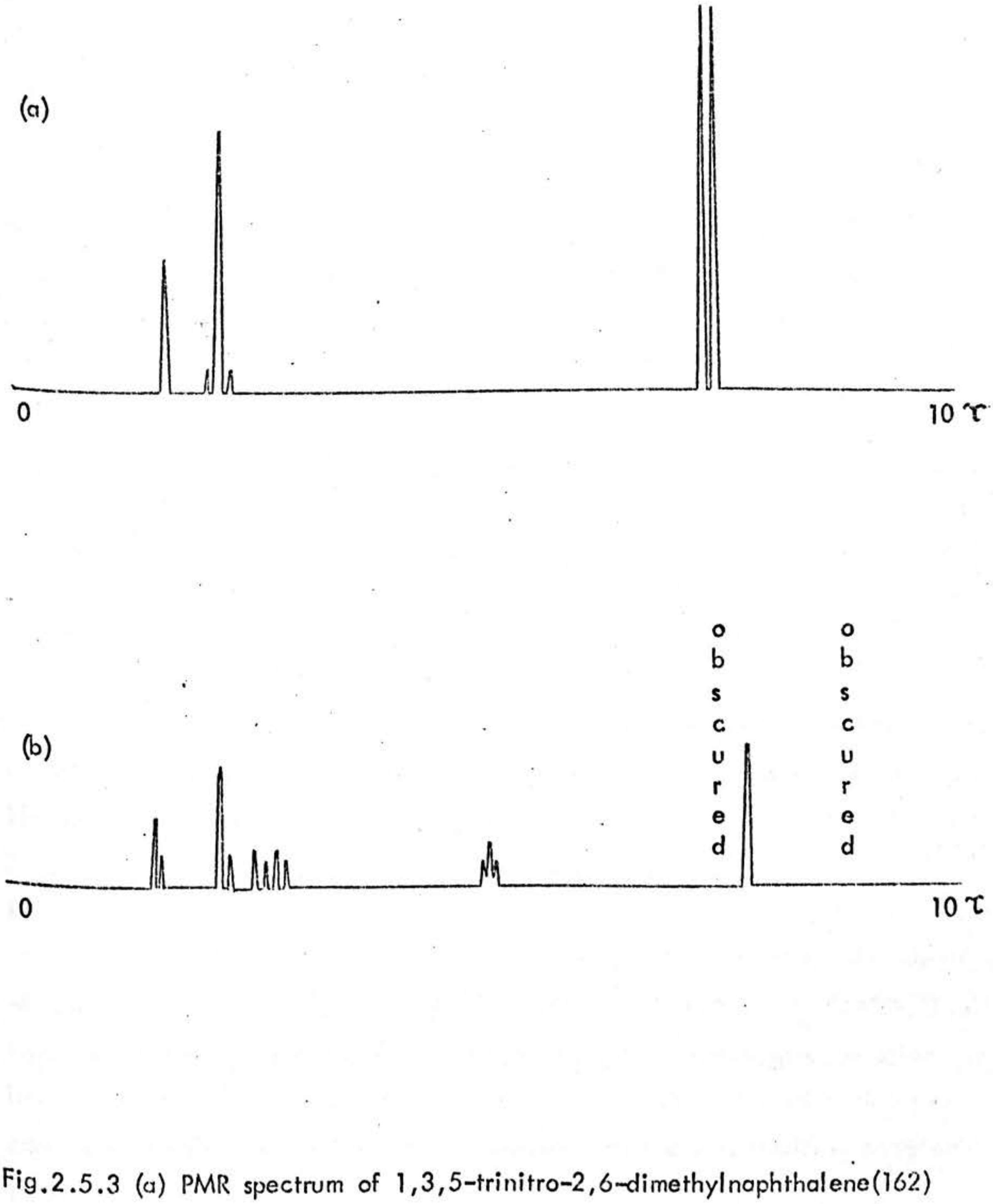


Fig.2.5.3 (a) PMR spectrum of 1,3,5-trinitro-2,6-dimethylnaphthalene(162) in DMSO-d_6 (b) Spectrum 12 minutes after the addition of 3 equivalents of diethylamine.

(D) Other amines

The PMR spectra of the products obtained on reaction of benzylamine or hydrazine hydrate with compound (162) in d_6-DMSO are difficult to interpret due to obscuration by base/solvent peaks. It would appear, however, that stable addition complexes are not formed.

(E) Sulphite ion

The PMR spectrum of the products of reaction of from 1-3 equivalents of sulphite ion with compound (162) in aqueous d_6-DMSO is shown in fig.2.5.4(b). The formation of a C-4 mono-addition complex (168) may be postulated.

(168)

The visible absorbtion maximum of an aqueous DMSO solution containing 2 equivalents of sulphite ion and compound (162) occurs at 526nm. This may be assigned to compound (168).

2.5.2 1,4,5-Trinitro-2,6-dimethylnaphthalene(169)

(A) Hydroxide ion

PMR indicates that a mixture of products is obtained for the reaction of one equivalent of deuterioxide ion with compound (169) in d_6-DMSO. The PMR spectrum shows what appears to be an AB quartet overlapped by other lines in the aromatic region. A multiplet occurs in the mid-field region and may be partly due to the H-3 proton resonance of the C-3 addition complex (170).

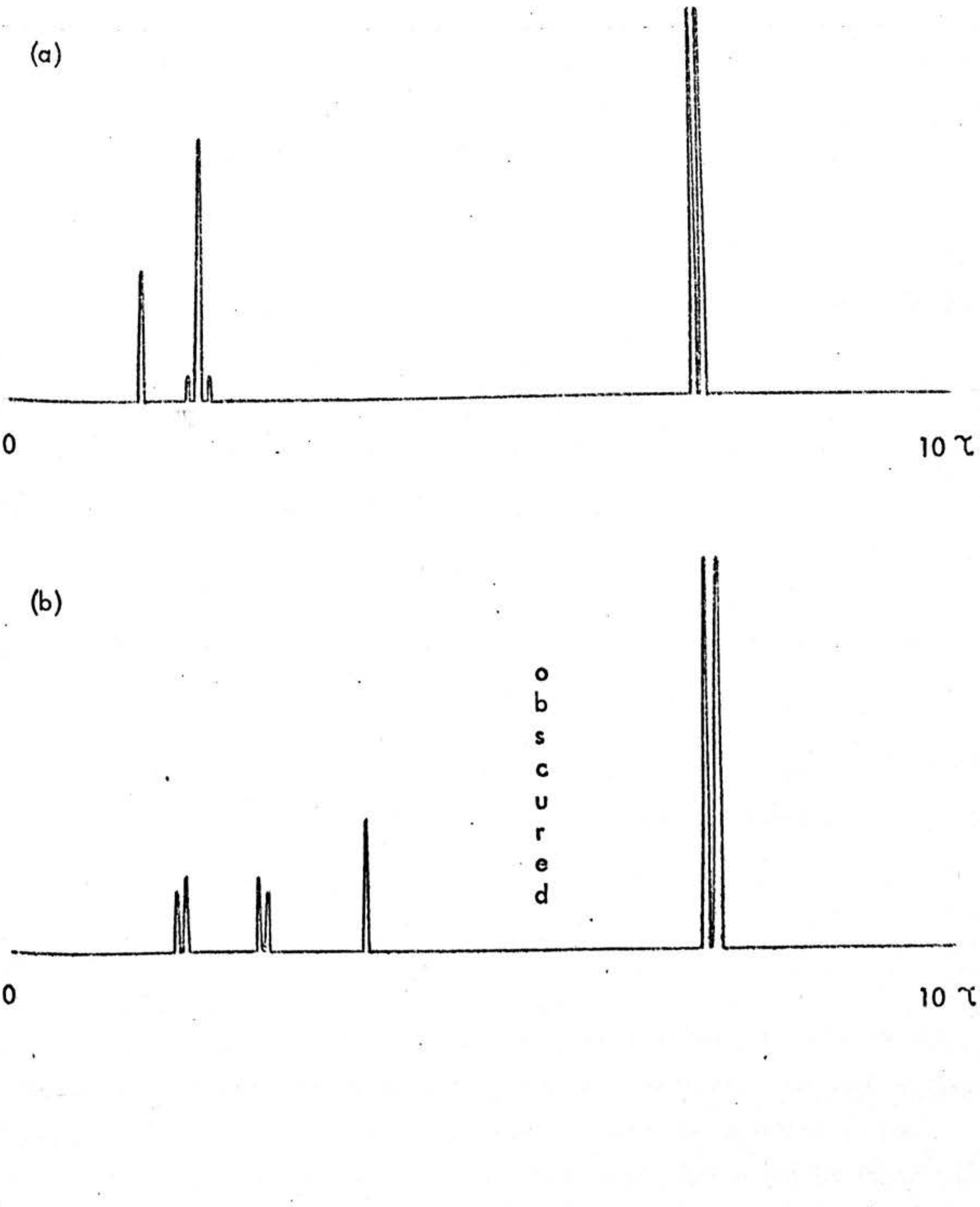
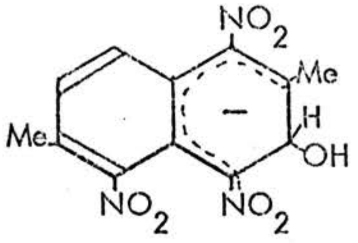
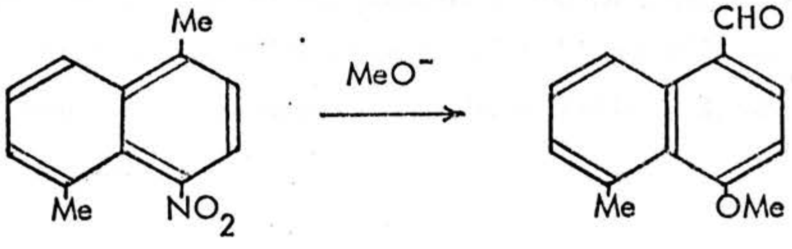


Fig.2.5.4 (a) PMR spectrum of 1,3,5-trinitro-2,6-dimethylnaphthalene(162) in DMSO-d_6 (b) Spectrum after the addition of 3 equivalents of aqueous sodium sulphite.



(170)

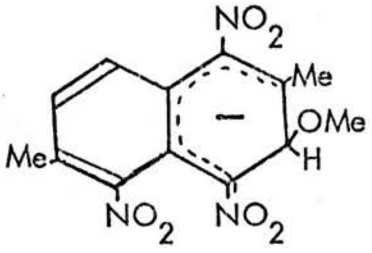
The PMR spectrum also shows a line at $\tau \sim 0$ which is indicative of aldehyic protons. It has previously been noted that the conditions employed for base induced coupling of 4-nitro-1,5- and 1,8-dimethylnaphthalenes[200] have succeeded in oxidation of the 1-methyl to an aldehyde group. The 4-nitro group is also replaced by a methoxy group in this process.



(171)

(B) Methoxide ion

A PMR spectrum showing broadened resonances is obtained for the products of reaction of less than one equivalent of methoxide ion with compound (169) in d_6-DMSO. A broad mid-field multiplet from the spectrum of the product of reaction of methoxide ion with compound (169) might be taken to indicate the simultaneous formation of C-3 addition product (173) and free radicals.

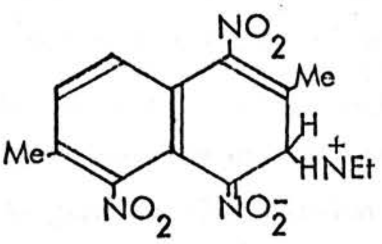


(173)

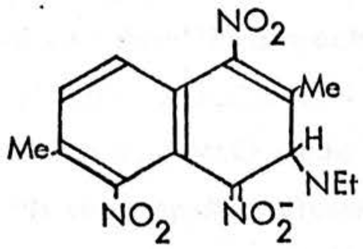
The visible absorbtion maximum of a solution containing 0.5-1 equivalent of methoxide ion and compound (169) in DMSO occurs at 465nm and this solution is paramagnetic, but unlike the reaction of methoxide ion with compound (162) a transient addition complex was not obviously given (See section 2.5.1(B)).

(C) Amine bases

The PMR spectrum of the products of the reaction of diethylamine and compound (169) in d_6-DMSO shows a mid-field multiplet which possibly indicates the formation of an addition complex(probably C-3) which may exist as the zwitterion (174) or anion (175).



(174)



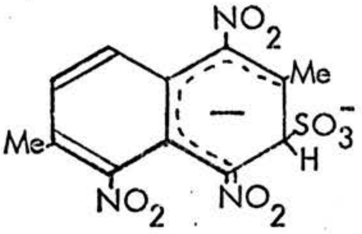
(175)

The PMR spectra of the products of reaction of benzylamine and hydrazine hydrate and compound (169) are not consistent with the formation of stable addition complexes but indicate the formation of miscellaneous unknown products.

(D) Sulphite ion

The PMR spectrum of the products of reaction of 1-3 equivalents of sodium sulphite with compound (169) in aqueous d_6-DMSO is shown in fig.2.5.5(b). Formation of the C-3 mono-addition complex (176) is indicated.

The visible absorbtion maximum of a solution containing 3 equivalents of sulphite ion and compound (169) occurs at 424nm and is possibly due to compound (176), although this is at rather a short wavelength compared with other sulphite complexes.[121]

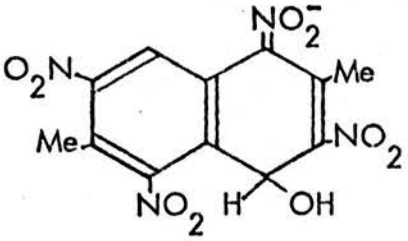


(176)

2.5.3 1,3,5,7-Tetranitro-2,6-dimethylnaphthalene(177)

(A) Hydroxide ion

The low solubility of compound (177) in d_6-DMSO necessitates the use of FT PMR and so makes the observation of any short lived species formed by the reaction of base with compound (177) difficult. Reaction of 1 equivalent of hydroxide ion with compound (177) in d_6-DMSO might be expected to give the C-4 addition product (178) very rapidly followed by decomposition in a manner analogous to the reaction of compound (162) with hydroxide ion.



(178)

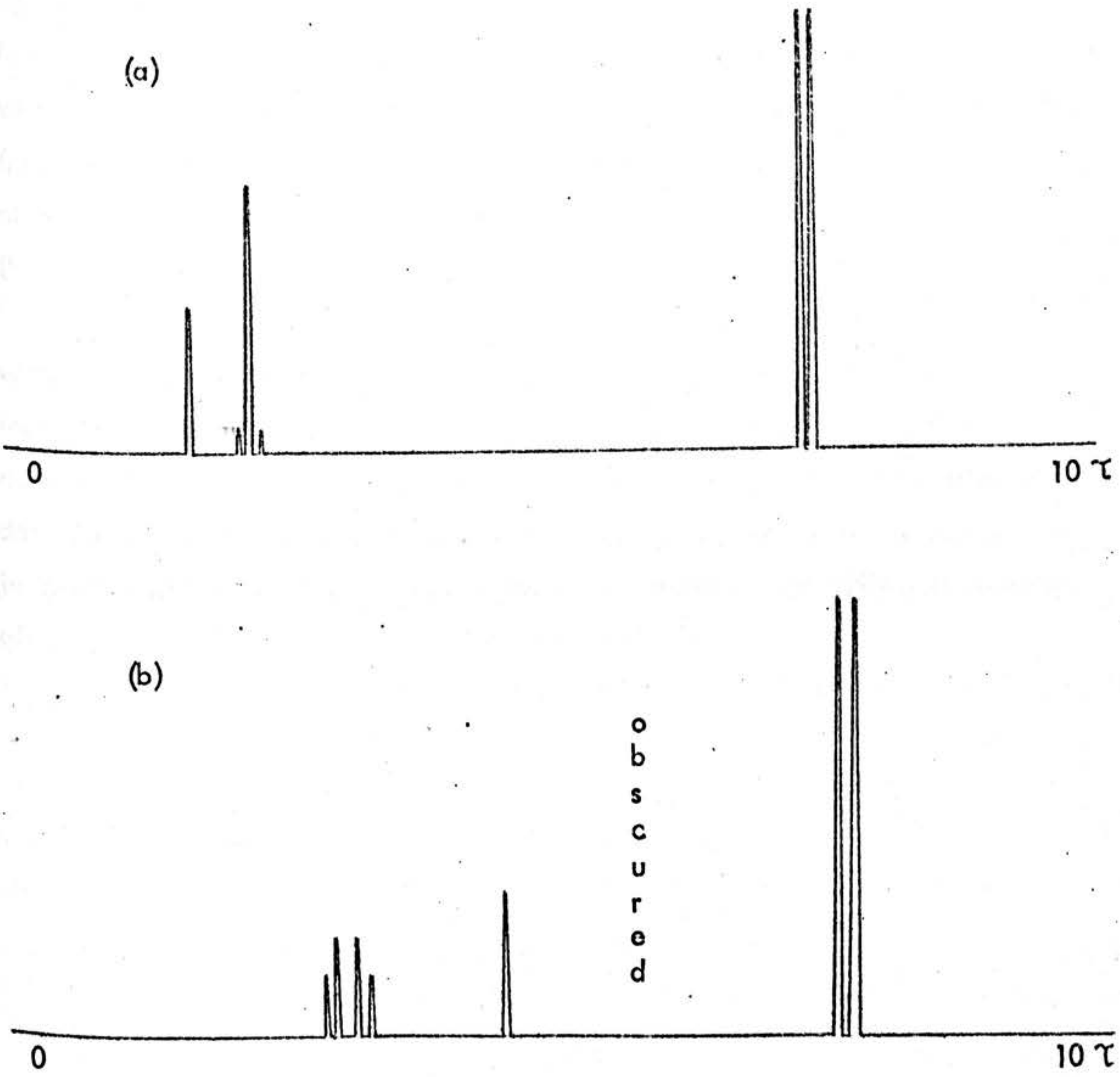
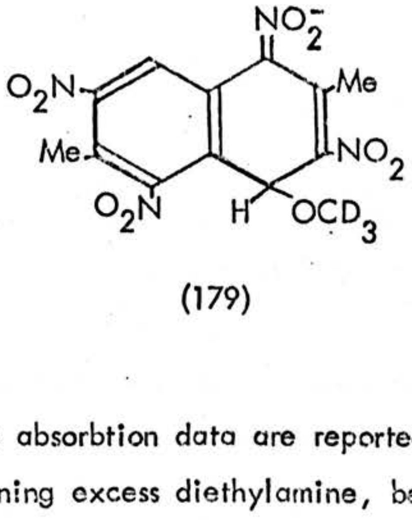


Fig.2.5.5 (a) PMR spectrum of 1,4,5-trinitro-2,6-dimethylnaphthalene(169) in DMSO-d_6 (b) Spectrum after the addition of 3 equivalents of sodium sulphite.

The visible absorbtion maximum of a DMSO solution containing 2 equivalents of hydroxide ion and compound (177) initially occurs at 501nm, however, a slow increase of absorbance and shift of the band to 505nm occurs with time. This may be explained by rapid formation of an addition complex (probably C-4(178)) and subsequent decomposition to give products with λ_{max} at 505nm.

(B) Methoxide ion

The PMR spectrum of the products of reaction of d_3-methoxide ion with compound (177) in d_6-DMSO is poorly resolved probably due to the formation of free radicals. It is possible that an unstable C-4 addition complex (179) is formed. This is possibly supported by the visible absorbtion data for the reaction of 4 equivalents of methoxide ion with compound (164) in DMSO which are that a visible absorbtion maximum at 498nm is rapidly given which slowly decreases in intensity with time.



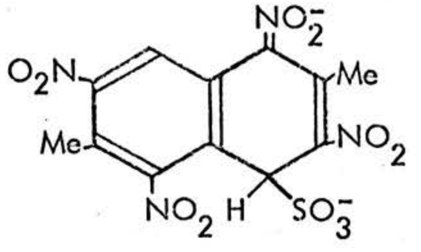
(179)

(C) Amines

Only the visible absorbtion data are reported. The visible absorbtion maxima of solutions containing excess diethylamine, benzylamine or hydrazine hydrate and compound (177) in DMSO occur at 510, 507 and 503 respectively. The formation of C-4 addition complexes(zwitterionic or anionic) may be postulated.

(D) Sulphite ion

The PMR spectrum of the products of reaction of 1-3 equivalents of sulphite ion with compound (177) in aqueous d_6-DMSO(1:2) is shown in fig.2.5.6(b). The spectrum is consistent with formation of the C-4 addition complex (180).



(180)

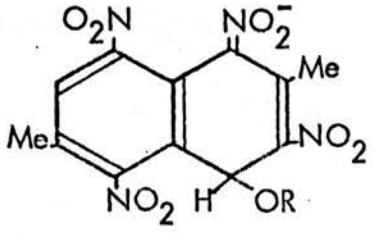
The visible absorbtion maximum of a solution containing 3 equivalents of sulphite ion and compound (164) in aqueous DMSO occurs at 508nm and is probably due to compound (180).

2.5.4 1,3,5,8-Tetranitro-2,6-dimethylnaphthalene(181)

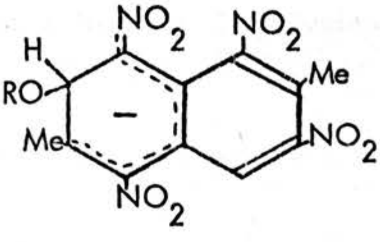
(A) Hydroxide and methoxide ion

PMR shows that 1 equivalent of deuterioxide or d_3-methoxide ion reacts with compound (181) in d_6-DMSO to produce a mixture of products. Low-field resonances suggest the presence of aldehydic species in small quantities.

The visible absorbtion maxima of solutions containing 2 equivalents of hydroxide or methoxide ion and compound (181) in d_6-DMSO occur at 501 and 492nm respectively. Any transient addition complexes may result from addition of base at C-4(182) or C-7(183), but addition at C-7 has been noted for reaction with 1,3,5,8-tetranitronaphthalene.[26]



(182)



(183)

R = H,Me

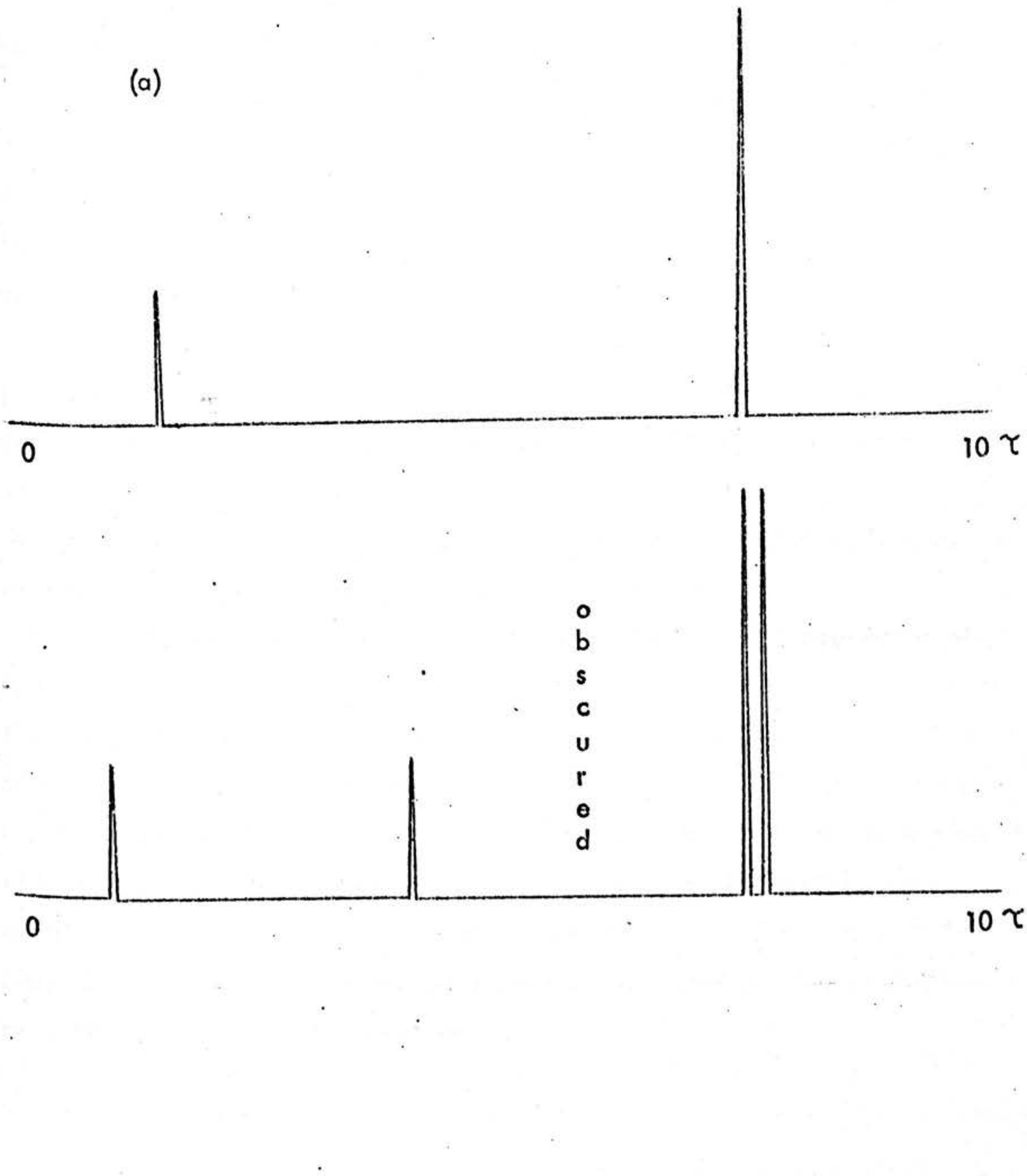


Fig.2.5.6 (a) PMR spectrum of 1,3,5,7-tetranitro-2,6-dimethylnaphthalene(177) in DMSO-d_6 (b) Spectrum after the addition of 3 equivalents of sodium sulphite.

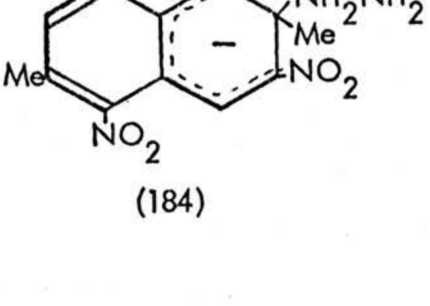
(B) Amines

The PMR spectrum of the products of reaction of diethylamine and compound (181) in d_6-DMSO is indicative of the formation of aldehydic species.

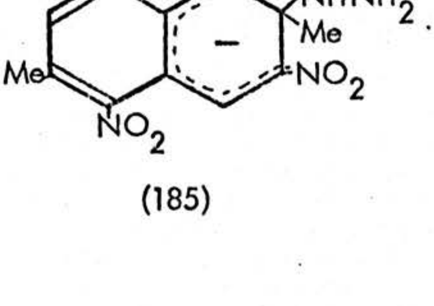
The visible absorbtion maximum of a solution containing excess diethylamine and compounds (181) in DMSO occurs at 509nm and this may indicate the rapid formation of an addition complex (C-4 or C-7) which may exist as the zwitterion or anion.

A PMR spectrum showing broadened resonances is obtained for the products of reaction of benzylamine with compound (181) in d_6-DMSO which probably indicates the formation of free radicals. The visible absorbtion maximum of a solution containing excess benzylamine and compound (181) in DMSO occurs at 585nm. It is possible that C-4 or C-7 addition products are formed on the reaction of benzylamine with compound (182).

The PMR spectrum of the product of reaction of 1 equivalent of hydrazine hydrate with compound (181) in d_6-DMSO is shown in fig.2.5.7(b). This shows the formation of a single product which is stable over a period of days. The chemical shifts of the aromatic protons are not consistent with the formation of a C-4 or C-7 adduct but indicate the formation of a product which may have been any one of 4 addition products (184)-(187), with addition occurring at an aromatic carbon bonded to a methyl group. It is difficult to distinguish between the 2 positions of addition. The possibility of zwitterionic or anionic complexes exists.



(184)



(185)

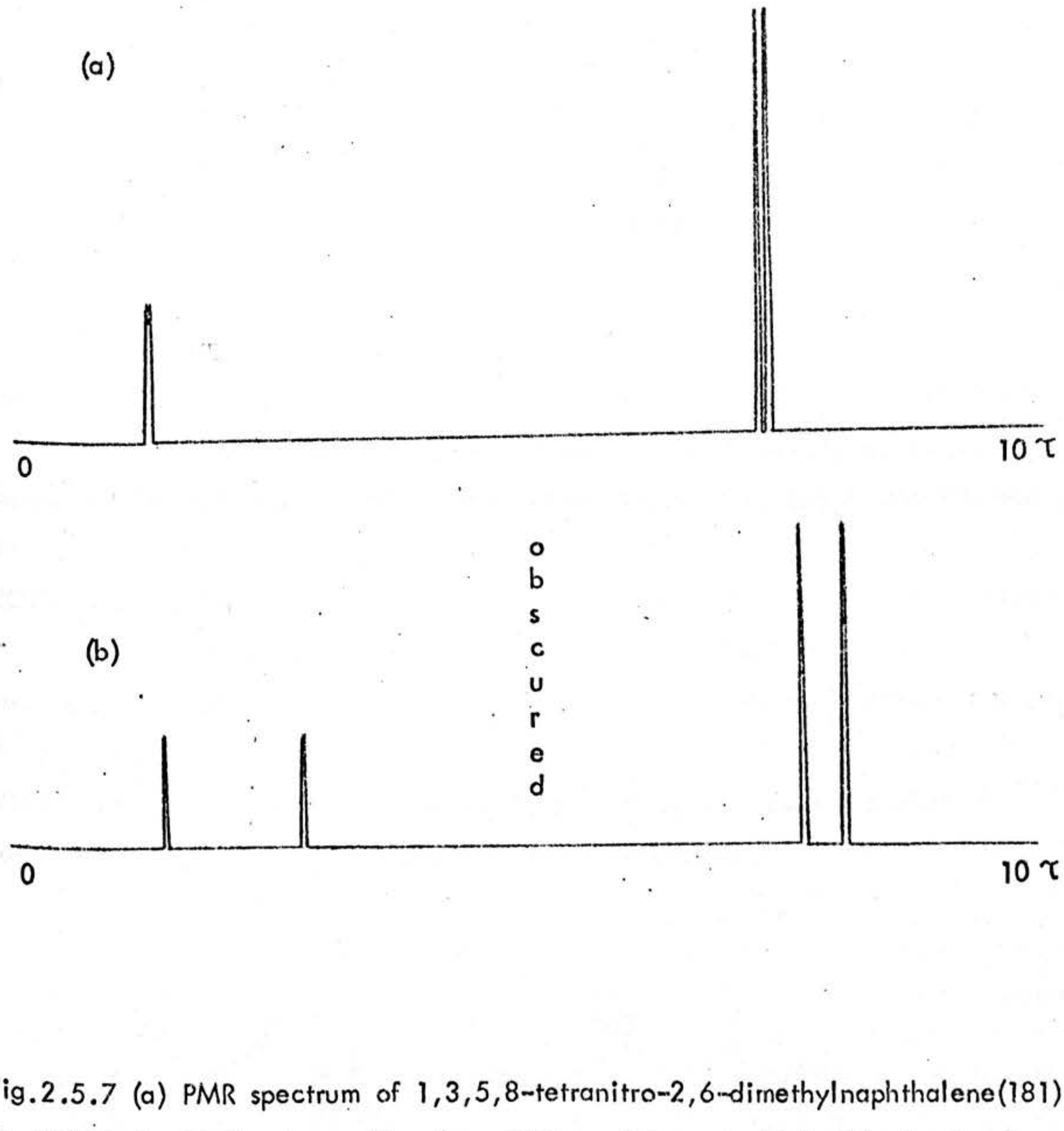
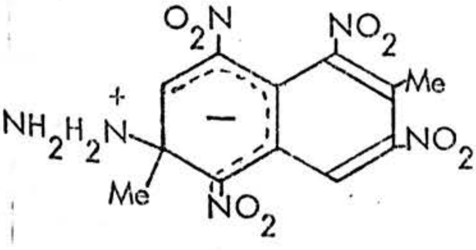
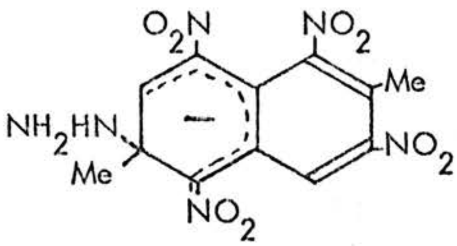


Fig.2.5.7 (a) PMR spectrum of 1,3,5,8-tetranitro-2,6-dimethylnaphthalene(181) in DMSO-d_6 (b) Spectrum after the addition of 1 equivalent of hydrazine hydrate.



(186)



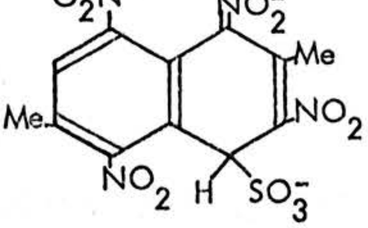
(187)

Over a period of 7 days the peaks due to the initial product decreased as those due to a new product, which is not identified, increased.

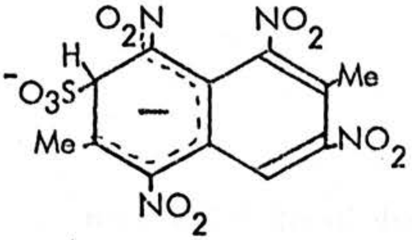
The visible absorbtion maximum of a solution containing excess hydrazine hydrate and compound (181) occurs at 544nm which is possibly due to an addition complex.

(C) Sulphite ion

The PMR spectrum of the products for the reaction of 1-3 equivalents of sulphite ion with compound (182) in aqueous d_6-DMSO is shown in fig.2.5.8(b). The formation of 2 addition complexes (C-4 (188) and C-7 (189)) is indicated. The minor product slowly disappears over a period of several weeks, leaving the major component unchanged.



(188)



(189)

Whether compound (188) or (189) is the major component is open to question.

The visible absorbtion maximum of a solution containing 1

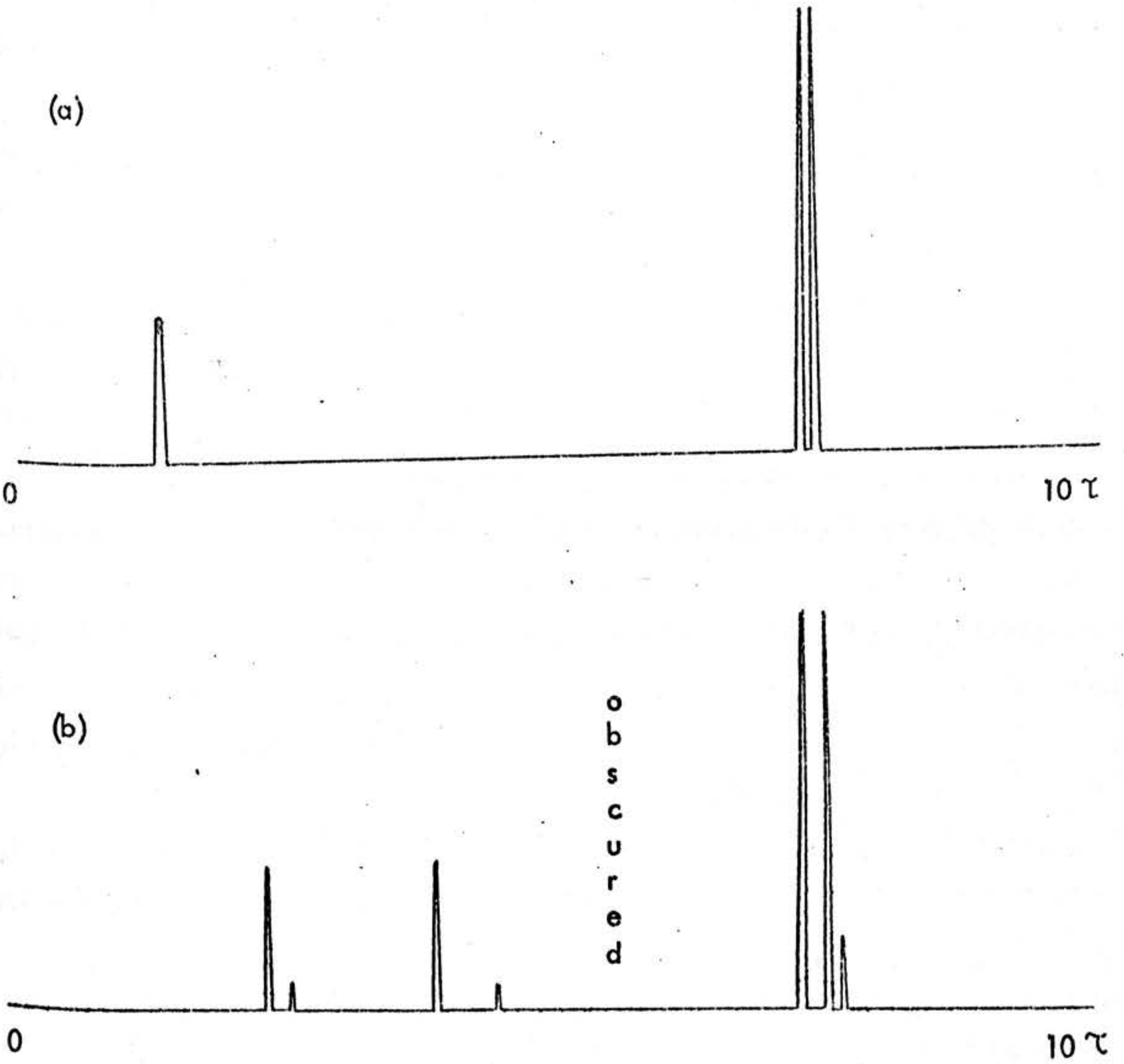


Fig.2.5.8 (a) PMR spectrum of 1,3,5,8-tetranitro-2,6-dimethylnaphthalene(181) in DMSO-d_6 (b) Spectrum after the addition of 3 equivalents of sodium sulphite.

equivalent of sulphite ion and compound (181) in aqueous DMSO occurs at 513nm and is probably due to a mixture of the compounds (188) and (189).

2.5.5 1,4,5,8-Tetranitro-2,6-dimethylnaphthalene(190)

(A) Hydroxide ion

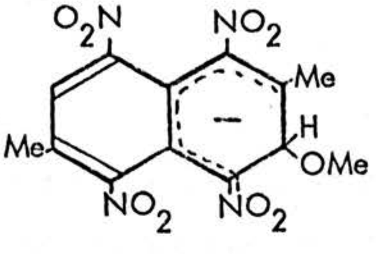
PMR indicates that 1 equivalent of deuterioxide ion reacts with compound (190) in d_6-DMSO to give a complex mixture of products including species containing aldehydic groups.

The visible absorbtion maximum of a solution of hydroxide ion and compound (190) in DMSO occurs at 430nm and is probably due to the products mentioned above.

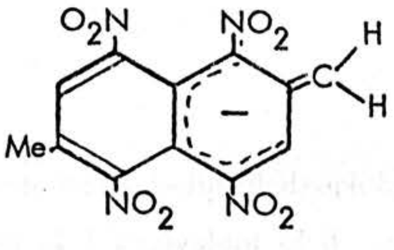
(B) Methoxide ion

PMR shows that 1 equivalent of d_3-methoxide ion reacts with compound (190) in d_6-DMSO(fig.2.5.9(b)) to possibly give 2 products. One of these could be the C-3 adduct (191)(resonances denoted by letter b), but the other has unknown composition(resonances denoted by letter d). Alternatively, proton abstraction from the 2-Me group may occur to give compound (192)(resonances denoted by letter c).

The PMR spectrum of compound (192) would be expected to show 2 singlets in the aromatic region due to protons H-3 and H-7 and a mid-field AB quartet due to coupled olefinic protons.



(191)



(192)

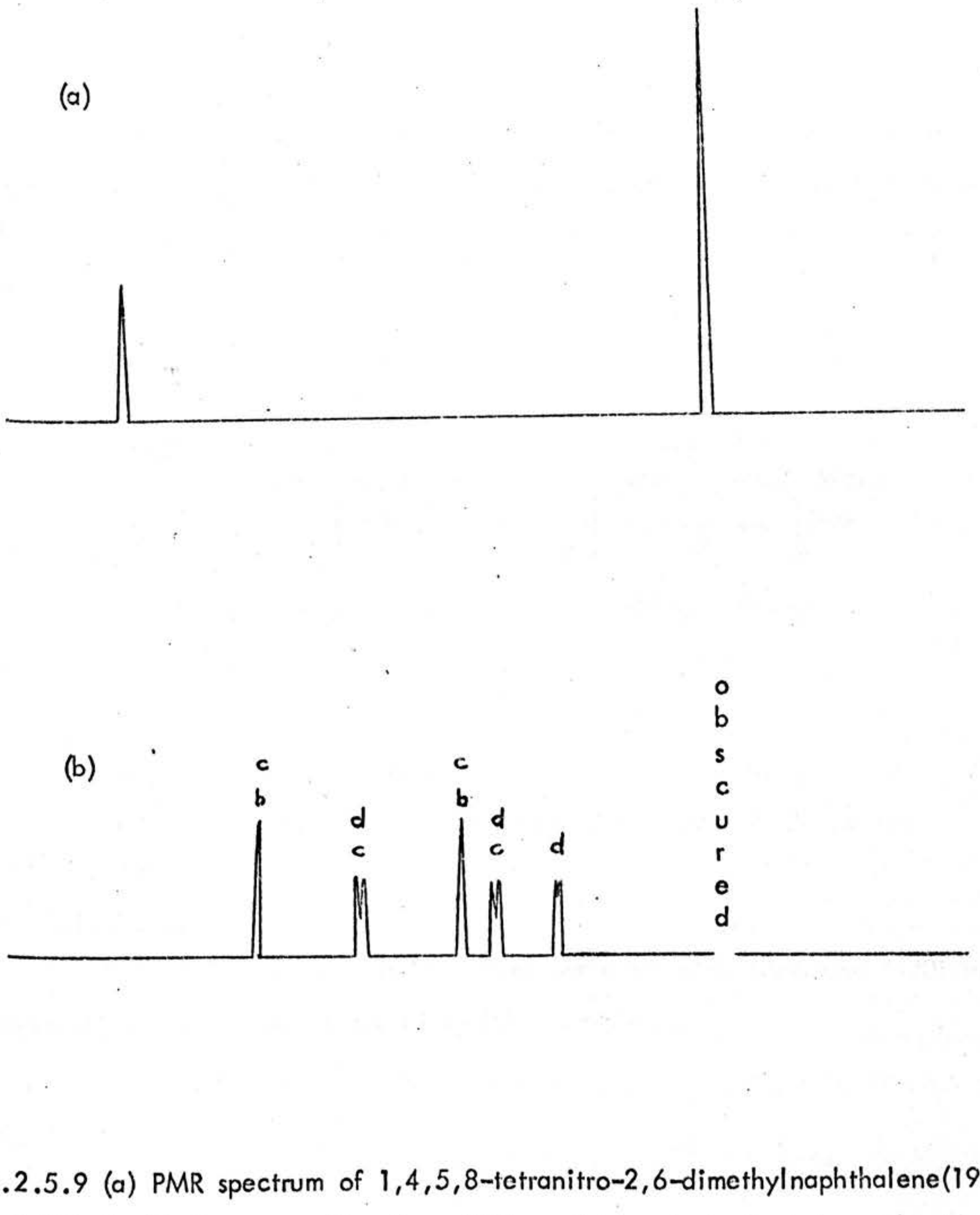
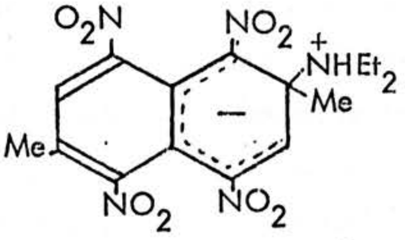


Fig.2.5.9 (a) PMR spectrum of 1,4,5,8-tetranitro-2,6-dimethylnaphthalene(190) in DMSO-d_6 (b) Spectrum after the addition of 1 equivalent of d_3-methoxide ion.

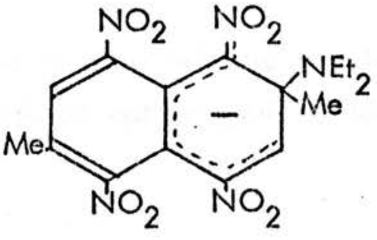
The visible absorbtion maximum of a solution containing methoxide ion and compound (190) in DMSO occurs at 440nm and may be assigned to the 2 products mentioned above.

(C) Amines

The PMR spectrum of the product of reaction of diethylamine with compound (190) in dimethylacetamide(DMA) indicates that the formation of an addition complex may occur. This is probably the C-2 adduct which could exist as the zwitterion (193) or anion (194).



(193)



(194)

PMR shows that benzylamine and hydrazine hydrate react with compound (190) in d_6-DMSO to give mixtures of products which are not readily identified.

(D) Sulphite ion

PMR shows that sulphite ion does not react with compound (190) in aqueous d_6-DMSO to give a stable addition complex.

Experimental

Spectrometers used for PMR measurements were as follows:- 60MHz, Perkin Elmer R10; 90MHz CW, Perkin Elmer R32; 90MHz FT, Perkin Elmer R32 with Nicolet TT4 FT unit; and the 220MHz PCMU instrument. Generally PMR spectra were recorded of samples containing 0.1mmole nitroaromatic using TMS as an internal standard. All samples for PMR measurements were generated in situ except those involving sulphite reaction. Visible absorbtion spectra were usually measured of $3cm^3$ of solutions containing nitroaromatic at concentrations of $5\times10^{-5}M$ in 10nm silica cells on Perkin Elmer SP1700 or SP8000 spectrophotometers. The stopped-flow spectrophotometer used was manufactured by Applied Photophysics and operated by mixing equal volumes of 2 reactant solutions. The absorbance of the reactant mixture was determined by irradiation with monochromatic light through an optical path of 10nm.

2.6 Polynitro-1,5-dimethylnaphthalenes

2.6.1 2,4,8-Trinitro-1,5-dimethylnaphthalene(93)

Compound (93)(0.0291g) was dissolved in d_6-DMSO and the PMR spectrum recorded(fig.2.2.1(a)):- τ 1.24(1H,s), 1.70 and 2.16(2H,ABq,J_{AB} 8.0Hz), 7.46(3H,s) and 7.52(3H,s).

(A) Deuterioxide and hydroxide ion

Sodium deuterioxide in $D_2O(5M;0.01cm^3)$ was added to a solution containing compound (93) in d_6-DMSO$(0.4cm^3)$. The 220MHz PMR spectrum (fig.2.2.1(b)) was recorded to reveal compound (94):- τ 1.34(1H,s), 2.50 and 2.67(2H,ABq,J_{AB} 8.4Hz) 4.05(1H,s), 5.08(1H,s) and 7.83(3H,s). One equivalent of 1M sodium hydroxide$(0.0006cm^3)$ was added to a $2.6\times10^{-4}M$ solution of compound (93) in DMSO$(3cm^3)$ and the UV-visible absorbtion spectrum recorded(fig.2.2.2(a)); λ_{max} values were at 400 and 560nm. Ten equivalents of 0.5M sodium hydroxide$(0.003cm^3)$ were added to a $5\times10^{-5}M$ solution of compound (93) in DMSO$(3cm^3)$ and the spectrum recorded(fig.2.2.2 (b)); λ_{max} values were at 400 and 560nm. One hundred equivalents of 1M sodium hydroxide$(0.015cm^3)$ were added to a $5\times10^{-5}M$ solution of compound (93) in DMSO$(3cm^3)$; λ_{max} was less than 350nm.

Equal volumes($1.5cm^3$) of solutions containing 0.1 equivalent of sodium hydroxide($2 \times 10^{-4}M$) and compound (93)($2 \times 10^{-3}M$) in DMSO/H_2O(9:1) were mixed and the visible spectrum recorded within 50 seconds of mixing (fig.2.2.3); λ_{max} was at 525nm.

The stopped-flow trace obtained on rapid mixing of equal volumes of solutions containing 0.05 equivalent of sodium hydroxide($5 \times 10^{-5}M$) and compound (93)($10^{-3}M$) in DMSO/H_2O(9:1) shows 3 steps(fig.2.2.4(a)). The stopped-flow traces obtained on rapid mixing of solutions containing 40 equivalents of sodium hydroxide($5 \times 10^{-3}M$) with compound (93)($1.25 \times 10^{-4}M$) in DMSO/H_2O(9:1) are shown in (fig.2.2.4(b)-(d)). The stopped-flow spectrum obtained by measuring the absorbance at 10nm intervals at the infinity position after mixing 244 equivalents of sodium hydroxide(0.025M) with compound (93)($10^{-4}M$) in DMSO/H_2O(9:1) solution showed an absorbtion maximum at 560nm(fig.2.2.5).

(B) Triethylamine

Compound (93)(0.021g) was dissolved in d_6-DMSO($0.5cm^3$) and triethylamine($0.01cm^3$) added. The PMR spectrum(220MHz) was recorded within 5 minutes of mixing(fig.2.2.6(b)):- τ 1.35(1H,s),2.54 and 2.72(2H,ABq,J_{AB} 8Hz),4.09(1H,s),5.12(1H,s) and 7.86(3H,s).

(C) Diethylamine and deuterioxide

Compound (93)(0.0388g) was dissolved in d_6-DMSO($0.4cm^3$) and diethylamine($0.014cm^3$) added. The PMR spectrum(90MHz) was recorded and is identical to that obtained for the product of reaction of triethylamine and compound (93) in d_6-DMSO. Sodium deuterioxide in D_2O(5M;$0.1cm^3$) was added and the spectrum recorded:- τ 2.72 and 2.95(2H,ABq,J_{AB} 8.0Hz), 3.12 and 5.04(2H,ABq,J_{AB} 2Hz),4.16(1H,s) and ~7.65(3H,s).

(D) Benzylamine

Compound (93)(0.029g) was dissolved in d_6-DMSO($0.5cm^3$) and 1 equivalent of benzylamine($0.01cm^3$) added. The PMR spectrum(220MHz) was recorded and this showed the formation of compound (94) and another species (fig.2.2.6(c)). This latter species gave the following spectrum:- τ 1.27(1H,s), other aromatic lines obscured, 7.86(3H,s) and 8.24(3H,s).

PMR spectra(60MHz) recorded after 5 minutes reaction showed that 0.025,0.075,0.15 and 0.3cm^3(3-40 equivalents) of benzylamine reacted with compound (93)(0.020g) in d_6-DMSO(0.4cm^3) to give compounds (121) or (122) and (94) in the ratio of 2:3;1:1;4:3 and 16:9 respectively.

A few microlitres of the PMR sample containing 1 equivalent of benzylamine and compound (93) in d_6-DMSO were diluted in DMSO(3cm^3) and the UV-visible spectrum recorded(fig.2.2.7(a)); λ_{max} values were 395 and 560nm. Addition of an excess of benzylamine(0.01cm^3) gave a solution with λ_{max} = 544nm(fig.2.2.7(b)).

(E) <u>3-chloro and 3,4-dichlorobenzylamine</u>

Compound (93)(0.020g) was dissolved in d_6-DMSO(0.4cm^3) and 10 equivalents of 3-chlorobenzylamine(0.1cm^3). The PMR spectrum was recorded after 4 minutes and it indicated the formation of a mixture of compound (94); and another species which gave resonances at:- τ 1.41(1H,s), other aromatic lines obscured, 7.90(3H,s) and 8.24(3H,s), conversion of this to compound (94) was subsequently observed by PMR spectroscopy.

A 2.6×10^{-4}M solution of compound (93) in DMSO(3cm^3) was treated with a 10% solution of 3-chlorobenzylamine(0.0007cm^3) in DMSO and the UV-visible spectrum recorded; λ_{max} was 560nm.

An excess of 3-chlorobenzylamine(0.01cm^3) was added to a 5×10^{-5}M solution of compound (93) in DMSO(3cm^3) and the UV-visible spectrum recorded within 1 minute of mixing; λ_{max} was 537nm. This absorbtion maximum shifted to 545nm over a period of 17 hours.

Compound (93)(0.02g) was dissolved in d_6-DMSO(0.4cm^3) and 10 equivalents of 3,4-dichlorobenzylamine(0.1cm^3) added. The PMR spectrum (60MHz) was recorded and showed the formation of compound (94) and another species:- τ 1.39(1H,s), other aromatic lines obscured, 7.86(3H,s) and 8.22(3H,s).

A 2.6×10^{-4}M solution of compound (93) in DMSO was treated with 1 equivalent of 3,4-dichlorobenzylamine(0.08cm^3) and the UV-visible spectrum recorded; λ_{max} was 558nm.

An excess of 3,4-dichlorobenzylamine(0.01cm^3) was added to a 5×10^{-5}M solution of compound (93) in DMSO and the UV-visible spectrum recorded within 1 minute of mixing; λ_{max} was 533nm. This absorbtion maximum shifted to 555nm over a period of 6 hours.

(F) Hexamethyldisilazane(HMDS)

Compound (93)(0.0312g) was dissolved in d_6-DMSO(0.4cm^3) and hexamethyldisilazane(0.02cm^3) added. The PMR spectrum(90MHz) was recorded:- τ 1.34(1H,s),2.56 and 2.73(2H,ABq,J_{AB} 8.0Hz),4.06(1H,s),5.11(1H,s) and 7.84(3H,s).

(G) Hydrazine hydrate

One equivalent of hydrazine hydrate(0.005cm^3) was added to compound (93)(0.0311g) in d_6-DMSO(0.4cm^3) and the PMR spectrum recorded (fig.2.2.8(b)). The formation of compound (94) and another species occured:- τ 1.39(1H,s),2.84 and 2.85(2H,ABq,J_{AB} 8Hz),7.84(3H,s) and 8.43(3H,s).

A few microlitres of the PMR sample were diluted in DMSO(3cm^3) and the visible absorbtion spectrum recorded; λ_{max} was at 557nm.

(H) Sulphite ion

Compound (93)(0.0344g) was dissolved in d_6-DMSO(0.6cm^3) with warming and magnetic stirring in a 10cm^3 QF stoppered conical flask. Aqueous sodium sulphite solution(1M;0.3cm^3) was added and after 5 minutes 0.4cm^3 of the filtered solution was examined by 90MHz FT PMR spectroscopy. The spectrum showed the formation of 2 species(fig.2.2.9(b)):- τ 2.41 and 2.64(2H,ABq,J_{AB} 8.4Hz),3.49(1H,s),7.94(3H,s) and 8.07(3H,s); and τ 1.96 (1H,s),3.62 and 4.55(2H,ABq,J_{AB} 6-7Hz),7.62(3H,s), other methyl resonance obscured(~ 7.4).

(I) Methoxide ion(in methanol)

Compound (93)(0.001g) was dissolved in CD_3OD(0.4cm^3) and the 90MHz FT PMR spectrum recorded(fig.2.2.10(a)):- τ 1.54(1H,s),1.90 and 2.21(2H,ABq,J_{AB} 7.9Hz),7.37(3H,s) and 7.42(3H,s).

Addition of 1 equivalent of 2M sodium methoxide-d_3(0.002cm^3)

yielded a product with the PMR spectrum shown in fig.2.2.10(b):- τ 1.30 (1H,s),2.64 and 2.73(2H,ABq,J_{AB} 8Hz),5.25(1H,s),6.09(1H,s) and 7.73(3H,s).

Addition of a total of 3 equivalents of base gave a compound with the PMR spectrum shown in fig.2.2.10(c):- τ 2.61 and 2.78(2H,ABq,J_{AB} 8.3Hz),3.26 and 4.61(2H,ABq,J_{AB} 1.4Hz),3.59(1H,s) and 7.52(3H,s).

(J) Diethylamine(in methanol)

Compound (93)(0.001g) was dissolved in CD_3OD(0.4cm^3) and 75 equivalents of diethylamine(0.025cm^3) added. The 90MHz FT PMR spectrum was recorded to show that compound (94) was the only product formed.

(K) Diethylamine and triethylamine(in DMSO/methanol)

The visible absorbtion maximum of a 5×10^{-5}M solution of compound (93) and up to 1600 equivalents of diethylamine(0.026cm^3) or triethylamine (0.034cm^3) in DMSO/methanol(1:1,2:1,4:1 and 9:1) occurred at 560nm. The UV-visible spectrum for the reaction of 800 equivalents of diethylamine with compound (93) in DMSO/methanol(2:1) is shown in fig.2.2.11.

(L) Ethoxide ion(in DMSO and ethanol)

Compound (93)(0.0197g) was dissolved in d_6-DMSO(0.4cm^3) and 1 equivalent of 2M sodium ethoxide(0.03cm^3) added. The 60MHz PMR spectrum was recorded:- τ 1.40(1H,s),2.55 and 2.85(2H,ABq,J_{AB} 8Hz),4.14(1H,s),5.16 (1H,s) and 7.86(3H,s).

The spectrum was unchanged after the addition of a further 2 equivalents of sodium ethoxide(0.06cm^3), but with a total of 6 equivalents of base(0.18cm^3) a new spectrum was obtained:- τ 2.70 and 2.93(2H,ABq,J_{AB} ~8Hz),3.28 and 4.98(2H,ABq,J_{AB} 2Hz),3.61(1H,s) and 7.62(3H,s).

The visible absorbtion spectrum shown in fig.2.2.12 was obtained by measuring the absorbance at 10nm intervals(490-610nm) at the infinity position of the reaction, after mixing 200 equivalents of sodium ethoxide (0.02M) with compound (93)(10^{-4}M) in ethanol. Maxima at 520 and 560nm occurred.

(M) Tert-butoxide ion(in DMSO/t-butanol and t-butanol)

Compound (93)(0.026g) was dissolved in d_6-DMSO(0.4cm^3) and 1 equivalent of 1M sodium tert-butoxide in t-butanol(0.06cm^3) added. The spectrum was recorded and showed the formation of compound (94) only. No change occurred on addition of a further 0.2cm^3 of base.

The visible absorbtion spectrum in fig.2.2.13 was obtained by measuring the absorbance at 10nm intervals(450–600nm) at the infinity position of the reaction 8 seconds after mixing 200 equivalents of 0.02M sodium tert-butoxide with compound (93)(10^{-4}M) in t-butanol. Three overlapping maxima at 500,530 and ~550nm were observed.

The visible absorbtion spectrum in fig.2.2.14 was obtained by measuring the absorbance at 10nm intervals(500–580nm) at the infinity position of the reaction, after mixing 20 equivalents of 0.002M sodium tert-butoxide with compound (93)(10^{-4}M) in DMSO/t-butanol(1:1). Absorbtion maxima occurred at ~540 and 560nm.

2.6.2 2,4,6,8-Tetranitro-1,5-dimethylnaphthalene(98)

Compound (98)(0.0336g) was dissolved in d_6-DMSO(0.4cm^3) and the spectrum recorded(fig.2.2.15(a)):- τ 1.04(2H,s) and 7.49(6H,s).

(A) Deuterioxide and hydroxide ion

Compound (98)(0.0366g) was dissolved in d_6-DMSO(0.4cm^3) and 1 equivalent of 5M sodium deuterioxide in D_2O(0.02cm^3) added. The 90MHz PMR spectrum was recorded after 5 minutes reaction(fig.2.2.15(b)):- τ 1.24 (1H,s),1.74(1H,s),4.04(1H,s),4.97(1H,s) and 7.92(3H,s).

The spectrum was re-recorded after 40 minutes reaction time (fig.2.2.15(c)):- τ 1.15(1H,s),1.32(1H,s),1.78(1H,s),2.11(1H,s) and 7.82(3H,s).

A few microlitres of the PMR sample were then diluted in DMSO (3cm^3) and the UV-visible spectrum recorded; λ_{max} was at 540nm.

The visible absorbtion spectrum shown in fig.2.2.16 was obtained by measuring the absorbance at 10nm intervals(480–570nm) at the infinity position of the reaction, after rapidly mixing 11 equivalents of 0.002M sodium hydroxide with compound (98)(1.827 x 10^{-4}M) in DMSO/H_2O(9:1). Absorbtion maxima occurred at 520 and 540nm.

(B) Diethylamine and triethylamine

Compound (98)(0.0336g) was dissolved in d_6-DMSO(0.5cm^3) and 1 equivalent of diethylamine($0.01cm^3$) added. The PMR spectrum(220MHz) was recorded(fig.2.2.17(b)):- τ 1.10(1H,s),1.34(1H,s)1.72(1H,s),2.06(1H,s) and 7.85(3H,s).

Three samples containing compound (98)(0.0336g) dissolved in d_6-DMSO($0.5cm^3$) were treated separately with 0.3,0.5 and 1 equivalent of triethylamine($0.004,0.007,0.012cm^3$). The PMR spectra were recorded after 5 minutes and showed the formation of compounds (101) and (100):- τ 1.28 (1H,s),1.73(1H,s),4.04(1H,s),4.96(1H,s) and 7.88(3H,s).

Fifty equivalents of triethylamine($0.001cm^3$) was added to a solution of compound (98) in DMSO(4×10^{-5}M) and the UV-visible spectrum recorded; λ_{max} was at 540nm.

(C) Benzylamine

Compound (98)(0.0336g) was dissolved in d_6-DMSO($0.5cm^3$) and 1 equivalent of benzylamine($0.01cm^3$) added. The PMR spectrum(220MHz) was recorded after 5 minutes(fig.2.2.18(b)):- τ 1.23(1H,s),2.00(1H,s),7.86(3H,s) and 8.21(3H,s).

Similar PMR spectra(90MHz) were produced for the products of reaction of 2 or 10 equivalents of benzylamine(0.02 or $0.1cm^3$) with compound (98)(0.0336g) in d_6-DMSO($0.4cm^3$).

Stopped-flow spectrophotometry showed 2 reaction steps on rapidly mixing DMSO solutions of 100 or 500 equivalents of benzylamine(0.02 or 0.10M) with compound (98)(fig.2.2.19(a)).

Fifty equivalents of benzylamine($0.0007cm^3$) were added to a 4×10^{-5}M solution of compound (98) in DMSO and the UV-visible spectrum recorded; λ_{max} was at 530nm.

(D) Hexamethyldisilazane(HMDS)

Compound (98)(0.0315g) was dissolved in d_6-DMSO($0.4cm^3$) and 1 equivalent of hexamethyldisilazane($0.02cm^3$) added. The PMR spectrum(90MHz) was recorded and is shown in fig.2.2.20(b). The formation of compound (100) and another species occurred:- τ 1.62(1H,s),2.19(1H,s),7.95(3H,s) and 8.35 (3H,s).

The spectrum was re-recorded after 40 minutes and showed only compound (101)(fig.2.2.20(c)).

(E) Hydrazine hydrate

Compound (98)(0.0328g) was dissolved in d_6-DMSO(0.4cm^3) and 1 equivalent of hydrazine hydrate(0.005cm^3) added. The PMR spectrum(90MHz) was recorded after 5 minutes(fig.2.2.21(b)) and showed the formation of compound (100); and another species which gave the following spectrum:- τ 1.37(1H,s),2.14(1H,s),7.86(3H,s) and 8.36(3H,s).

The spectrum was re-recorded after 30 minutes and showed only compound (101).

A few microlitres of the PMR sample were diluted in DMSO(3cm^3) and the UV-visible spectrum recorded; λ_{max} was at 524nm.

(F) Sulphite ion

Compound (98)(0.034g) was dissolved in d_6-DMSO(0.6cm^3) in a stoppered 10cm^3 QF conical flask and 3 equivalents of 1M aqueous sodium sulphite solution(0.3cm^3) added, with magnetic stirring. After 5 minutes the PMR spectrum(90MHz) of filtered reaction mixture was recorded(fig.2.2.22(b)):- τ 1.77(1H,s),3.48(1H,s),7.60(3H,s) and 7.93(3H,s).

2.7 Polynitro-1,8-dimethylnaphthalenes

2.7.1 2,4,5-Trinitro-1,8-dimethylnaphthalene(106)

Compound (106)(0.0291g) was dissolved in d_6-DMSO(0.4cm^3) and the PMR spectrum(90MHz) recorded(fig.2.3.1(a)):- τ 1.13(1H,s),1.53 and 2.12 (2H,ABq,J_{AB} 8Hz),6.95(3H,s) and 7.07(3H,s).

(A) Hydroxide ion

Compound (106)(0.0507g) was dissolved in d_6-DMSO(0.4cm^3) and 1 equivalent of 5M sodium deuterioxide in D_2O(0.05cm^3) added. The PMR spectrum(90MHz) was recorded and showed that 2 products were formed (fig.2.3.1(b)); compound (142):- τ 1.34(1H,s),2.38 and 2.69(2H,ABq,J_{AB} 8.0Hz),3.76(1H,s),4.66(1H,s) and 7.41(3H,s); and compound (143):- τ 1.51 (1H,s), other aromatic lines obscured, 7.30(3H,s) and 8.22(3H,s).

Compound (106)(0.03g) was dissolved in d_6-DMSO(0.4cm^3) and diethylamine(0.04cm^3) added(See section C for the spectral parameters of the product of this reaction). This was followed by the addition of 5M sodium deuterioxide in D_2O(0.04cm^3). The PMR spectrum(90MHz) of this mixture was recorded:- τ 2.62 and 2.86(2H,ABq,J_{AB} 8Hz), low-field doublet of ABq obscured, 4.81(2H,ABq,J_{AB} 2.6Hz),4.11(1H,s) and 7.48(3H,s).

(B) Methoxide ion

Compound (106)(0.0291g) was dissolved in d_6-DMSO(0.4cm^3) and 1 equivalent of 2M sodium methoxide-d_3 in CD_3OD(0.05cm^3) added. The PMR spectrum(90MHz) was recorded(fig.2.3.2(b)). This indicated the formation of compound (142) and another species:- τ 1.24(1H,s),2.40 and 2.94(2H,ABq, J_{AB} 8.0Hz),7.36(3H,s) and 8.12(3H,s).

A further 2 equivalents of 2M sodium methoxide-d_3 in CD_3OD was added and the PMR spectrum recorded(fig.2.3.2(c)):- τ 1.24(1H,s),2.40 and 2.94(2H,ABq,J_{AB} 8.0Hz),7.36(3H,s) and 8.12(3H,s).

A few microlitres of this PMR sample were diluted in DMSO(3cm^3) and the UV-visible spectrum recorded; λ_{max} was at 549nm.

(C) Diethylamine

Compound (106)(0.02g) was dissolved in d_6-DMSO(0.4cm^3) and 3.5 equivalents of diethylamine(0.025cm^3) added. The PMR spectrum(90MHz) was recorded(fig.2.3.3(b)):- τ 1.35(1H,s),2.41 and 2.74(2H,ABq,J_{AB} 8.3Hz), 3.82(1H,s),4.76(1H,s) and 7.40(3H,s).

No change in the spectrum was observed after the addition of a further 7 equivalents of diethylamine(0.05cm^3).

A few microlitres of this PMR sample were diluted in DMSO(3cm^3) and the UV-visible spectrum recorded; λ_{max} was at 558nm.

(D) Benzylamine

Compound (106)(0.0291g) was dissolved in d_6-DMSO(0.4cm^3) and 2.5 equivalents of benzylamine(0.025cm^3) added. The PMR spectrum(90MHz) was recorded after 5 minutes and it showed the formation of compound (142) and another species(fig.2.3.4(b)). This latter species gave the following PMR spectrum:- τ 1.23(1H,s), other aromatic lines obscured, 7.12(3H,s) and 8.20 (3H,s).

After 1 hour the spectrum showed only the presence of compound (142).

Five equivalents of benzylamine(0.05cm^3) reacted with compound (106)(0.0291g) in d_6-DMSO(0.4cm^3) to give a spectrum similar to that obtained for the products of reaction of 2.5 equivalents of base.

(E) Hexamethyldisilazane(HMDS)

Compound (106)(0.028g) was dissolved in d_6-DMSO(0.4cm^3) and hexamethyldisilazane(0.025cm^3) added. The PMR spectrum(90MHz) was recorded and showed that only compound (142) was formed.

(F) Hydrazine hydrate

Compound (106)(0.0291g) was dissolved in d_6-DMSO(0.4cm^3) and 2 equivalents of hydrazine hydrate(0.01cm^3) added. The PMR spectrum(90MHz) recorded(fig.2.3.5(b)):- τ 1.22(1H,s),2.40 and 2.93(2H,ABq,J_{AB} 8.0Hz), 7.22(3H,s)and 8.34(3H,s).

(G) Sulphite ion

Compound (106)(0.0289g) was dissolved in d_6-DMSO(0.4cm^3) in a stoppered 10cm^3 QF conical flask and 2 equivalents of 1M sodium sulphite in D_2O(0.2cm^3) added with magnetic stirring. The PMR spectrum(90MHz) of 0.4cm^3 of the filtered reaction mixture was recorded(fig.2.3.6(b)):- τ 2.39 and 2.80(2H,ABq,J_{AB} 8.0Hz),3.56(1H,s),7.46(3H,s) and 7.70(3H,s).

A few microlitres of the PMR sample were diluted by DMSO(3cm^3), and the UV-visible spectrum recorded; λ_{max} was at 534nm.

2.7.2 2,4,5,7-Tetranitro-1,8-dimethylnaphthalene(107)

Compound (107)(0.0336g) was dissolved in d_6-DMSO(0.4cm^3) and the PMR spectrum(90MHz) recorded(fig.2.3.7(a)):- τ 0.97(2H,s) and 7.07 (3H,s).

(A) Deuterioxide ion

Compound (107)(0.0336g) was dissolved in d_6-DMSO(0.4cm^3) and 1 equivalent of 5M sodium deuterioxide in D_2O(0.025cm^3) added. The PMR spectra(90MHz) was recorded(fig.2.3.7(b)):- τ 1.42(1H,s),1.71(1H,s),3.82 (1H,s),4.67(1H,s) and 7.30(3H,s).

(B) Methoxide ion

Compound (107)(0.0336g) was dissolved in d_6-DMSO(0.4cm^3) and 1 equivalent of 2M sodium methoxide-d_3 in CD_3OD(0.05cm^3) added. The PMR spectrum(90MHz) was recorded and the formation of compound (109) and another species noted(fig.2.3.8(b)):- τ 1.27(1H,s),1.77(1H,s),8-Me line obscured and 8.02(3H,s).

(C) Diethylamine

Compound (107)(0.035g) was dissolved in d_6-DMSO(0.4cm^3) and 2 equivalents of diethylamine(0.02cm^3) added. The PMR spectrum(90MHz) was recorded(fig.2.3.9(b)) and it showed that only compound (109) was formed.

A few microlitres of the PMR sample were diluted in DMSO(3cm^3) and the UV-visible spectrum recorded; λ_{max} was at 535nm.

(D) Benzylamine

Compound (107)(0.0336g) was dissolved in d_6-DMSO(0.4cm^3) and 2 equivalents of benzylamine(0.025cm^3) added. The PMR spectrum(90MHz) was recorded and the formation of compound (109) and another species noted (fig.2.3.10(b)):- τ 1.25(1H,s),1.85(1H,s),7.03(3H,s) and 8.09(3H,s).

(E) Hexamethyldisilazane

Compound (107)(0.0336g) was dissolved in d_6-DMSO(0.4cm^3) and 1.5 equivalents of hexamethyldisilazane(0.025cm^3) added. The PMR spectrum (90MHz) was recorded and the formation of compound (109) indicated.

(F) Hydrazine hydrate

Compound (107)(0.030g) was dissolved in d_6-DMSO(0.4cm^3) and 1 equivalent of hydrazine hydrate(0.005cm^3) added. The PMR spectrum(90MHz) was recorded and the formation of compound (109) indicated(fig.2.3.11(b)). Addition of 5 equivalents of base(0.025cm^3) to compound (107)(0.030g) in d_6-DMSO(0.4cm^3) resulted in the formation of a different product as shown by the PMR spectrum(90MHz)(fig.2.3.11(c)):- τ 1.26(1H,s),1.82(1H,s),7.13 (3H,s) and 8.23(3H,s).

(G) Sulphite ion

Compound (107)(0.0627g) was dissolved in d_6-DMSO(0.8cm^3) in a stoppered $10cm^3$ QF conical flask and 1 equivalent of 1M sodium sulphite in $D_2O(0.2cm^3)$ added with magnetic stirring. The PMR spectrum(90MHz) was recorded but it only showed a mixture of decomposition products.

2.8 Polynitro-2,3-dimethylnaphthalenes

2.8.1 1,5,7-Trinitro-2,3-dimethylnaphthalene(156)

Compound (156)(0.0291g) was dissolved in d_6-DMSO($0.4cm^3$) and the PMR spectrum(90MHz) recorded(fig.2.4.1(a)):- τ 1.67(1H,s),1.13 and 1.48 (2H,ABq,J_{AB} 1.8Hz),7.39(3H,s) and 7.58(3H,s).

(A) Deuterioxide ion

Compound (156)(0.0215g) was dissolved in d_6-DMSO($0.4cm^3$) and 5M sodium deuterioxide in $D_2O(0.025cm^3)$ added. The PMR spectrum(90MHz) was recorded but showed only the formation of decomposition products.

(B) Methoxide ion

Compound (156)(0.012g) was dissolved in d_6-DMSO($0.4cm^3$) and 1 equivalent of 2M sodium methoxide-d_3 in $CD_3OD(0.02cm^3)$ added. The PMR spectrum(90MHz) was recorded:- τ 1.09 and 3.98(2H,ABq,J_{AB} 2Hz),1.57 (1H,s),7.66(3H,s) and 7.90(3H,s).

(C) Diethylamine

Compound (156)(0.0183g) was dissolved in d_6-DMSO($0.4cm^3$) and 1.5 equivalents of diethylamine($0.01cm^3$) added. The PMR spectrum(90MHz) was recorded but no well defined product was indicated.

(D) Sulphite ion

Compound (156)(0.02g) was dissolved in d_6-DMSO($0.4cm^3$) in a stoppered $10cm^3$ QF conical flask and 1M sodium sulphite in $D_2O(0.2cm^3)$ added with magnetic stirring. The PMR spectrum(90MHz) of $0.4cm^3$ of the filtered reaction mixture was recorded(fig.2.4.1(b)):- τ 1.30(1H,s),1.33 and 4.17(2H,ABq,J_{AB} 1.8Hz),7.67(3H,s) and 7.87(3H,s).

A few microlitres of the PMR sample were diluted by DMSO($3cm^3$), and the UV-visible spectrum recorded; λ_{max} was at 543nm.

2.8.2 1,4,5,7-Tetranitro-2,3-dimethylnaphthalene(161)

Compound (161)(0.0336g) was dissolved in d_6-DMSO($0.4cm^3$) and the PMR spectrum recorded(fig.2.4.2(a)):- τ 0.93 and 1.36(2H,ABq,J_{AB} 2Hz), 7.44(3H,s) and 7.47(3H,s).

(A) Deuterioxide ion, diethylamine and benzylamine

Compound (161)(0.0205g) dissolved in d_6-DMSO(0.4cm^3) reacted with 5M sodium deuterioxide(0.02cm^3), diethylamine(0.02cm^3) or benzylamine (0.02cm^3) to give products which gave PMR spectra(90MHz) which showed broadened resonances.

(B) Sulphite ion

Compound (161)(0.0672g) was dissolved in d_6-DMSO(1.2cm^3) in a stoppered 10cm^3 QF conical flask and 3 equivalents of 1M sodium sulphite in D_2O(0.6cm^3) added with magnetic stirring. The PMR spectrum(90MHz) of 0.4cm^3 of the filtered reaction mixture was recorded(fig.2.4.2(b)):- τ 1.43 and 4.30(2H,ABq,J_{AB} 1.8Hz),7.74(3H,s) and 7.76(3H,s).

A 5×10^{-5}M solution(3cm^3) of compound (161) in aqueous DMSO(2:3) was reacted with excess sodium sulphite and the UV-visible spectrum recorded; λ_{max} was at 527nm.

Stopped-flow spectrophotometry shows only 1 reaction step on mixing solutions containing 5×10^{-4}M sodium sulphite and 5×10^{-5}M compound (161) in DMSO/H_2O(4:1)(fig.2.4.3).

2.9 Polynitro-2,6-dimethylnaphthalenes

2.9.1 1,3,5-Trinitro-2,6-dimethylnaphthalene(162)

Compound (162)(0.0291g) was dissolved in d_6-DMSO and the PMR spectrum(90MHz) recorded(fig.2.5.1(a)):- τ 1.40(1H,s),2.03 and 2.06(2H,ABq, J_{AB} 9.2Hz),7.45(3H,s) and 7.48(3H,s).

(A) Hydroxide ion

Compound (162)(0.0425g) was dissolved in d_6-DMSO(0.4cm^3) and 0.86 equivalent of 5M sodium hydroxide in H_2O(0.025cm^3) added. The PMR spectrum(90MHz) was recorded after 4 minutes and showed the formation of several products(fig.2.5.1(b)). One product appeared to have the following spectral parameters:- τ 2.15 and 2.76(2H,ABq,J_{AB} 8Hz),5.16(multiplet or overlapping doublets),7.82(3H,s) and 7.86(3H,s). Another product gave a doublet that appeared to be the high-field half of an AB quartet at τ 2.57

(J_{AB}~9Hz), but the other lines were obscured. The PMR spectrum did not change markedly over 1 hour. Solutions(1.5cm^3) containing 100 equivalents of 0.05M sodium hydroxide and compound (162) in DMSO/H_2O(7:3) were mixed and the visible absorbtion spectrum recorded immediately. The absorbtion maximum occurred at 508nm, but over a period of 20 minutes this was observed to shift to 515nm.

The visible absorbtion spectrum in fig.2.5.2 was obtained by measuring the absorbance at 10nm intervals(470-560nm) at the infinity position of the reaction after 364 equivalents of 0.02M sodium hydroxide were mixed with 5.5×10^{-5}M compound (162) in aqueous DMSO(1:4). A broad absorbtion maximum at 511nm was obtained.

(B) Methoxide ion

Compound (162)(0.0412g) was dissolved in d_6-DMSO(0.4cm^3) and 0.85 equivalent of 2M sodium methoxide-d_3 in CD_3OD(0.06cm^3) added. The FT PMR spectrum(90MHz) was recorded(accumulated within 7 minutes of mixing) and it showed the formation of several products. The aromatic region was confused but one of the products appeared to give the following spectrum(fig.2.5.1(c)):- τ 2.17 and 2.73(2H,ABq,J_{AB} 9Hz), 5.13(multiplet) and 7.80(methyl lines).

Solutions containing 0.5 equivalent of 0.2M sodium methoxide (0.0035cm^3) in methanol and 4×10^{-4}M compound (162) in DMSO(3.5cm^3) were mixed and the UV-visible spectrum recorded after 2 minutes reaction. A visible absorbtion maximum at 511nm occurred, but the intensity of this decreased rapidly with time. After 20 minutes the absorbtion maximum which had decreased in intensity and shifted to 520nm started to increase in intensity again. After 100 minutes reaction time this band had shifted to 524nm.

The product of reaction of 10^{-4}M solution of compound (162) in DMSO with 1 equivalent of 0.2M sodium methoxide in methanol(0.00175cm^3) gives similar UV-visible absorbtion spectra to those for reaction with 0.5 equivalent of base, except that the process is relatively faster.

The EPR spectrum(9 GHz) of a DMSO solution containing 10^{-3}M compound (162)(1 cm^3) and 1 equivalent of 0.2M sodium methoxide in methanol (0.005cm^3), was recorded.

A low intensity broad resonance was observed to develop over a period of 25 minutes.

A 10^{-3}M solution of compound (162) in DMSO(1cm^3) was reacted with 10 equivalents of 0.2M sodium methoxide in methanol and the EPR spectrum recorded. A medium intensity broad resonance(g=2.026) was observed.

(C) Diethylamine

Compound (162)(0.0216g) was dissolved in d_6-DMSO(0.4cm^3) and 3 equivalents of diethylamine(0.025cm^3) added. The PMR spectrum(90MHz) was recorded and it showed the formation of several products(fig.2.5.3(b)). Two pairs of the high-field doublets of AB quartets occur at τ 2.54 and 2.74 (J_{AB} 8Hz); a multiplet occurs at τ 5.14 and a methyl resonance at τ 7.80. It is probable that the 2 aromatic doublets are due to 2 different compounds.

(D). Other amines

Compound (162)(0.0225g) was dissolved in d_6-DMSO(0.4cm^3) and benzylamine(0.025cm^3) added. The PMR spectrum(90MHz) was recorded and showed that several ill-defined products were formed.

Compound (162)(0.0446g) was dissolved in d_6-DMSO(0.4cm^3) and hydrazine hydrate(0.025cm^3) added. The PMR spectrum(90MHz) was recorded and showed that a complex mixture of unidentified products were formed.

(E) Sulphite ion

Compound (162)(0.060g) was dissolved in d_6-DMSO(1.2cm^3) in a stoppered 10cm^3 QF conical flask and 3 equivalents of 1M sodium sulphite in D_2O added with magnetic stirring. The PMR spectrum(90MHz) of 0.4cm^3 of the filtered reaction mixture was recorded(fig.2.5.4(b)):- τ 1.77 and 2.66 (2H,ABq,J_{AB} 8.0Hz),3.80(1H,s),7.53(3H,s) and 7.72(3H,s).

A few microlitres of the PMR sample were diluted with DMSO(3cm^3) and the UV-visible spectrum recorded; λ_{max} was at 526nm.

2.9.2 1,4,5-Trinitro-2,6-dimethylnaphthalene(169)

Compound (169)(0.0291g) was dissolved in d_6-DMSO(0.4cm^3) and the PMR spectrum recorded(fig.2.5.5(a)):- τ 1.43(1H,s),1.99 and 2.03

(2H,ABq,J_{AB} 9.0Hz),7.39(3H,s) and 7.46(3H,s).

(A) Hydroxide ion

Compound (169)(0.0406g) was dissolved in d_6-DMSO(0.4cm^3) and 5M sodium deuterioxide in D_2O(0.025cm^3) added. The PMR spectrum(90MHz) was recorded(accumulation within 7 minutes of mixing) and this showed that at least 2 products were formed. One of these gave a singlet at τ 0.15 and the other compound probably gave the following spectrum:- τ 2.87 and 3.14(2H, ABq,J_{AB} 7Hz),5.09(partly obscured doublet or multiplet),7.67(3H,s) and 8.04 (3H,s).

(B) Methoxide ion

Compound (169)(0.0417g) was dissolved in d_6-DMSO(0.4cm^3) and 0.84 equivalent of 2M sodium methoxide-d_3(0.06cm^3) added. The FT PMR spectrum(90MHz) was recorded(accumulation within 10 minutes of mixing) and although broadened it showed overlapping aromatic resonances; a multiplet at τ 5.09 and methyl lines at τ .7.67 and 8.01.

Compound (169)(0.006g) was dissolved in DMSO(0.1cm^3) and 1 equivalent of 2M sodium methoxide(0.01cm^3) was added. The EPR spectrum was recorded and this showed a broad resonance(g=2.033).

A 4×10^{-4}M solution(3cm^3) of compound (169) in DMSO was reacted with 0.5 equivalent of 0.2M sodium methoxide in MeOH and the UV-visible spectrum recorded. A visible absorbtion maximum at 465nm increased in intensity with time.

A 10^{-4}M solution of compound (169) in DMSO(3.5cm^3) was reacted with 1 equivalent of 0.2M sodium methoxide in methanol(0.00175cm^3) and the UV-visible spectrum recorded. A visible absorbtion maximum at 465nm occurred and this increased in intensity with time.

(C) Amine bases

Compound (169)(0.0291g) was dissolved in d_6-DMSO(0.4cm^3) and 2 equivalents of diethylamine added(0.02cm^3). The FT PMR spectrum(90MHz) was recorded(accumulation within 3 minutes of mixing) and this showed that several products were formed. The major product gave the following spectrum:- τ 2.88 and 3.05(2H,ABq,J_{AB} 8Hz),5.15(multiplet),7.69(3H,s) and 8.03(3H,s).

Compound (169)(0.044g) was dissolved in d_6-DMSO(0.4cm^3) and benzylamine added(0.025cm^3). The PMR spectrum was recorded and this showed that several products were formed. Obscuration by benzylamine lines made assignment difficult.

Compound (169)(0.041g) was dissolved in d_6-DMSO(0.4cm^3) and hydrazine hydrate added(0.025cm^3). The PMR spectrum(90MHz) was recorded and this showed that a complex mixture of products was formed.

(D) Sulphite ion

Compound (169)(0.06g) was dissolved in d_6-DMSO(1.2cm^3) in a stoppered 10cm^3 QF conical flask and 3 equivalents of 1M sodium sulphite in D_2O(0.6cm^3) added with magnetic stirring. The FT PMR spectrum(90MHz) of 0.4cm^3 of the filtered reaction mixture was recorded(fig.2.5.5(b)):- τ 2.81 and 3.04(2H,ABq,J_{AB} 8.0Hz),4.43(1H,s),7.66(3H,s) and 7.86(3H,s).

A few microlitres of the PMR sample were diluted with DMSO(3cm^3) and the UV-visible spectrum recorded; λ_{max} was at 424nm.

2.9.3 1,3,5,7-Tetranitro-2,6-dimethylnaphthalene(177)

The FT PMR spectrum(90MHz) of a saturated d_6-DMSO solution containing compound (177) was recorded(fig.2.5.6(a)):- τ 1.35(2H,s) and 7.48 (6H,s).

(A) Hydroxide ion

Compound (177)(0.003g) was dissolved in d_6-DMSO(0.4cm^3) and 1 equivalent of 5M sodium deuterioxide in D_2O(0.004cm^3) added. The FT PMR spectrum(90MHz) was recorded and this showed that several products were formed. Resonances of greatest intensity occurred at τ 1.33 and 3.77 with the methyl region obscured by solvent lines.

A 5×10^{-5}M solution of compound (177) in DMSO(3cm^3) was reacted with 0.2M aqueous sodium hydroxide(0.003cm^3) and the UV-visible spectrum recorded. A visible absorbtion maximum at 501nm was observed and this increased in intensity and shifted to 505nm with time(over a period of 2 hours).

(B) Methoxide ion

Compound (177)(0.004g) was dissolved in d_6-DMSO(0.4cm^3) and 2M sodium methoxide-d_3(0.01cm^3) added. The FT PMR spectrum(90MHz) was recorded but this only showed broadened lines due to a mixture of products.

A 5×10^{-5}M solution of compound (177) in DMSO(3cm^3) was reacted with 0.2M sodium methoxide(0.003cm^3) and the UV-visible spectrum recorded. A visible absorbtion maximum occurred at 498nm and this slowly decreased in intensity with time.

(C) Amines

PMR spectra of the products of reaction of amines with compound (177) in d_6-DMSO were not recorded.

A 5×10^{-5}M solution of compound (177) in DMSO(3cm^3) was reacted with diethylamine(0.005cm^3) and the UV-visible spectrum recorded; λ_{max} was at 510nm.

Similarly, the absorbtion maxima of solutions containing 5×10^{-5}M compound (177) in DMSO and benzylamine(0.0016cm^3) and hydrazine hydrate (0.002cm^3) occurred at 507 and 503nm respectively.

(D) Sulphite ion

Compound (177)(0.06g) was dissolved in d_6-DMSO(1.2cm^3) in a stoppered 10cm^3 QF conical flask and 3 equivalents of sodium sulphite added with magnetic stirring. The FT PMR spectrum(90MHz) of 0.4cm^3 of the filtered reaction mixture was recorded(fig.2.5.6(b)):- τ 0.78(1H,s),3.92(1H,s), 7.50(3H,s) and 7.67(3H,s).

A few microlitres of the PMR sample were diluted in DMSO(3cm^3) and the UV-visible spectra recorded; λ_{max} was at 508nm.

2.9.4 1,3,5,8-Tetranitro-2,6-dimethylnaphthalene(181)

Compound (181)(0.008g) was dissolved in d_6-DMSO(0.4cm^3) and the FT PMR spectrum(90MHz) recorded(fig.2.5.7(a)):- τ 1.22(1H,s),1.24(1H,s), 7.41(3H,s) and 7.47(3H,s).

(A) Hydroxide ion

Compound (181)(0.020g) was dissolved in d_6-DMSO(0.4cm^3) and 1 equivalent of 5M sodium deuterioxide(0.012cm^3) added. The FT PMR spectrum (90MHz) was recorded and it showed a mixture of products. The most prominent resonance was a multiplet at τ 5.26.

A 5×10^{-5}M solution of compound (181) in DMSO was reacted with 0.2M sodium hydroxide($0.006cm^3$) and the UV-visible spectrum recorded; λ_{max} was at 501nm.

(B) Methoxide ion

Compound (181)(0.007g) was dissolved in d_6-DMSO($0.4cm^3$) and 1 equivalent of 2M sodium methoxide-d_3 in CD_3OD($0.01cm^3$) added. The FT PMR spectrum(90MHz) was recorded and this showed a complex mixture of products.

(C) Amines

Compound (181)(0.0314g) was dissolved in d_6-DMSO($0.4cm^3$) and diethylamine($0.025cm^3$) added. The PMR spectrum(90MHz) was recorded and this showed 2 lines in the aromatic region at τ 0.5 and 1.45. Methyl lines occurred at τ 7.76 and 8.26.

A 5×10^{-5}M solution of compound (181) in DMSO was reacted with diethylamine($0.002cm^3$) and the UV-visible absorbtion recorded; λ_{max} was at 509nm.

Compound (181)(0.032g) was dissolved in d_6-DMSO($0.4cm^3$) and benzylamine($0.01cm^3$) added. The PMR spectrum(90MHz) was recorded but only broadened lines were given.

A 5×10^{-5}M solution of compound (182) in DMSO was reacted with benzylamine($0.0005cm^3$) and the UV-visible spectrum recorded; λ_{max} was at 585nm.

Compound (181)(0.020g) was dissolved in d_6-DMSO($0.4cm^3$) and hydrazine hydrate($0.005cm^3$) added. The FT PMR spectrum(90MHz) was recorded(fig.2.5.7(b)):- τ 1.34(1H,s),2.74(1H,s),7.81(3H,s) and 8.24(3H,s).

The spectrum was re-recorded after 7 days and a new product had formed:- τ 1.45(1H,s),2.45(1H,s),7.72(3H,s) and 8.52(3H,s).

A 5×10^{-5}M solution of compound (181) in DMSO was reacted with hydrazine hydrate($0.002cm^3$) and the UV-visible spectrum recorded; λ_{max} was at 544nm.

(D) Sulphite ion

Compound (181)(0.06g) was dissolved in d_6-DMSO($1.2cm^3$) in a stoppered $10cm^3$ QF conical flask and 3 equivalents of 1M sodium sulphite in

D_2O(0.6cm^3) added. The FT PMR spectrum(90MHz) was recorded and is shown in fig.2.5.8(b). Two products were formed:- τ 2.25(1H,s),3.88(1H,s),7.39 (3H,s) and 7.67(3H,s); and τ 2.49(1H,s),4.53(1H,s),7.82(3H,s) and the other methyl line obscured.

A few microlitres of the PMR sample were diluted with DMSO(3cm^3) and the UV-visible spectrum recorded; λ_{max} was at 513nm.

2.9.5 1,4,5,8-Tetranitro-2,6-dimethylnaphthalene(190)

Compound (190)(0.002g) was dissolved in d_6-DMSO(0.4cm^3) and the FT PMR spectrum(90MHz) recorded(fig.2.5.9(a)):- τ 1.21(2H,s) and 7.34(6H,s).

(A) Hydroxide ion

Compound (190)(0.0208g) was dissolved in d_6-DMSO(0.4cm^3) and 5M sodium deuterioxide in D_2O(0.02cm^3) added. The FT PMR spectrum(90MHz) was recorded and this showed that a mixture of products was formed.

A 5×10^{-5}M solution of compound (189) in DMSO(3cm^3) was reacted with 0.2M sodium hydroxide(0.003cm^3) and the UV-visible spectrum recorded; λ_{max} was at 443nm.

(B) Methoxide ion

Compound (190)(0.007g) was dissolved in d_6-DMSO(0.4cm^3) and 1 equivalent of 2M sodium methoxide-d_3(0.01cm^3) added. The FT PMR spectrum (90MHz) was recorded and this showed that 2 products were formed (fig.2.5.9(b)):- τ 2.57(1H,s),4.73(1H,s),7.48(3H,s) and 7.51(3H,s); and:- τ 3.68 and 5.09(doublets but possibly ABq,J_{AB} 3.6Hz),5.72(s),5.74(s) and methyl resonance(s) ~ 7.50(partly obscured).

A 5×10^{-5}M solution of compound (190) in DMSO(3cm^3) was reacted with 0.2M sodium methoxide in methanol(0.003cm^3) and the UV-visible spectrum recorded; λ_{max} was at 446nm.

(C) Amines

Dimethylacetamide(DMA) was saturated with compound (190) and diethylamine(0.02cm^3) added. The PMR spectrum(90MHz) was recorded:- τ 0.8(1H,s),3.2(1H,s), other lines obscured by solvent lines.

Compound (190)(0.0315g) was dissolved in DMA and benzylamine

($0.025cm^3$) added. The PMR spectrum(90MHz) was recorded and it showed that several unidentified products were formed.

A 5×10^{-5}M solution of compound (190) in DMSO was reacted with benzylamine($0.002cm^3$) and the UV-visible spectrum recorded; λ_{max} was at 550nm.

DMA was saturated with compound (190) and hydrazine hydrate ($0.015cm^3$) added. The PMR spectrum(90MHz) was recorded and showed that several products were formed.

A 5×10^{-5}M solution of compound (190) in DMSO($3cm^3$) was reacted with hydrazine hydrate($0.002cm^3$) and the UV-visible spectrum recorded; λ_{max} was at 377nm.

(D) Sulphite ion

Compound (190)(0.06g) was dissolved in d_6-DMSO($1.2cm^3$) in a stoppered $10cm^3$ QF conical flask and 3 equivalents of 1M aqueous sodium sulphite added with magnetic stirring. The FT PMR spectrum(90MHz) of $0.4cm^3$ of the filtered reaction mixture was recorded and this showed that a complex mixture of products was formed.

A few microlitres of the PMR sample was diluted with DMSO($3cm^3$) and the UV-visible spectrum recorded; λ_{max} was at 508nm.

CHAPTER THREE

KINETICS OF THE REACTION OF BASE WITH POLYNITRODIMETHYLNAPHTHALENES

3.1 2,4,8-Trinitro-1,5-dimethylnaphthalene

3.2 2,4,6,8-Tetranitro-1,5-dimethylnaphthalene

3.3 1,4,5,7-Tetranitro-2,3-dimethylnaphthalene

3.4 1,3,5-Trinitro-2,6-dimethylnaphthalene

3.1 2,4,8-Trinitro-1,5-dimethylnaphthalene(93)

3.1.1 Introduction

The reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine or triethylamine(50 - 1600 equivalents) in DMSO and DMSO/methanol (vol :vol :- 9:1,4:1,2:1 and 1:1) mixture has been studied in detail. Spectroscopic studies reported in the previous chapter have shown that under these conditions the amine abstracts a proton from a methyl group of 2,4,8-trinitro-1,5-dimethylnaphthalene. The proton abstraction reaction can be represented by the equation:-

$$XH \quad + \quad B \rightleftharpoons X^- \quad + \quad BH^+$$

where XH represents compound (93); B represents the amine base; X^- represents the 'benzyl-type' anion (94) and BH^+ is the conjugate acid of the base B.

3.1.2 Reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine in DMSO

The reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine (100 - 300 equivalents) in DMSO was followed by monitoring with time the absorbance of the 'benzyl-type' anion (94).

The reaction obeyed simple pseudo first order forward kinetics according to the following equation:-

$$\ln\left[\frac{x_e}{x_e - x}\right] = k_{1f}\, t \qquad (3.1)$$

where x_e is the concentration of species X^- (94) at equilibrium(in this case $x_e = [XH]_0$ where $[XH]_0$ is the initial concentration of compound (93)); x is the concentration of species X^- at time t and k_{1f} is the pseudo first order rate constant.

As the absorbance of the reaction solution at 560nm, where species X^- only absorbs, is proportional to x equation (3.1) may be rewritten:-

$$\ln\left[\frac{OD_e}{OD_e - OD_t}\right] = k_{1f}\, t \qquad (3.2)$$

or $$-\ln(OD_e - OD_t) + \text{constant} = k_{1f}t \qquad (3.3)$$

where OD_e = absorbance at infinite time and OD_t = absorbance at time t.

The data given in Table 3.1.1 was plotted according to equation (3.3) in fig.3.1.1 and a straight line obtained. The slope of this line gave the first order forward rate constant, k_{1f}, a value of $5.6 \times 10^{-3}s^{-1}$. This value is listed in Table 3.1.2 alongwith other values for k_{1f} derived from reaction involving other base concentrations and temperatures. These other reactions also gave linear first order kinetic plots.

Table 3.1.1 Absorbance values of species (94) for reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine in DMSO

$[XH]_0 = 5.116 \times 10^{-5}M$ Et_2NH = 300 equivalents Temp = 21.4°C

Time/s	OD_t	$OD_e - OD_t$	$-\ln(OD_e - OD_t)$
0	0.144	0.931	0.072
20	0.247	0.828	0.189
40	0.335	0.740	0.301
60	0.414	0.661	0.414
80	0.486	0.589	0.529
100	0.548	0.527	0.641
120	0.604	0.471	0.753
140	0.652	0.423	0.860
180	0.738	0.337	1.088
∞	1.013	0	∞

For pseudo first order reactions, a plot of k_{1f} against base concentration should give a straight line with slope equal to the second order forward rate constant, k_{2f} in accord with equation (3.4)

$$k_{1f} = k_{2f}[B] \qquad (3.4)$$

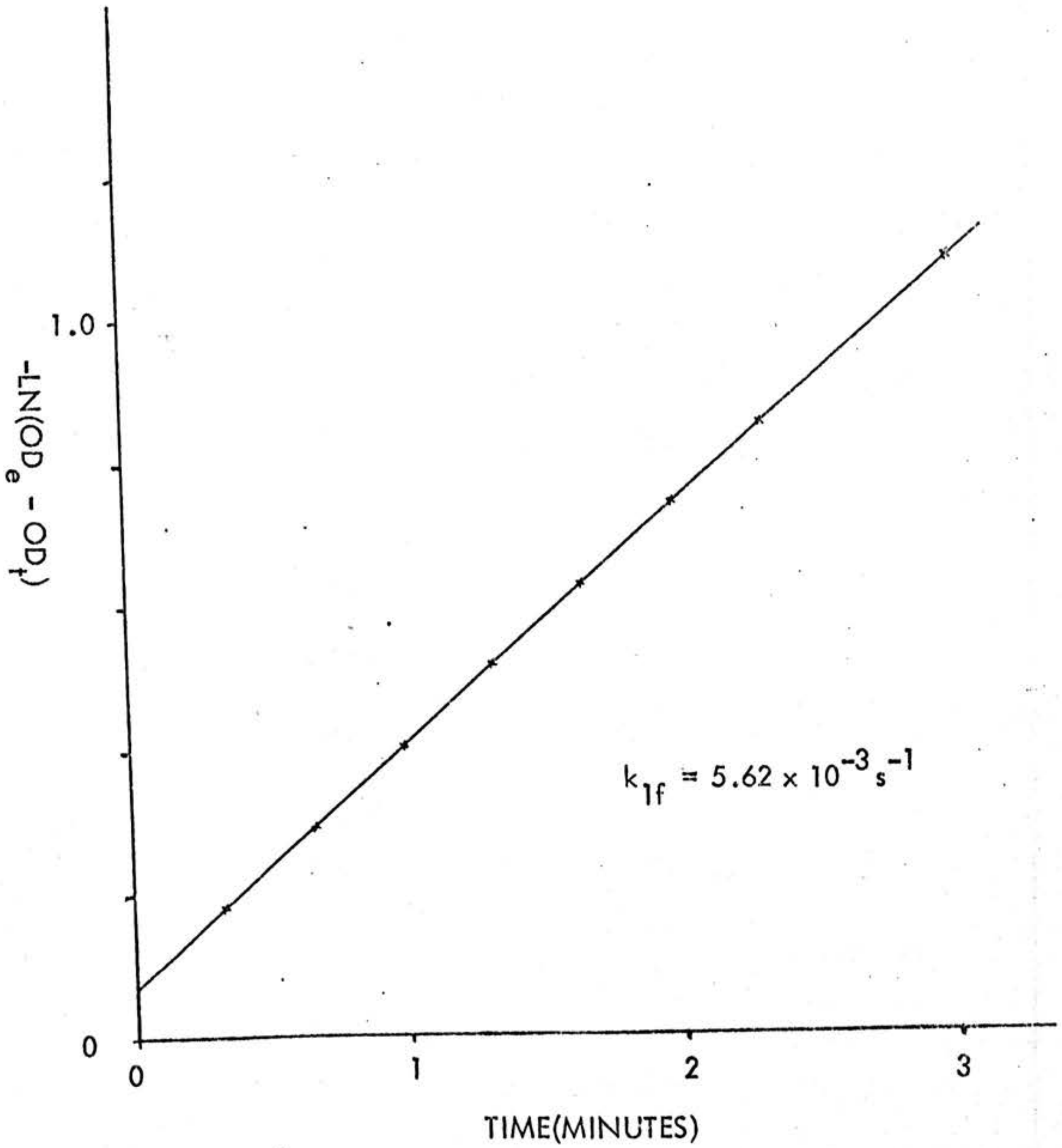


Fig.3.1.1 Pseudo 1st order forward kinetic plot as per equation (3.3) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93)(5.116×10^{-5}M) with 300 equivalents of diethylamine in DMSO at 21.4°C.

where $[B]$ is the base concentration. Such a plot is shown in fig.3.1.2. The k_{2f} values thus derived are listed in Table 3.1.2.

Table 3.1.2 Rate constants for reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine in DMSO

$[XH]_0 = 5.116 \times 10^{-5}M$

Temp.	Base equivalents	$10^3 k_{1f}/s^{-1}$	$k_{2f}/M^{-1}s^{-1}$
21.4°	100	1.93	
	200	3.81	0.368
	300	5.62	
30.5°	100	3.01	
	100	3.13	
	100	3.13	0.589
	200	5.93	
	300	9.33	
41.4°	100	5.38	
	100	5.50	
	200	10.23	
	200	10.30	0.971
	300	15.06	
	300	14.54	

Since in pure DMSO and using high base concentrations the reaction between 2,4,8-trinitro-1,5-dimethylnaphthalene and diethylamine goes to completion, the equilibrium constant for the reaction cannot be determined using the Benesi-Hildebrand equation(See section 3.1.3). However using low base concentrations(e.g. 10 equivalents) it is possible to obtain a measurable

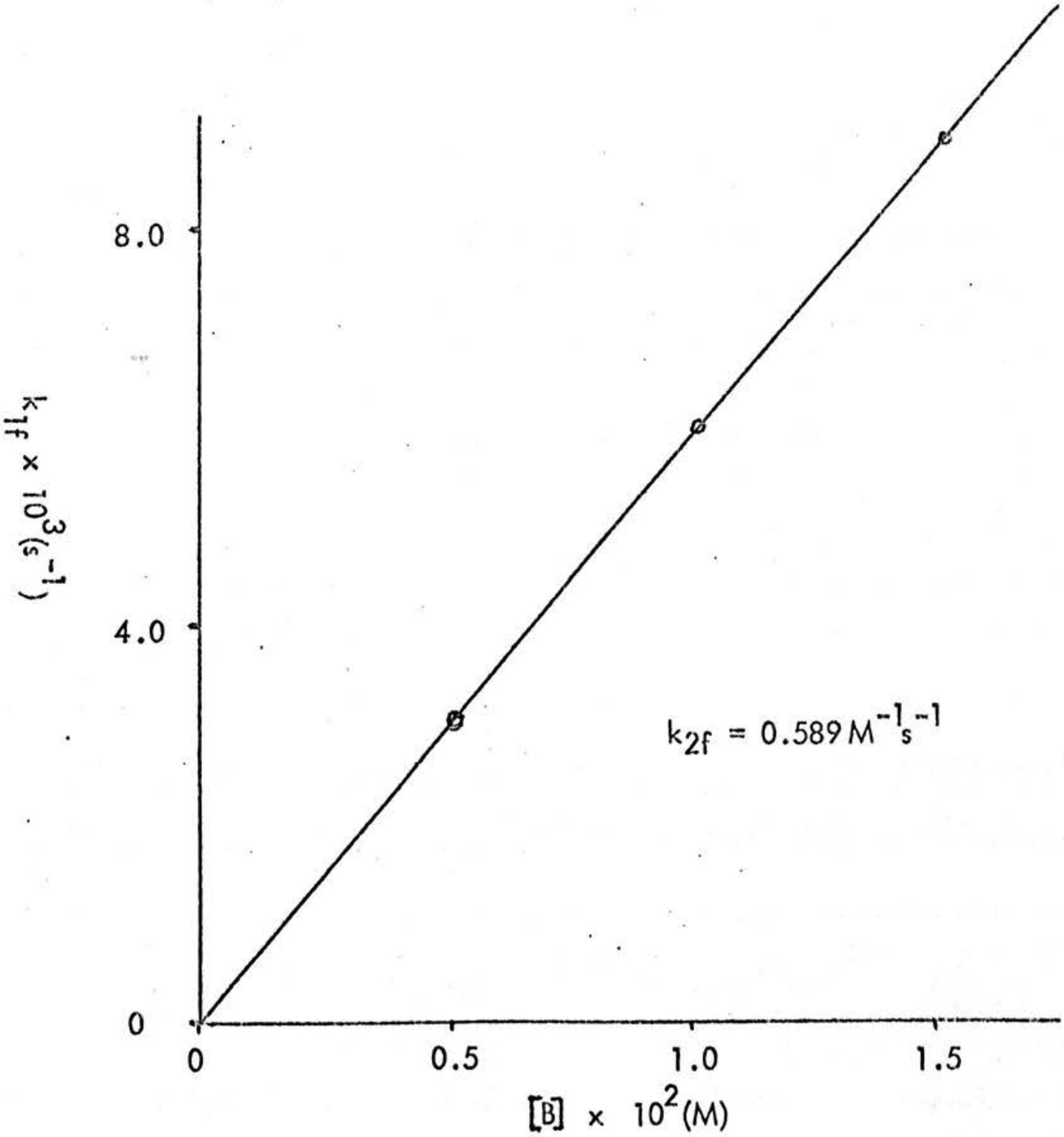


Fig.3.1.2 Plot of first order forward rate constant, k_{1f} against base concentration according to equation (3.4) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) with diethylamine in DMSO at 30.5°C.

equilibrium position. The 'spot-value' method employs equation (3.5)(derivation in Appendix 2.2.2):-

$$K = 1/(N\varepsilon_{X^-}^2 [XH]_0^2/OD_e^2 + 1 - \varepsilon_{X^-} [XH]_0 (1 + N)/OD_e) \qquad (3.5)$$

where N = number of equivalents of base, ε_{X^-} is the extinction coefficient of species X^- and the other symbols have their usual meaning. The extinction coefficient, ε_{X^-} required by equation (3.5) is given by the relationship $\varepsilon_{X^-} = OD_e/[XH]_0\ 1$. Both ε_{X^-} and K values are given in Table 3.1.3. The second order reverse rate constants, k_{2r}, for the reaction:-

$$XH + B \underset{k_{2r}}{\rightleftharpoons} X^- + BH^+$$

can be calculated from the relationship $k_{2r} = k_{2f}/K$. Values of k_{2r} derived in this way are listed in Table 3.1.3.

Table 3.1.3 Rate constants, equilibrium constants and extinction coefficients for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine in DMSO

Temp.	$k_{2f}/M^{-1}s^{-1}$	$k_{2r}/M^{-1}s^{-1}$ [a]	$\varepsilon_{X^-}/M^{-1}cm^{-1}$ [b]	K_{spot} [c]
21.4°	0.368	0.46	19700	0.817
30.5°	0.589	0.93	19600	0.662
41.4°	0.971	1.72	19300	0.577

a. k_{2r} from k_{2f}/K b. ε_{X^-} from $OD_e/[XH]_0$

c. K values derived according to equation (3.5)

Thermodynamic Parameters

The Arrhenius equation(equations (3.6) and (3.7) can be applied to the forward and reverse reaction under study:-

$$XH + B \rightleftharpoons X^- + BH^+$$

$$\ln k_{2f} = \ln A - E_a/RT \qquad (3.6)$$

$$\ln k_{2r} = \ln A' - E_a'/RT \qquad (3.7)$$

where E_a is the activation energy for the forward reaction and E_a' is the activation energy for the reverse reaction. Plots of $\ln k_{2f}$ and k_{2r} against $1/T$ gave values for E_a and E_a' respectively. An exemplary plot is shown in fig.3.1.3.

The enthalpy of activation and entropy of activation for the forward and reverse reactions were derived using the following relationships:-

$$\text{Enthalpy of activation} \quad \Delta H_f^* = E_a - RT$$

$$\Delta H_r^* = E_a' - RT$$

$$\text{Entropy of activation} \quad \Delta S_f^* = R\ln(Ah/k_BTe)$$

$$\Delta S_r^* = R\ln(A'h/k_BTe)$$

where A or A' is the Arrhenius frequency or pre-exponential factor and k_B = Boltzmann constant.

Program TD25 was used to process and plot the data. Fig.3.1.3 shows the Arrhenius plot for the forward reaction.

The overall enthalpy and entropy changes $\Delta H(= \Delta H_f^* - \Delta H_r^*)$ and $\Delta S(= \Delta S_f^* - \Delta S_r^*)$ respectively are listed in Table 3.1.4.

Table 3.1.4 Thermodynamic parameters for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine in DMSO

ΔH_f^*	ΔH_r^*	ΔH	ΔS_f^*	ΔS_r^*	ΔS
	$kJmol^{-1}$			$Jmol^{-1}K^{-1}$	
34.9	48.4	-13.5	-135	-87	-48

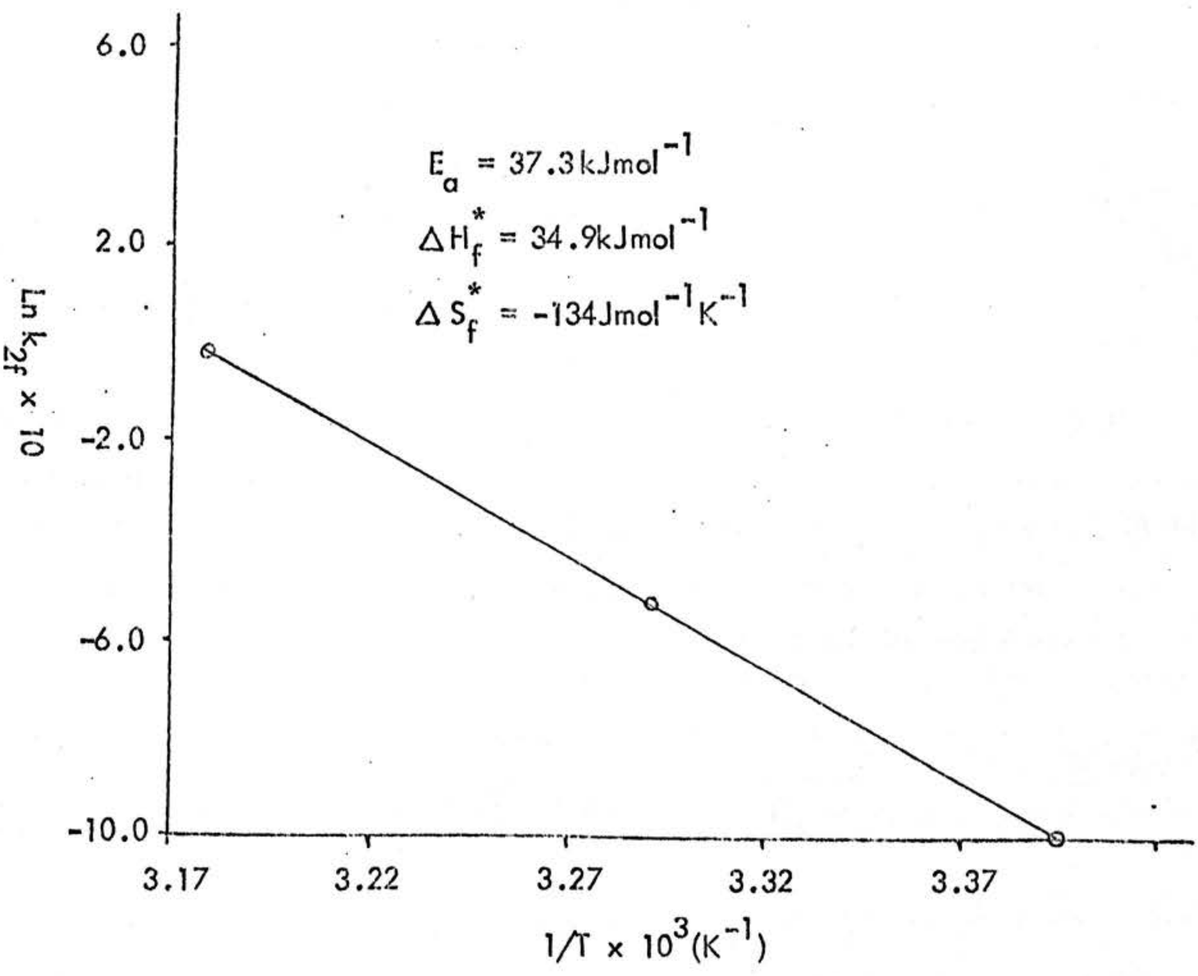


Fig.3.1.3 Arrhenius plot according to equation (3.6) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) with diethylamine in DMSO.

3.1.3 Reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine in DMSO/methanol

The reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine in DMSO/methanol (2:1 and 1:1) has been found to obey pseudo first order forward and second order reverse kinetics. The relevant kinetic equations are given below:-

$$\ln\left[\frac{a x_e + x(a - x_e)}{a(x_e - x)}\right] = \left[\frac{2a - x_e}{x_e}\right] k_{1f}\, t \qquad (3.8)$$

or $$\ln\left[\frac{a x_e + x(a - x_e)}{a(x_e - x)}\right] \Bigg/ \left[\frac{2a - x_e}{x_e}\right] = k_{1f}\, t \qquad (3.9)$$

or First order forward and second order reverse function = $k_{1f}t$ (3.10)

where $a = [XH]_0$ and x = concentration of species X^- at time t. (See Appendix 2.3.2 for derivation of equation (3.8)).

A knowledge of the extinction coefficient, ε of species X^- was necessary to determine values of x_e and x as only species X^- was measured experimentally with time.

The Benesi-Hildebrand equation (given below in 2 forms as equations (3.11) and (3.12)) was applied to calculate the ε value of species X^- at the monitoring wavelength and the equilibrium constant, K for the reaction:-

$$\frac{[XH]_0}{OD_e} = \frac{OD_e}{K\varepsilon_{X^-}^{2} l^{2}[B]} + \frac{1}{\varepsilon_{X^-} l} \qquad (3.11)$$

$$\frac{[B]}{OD_e} = \frac{[XH]_0 [B]\, \varepsilon_{X^-} l}{OD_e^{2}} - \frac{1}{K\varepsilon_{X^-} l} \qquad (3.12)$$

where the symbols represent the quantities already listed above and l = cell path length in cm.(See Appendix 2.1.2 and 2.1.3 for derivation of equations (3.11) and (3.12)).

A plot according to equation (3.11) of $[XH]_0/OD_e$ against $OD_e/[B]$ (with slope = $1/K\varepsilon_{X^-}^2 l^2$ and intercept = $1/\varepsilon_{X^-}l$) is dependent on the inverse of the base concentration. This treatment gives more weight to low base concentrations which are subject to greater error(by virtue of the small volumes of base handled and possibility of evaporation). This problem is overcome using equation (3.12) which on plotting $[B]/OD_e$ against $[XH]_0[B]/OD_e^2$ should give a plot (with slope = $\varepsilon_{X^-}l$ and intercept $-1/K\varepsilon_{X^-}l$) which is linearly dependent on the base concentration. Linear plots were obtained (see fig.3.1.4) from which values of ε_{X^-} and K were derived.

It can be seen from equation (3.9) that a plot of the function on the LHS of the equation against time should be a straight line of slope equal to k_{1f}. Straight lines were obtained as seen by the plots given in fig.3.1.5. The k_{1f} values derived from these plots are given in Table 3.1.5. The computer program KD12 was used to process and plot the absorbance-time data.

Plots of k_{1f} against $[B]$ gave straight lines with slopes equal to k_{2f} according to equation (3.4)(see fig.3.1.6). k_{2f} values so derived are given in Tables 3.1.5 & 6.

The second order reverse rate constant, k_{2r}, can be calculated from the value for k_{2f} using the relationship, $k_{2r} = k_{2f}/K$. Direct measurement of k_{2r} is also possible by adding methanol to a solution of compound (94) at equilibrium in DMSO and reversing the reaction:-

$$XH \quad + \quad B \underset{\text{methanol}}{\rightleftharpoons} X^- \quad + \quad BH^+$$

The reaction is reversed due to a decrease in the equilibrium constant value with an increase of methanol in the DMSO/methanol solvent mixture. The situation prior to the addition of methanol is that the reaction under study is second order in the forward direction and second order in the reverse direction. The kinetic equation which applies when methanol is added to reverse the reaction from right to left is given in equation (3.13):-

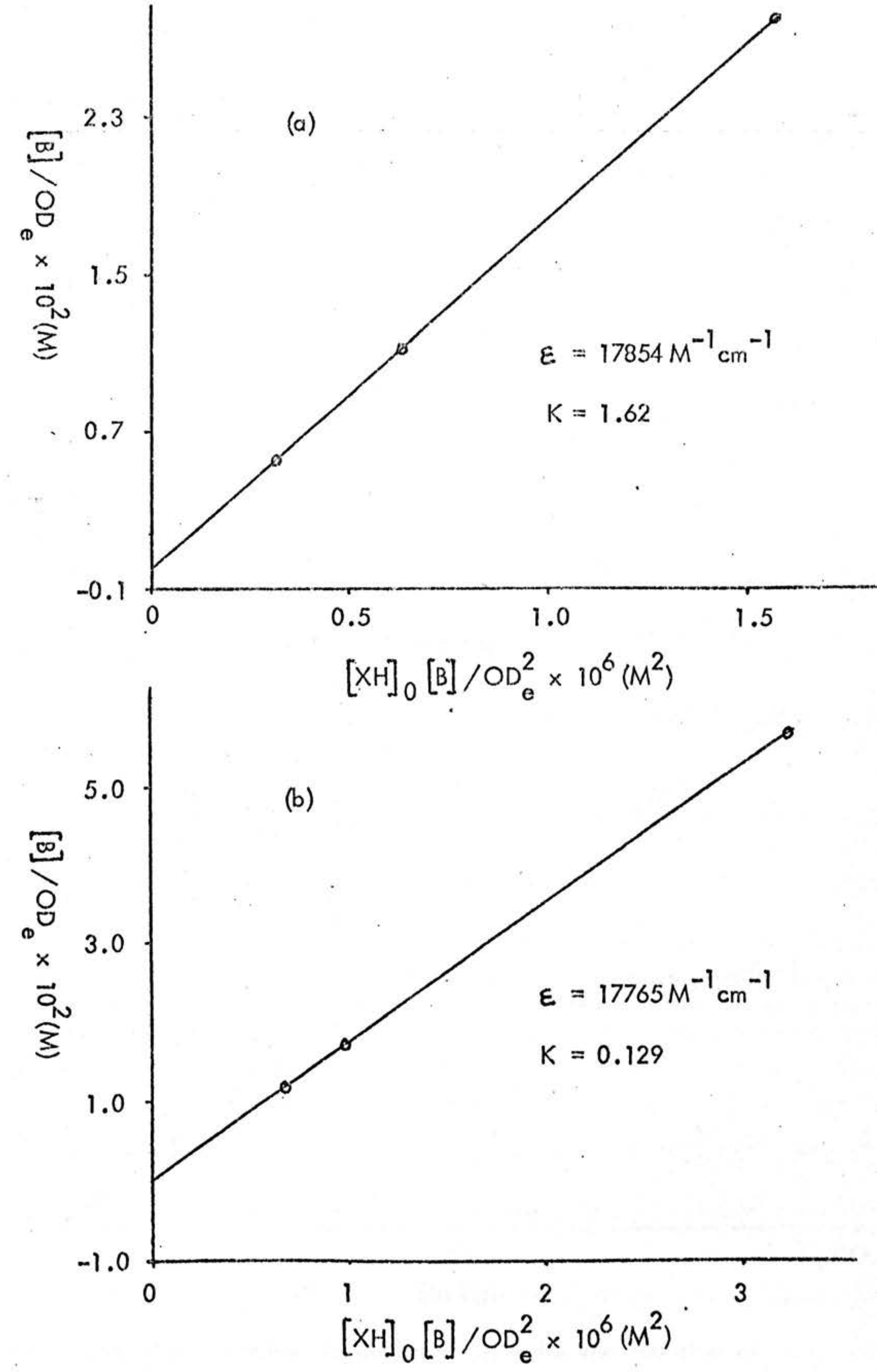


Fig.3.1.4 Benesi-Hildebrand plots according to equation (3.12) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) with diethylamine in:-
(a) DMSO/MeOH(2:1) at 31.5°C and (b) DMSO/MeOH(1:1) at 30.5°C.

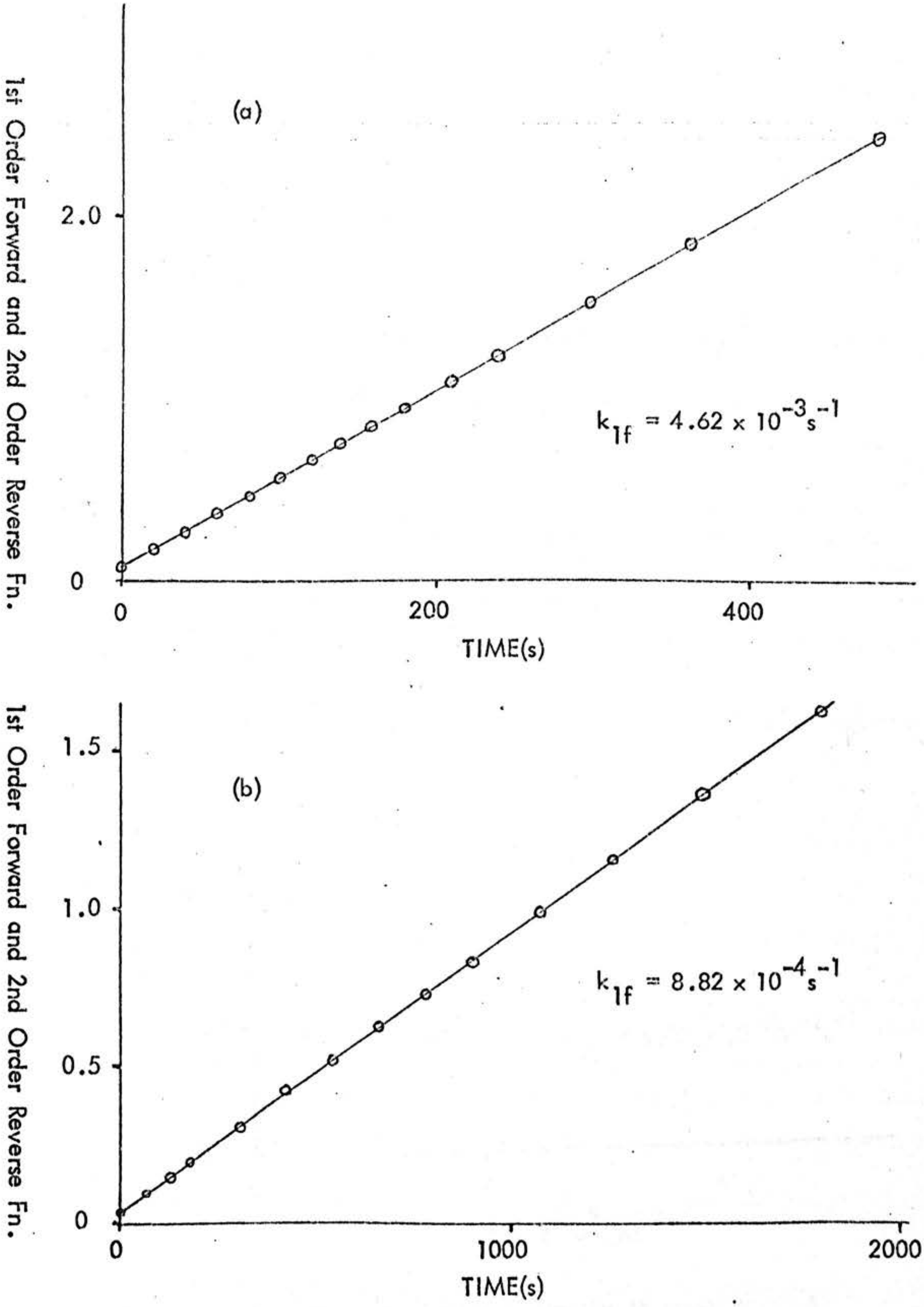


Fig.3.1.5 (a) Kinetic plot according to equation (3.9) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93)(6.796×10^{-5}M) with 500 equivalents of diethylamine in DMSO/MeOH(2:1) at 31.5°C and (b) Kinetic plot according to equation (3.9) for the reaction of compound (93)(5.108×10^{-5}M) with 300 equivalents of diethylamine in DMSO/MeOH(1:1) at 30.5°C.

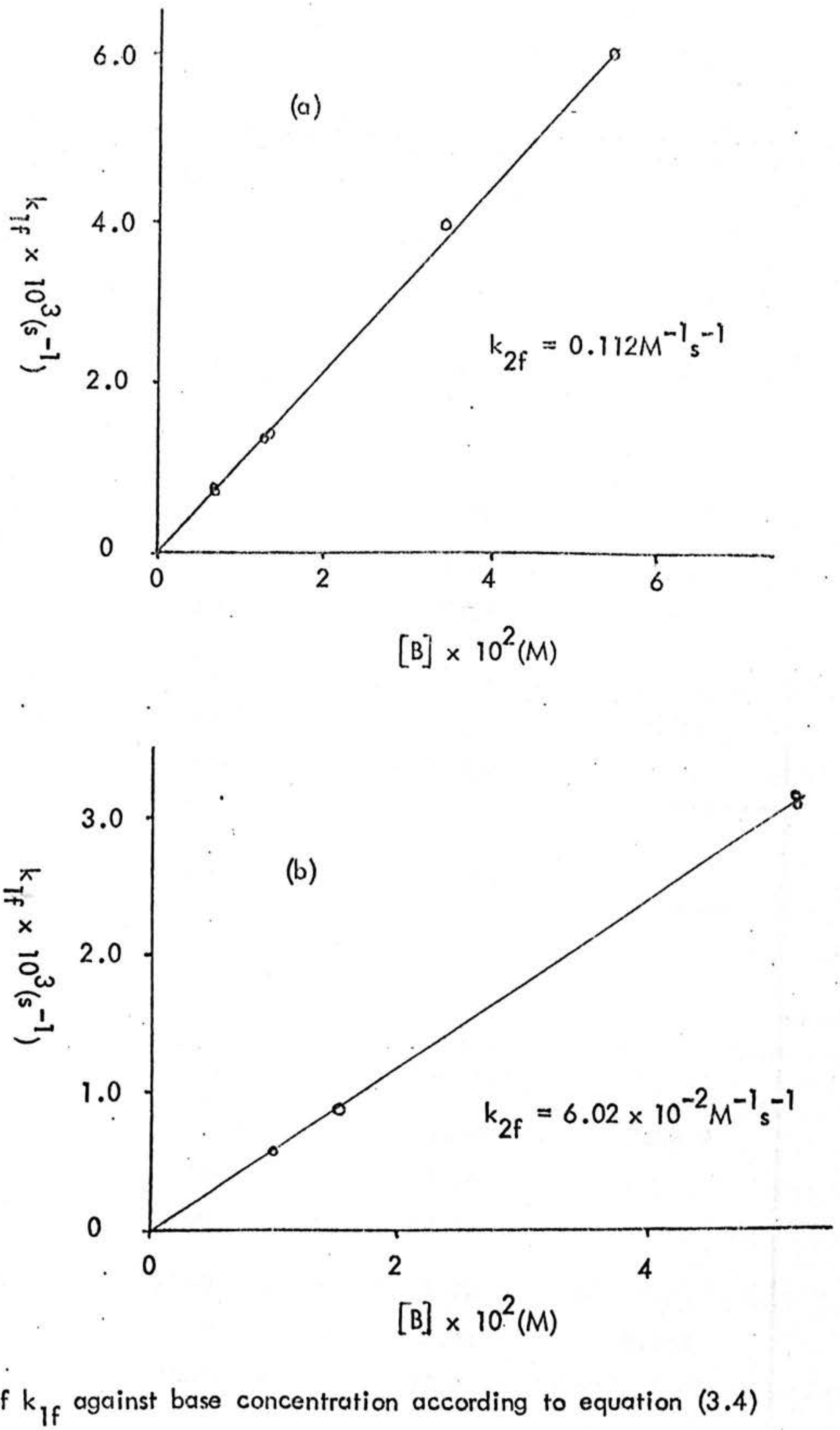


Fig.3.1.6 Plot of k_{1f} against base concentration according to equation (3.4) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) with diethylamine in:- (a) DMSO/MeOH(2:1) at 31.5°C and (b) DMSO/MeOH(1:1) at 30.5°C.

Table 3.1.5 Rate constants for reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine in DMSO/methanol solution

	Temp.	Base equivalents	$10^3 k_{1f}/s^{-1}$	$k_{2f}/M^{-1}s^{-1}$
DMSO/ MeOH(2:1)	31.5°	100	0.792	0.112
		200	1.44	
		500	4.00	
		800	5.99	
	41.0°	50	0.588	0.210
		100	1.16	
		200	2.89	
	51.5°	100	1.14	0.361
		200	4.83	
		500	12.26	
DMSO/ MeOH(1:1)	30.5°	200	0.563	0.0602
		300	0.882	
		1000	3.02	
		1000	3.10	
	41.0°	100	0.405	0.0879
		200	0.784	
		300	1.26	
		600	2.66	
		1000	4.11	
	52.25°	200	1.97	0.213
		300	2.98	
		1000	10.8	

Table 3.1.6 Rate constants, equilibrium constants and extinction coefficients for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine in DMSO/methanol solution

Temp.(C)	$k_{2f}/M^{-1}s^{-1}$	$k_{2r}/M^{-1}s^{-1}$	K^c	$\varepsilon_{BH}/M^{-1}cm^{-1}$ [d]	$\varepsilon_{BE}/M^{-1}cm^{-1}$ [e]	K_{BH} [f]	K_{BE} [g]	K_{spot} [h]
DMSO/MeOH(2:1)								
31.5°	0.112	0.86^a $-^b$	0.129	17800	17700	-	-	0.056
41.0°	0.210	2.35 -	0.092	18600	17200	0.077	0.067	0.041
51.5°	0.361	5.99 -	0.061	17700	17600	0.060	0.066	-
DMSO/MeOH(1:1)								
30.5°	0.060	- 0.50	-	17800	17800	0.110	0.129	-
41.0°	0.088	- 3.14	-	16700	16500	0.023	0.028	-
52.25°	0.213	- 10.0	-	18000	18100	0.022	0.021	0.011

a. k_{2r} measured directly. b. k_{2r} from k_{2f}/K_{BE}. c. K from k_{2f}/k_{2r} [a]. d. ε values derived according to eqn. (3.11).

e. ε values derived according to eqn. (3.12). f. K values derived from Benesi-Hildebrand eqn. (3.11).

g. K values derived from Benesi-Hildebrand eqn. (3.12). h. K values derived according to eqn. (3.5).

$$\ln\left[\left[\frac{x + ax_e/(a - x_e)}{x - x_e}\right]\left[\frac{a - x_e}{a + ax_e/(a - x_e)}\right]\right] = \left[\frac{a - x_e}{x_e(2a - x_e)}\right] k_{2r}\, t \qquad (3.13)$$

$$\text{or} \quad \ln\left[\left[\frac{x + ax_e/(a - x_e)}{x - x_e}\right]\left[\frac{a - x_e}{a + ax_e/(a - x_e)}\right]\right] \Big/ \left[\frac{a - x_e}{x_e(2a - x_e)}\right] = k_{2r}\, t \qquad (3.14)$$

or 2nd order reverse function $= k_{2r}\, t$ (3.15)

where the symbols have their usual meaning and a = concentration of XH in solution before reaction, times a dilution factor of $\frac{2}{3}$. A straight line plot, obtained using equation (3.14), of the data given in Table 3.1.7 is shown in fig.3.1.7. The slope of the plot gives a value for k_{2r} of $0.88 M^{-1}s^{-1}$.

The values of k_{2r} derived from plots for reactions at 2 other temperatures are also given in Table 3.1.6.

Table 3.1.7 Absorbance values of species (94) for the reversal of the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine in DMSO/methanol (2:1)

$[XH]_0 = 3.411 \times 10^{-5} M$ Et_2NH = 10 equivalents   Temp = 31.3°

Time/min	OD_t	2nd order reverse function
0	0.496	39270
50	0.467	41860
150	0.423	46570
250	0.386	51540
350	0.356	56520
500	0.318	64650
700	0.278	76880
∞	0.178	∞

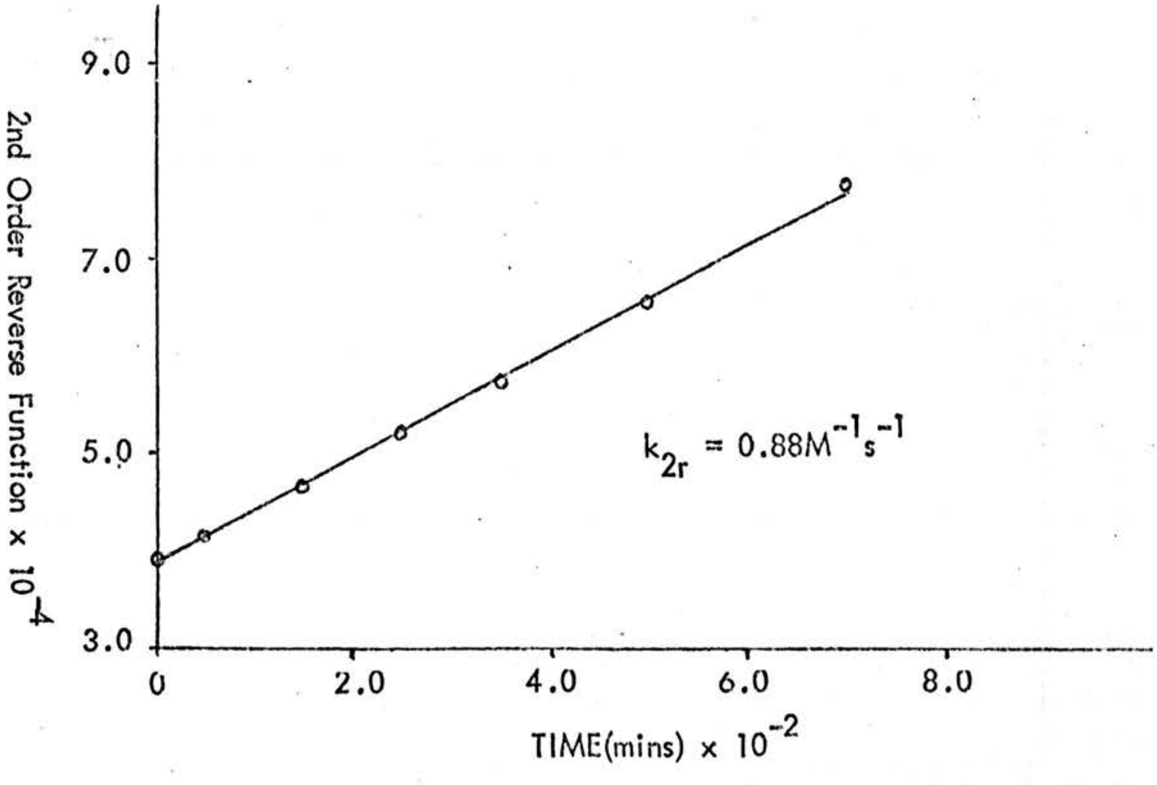


Fig.3.1.7 Kinetic plot according to equation (3.14) for reversal of the reaction involving 2,4,8-trinitro-1,5-dimethylnaphthalene(93)(3.411×10^{-5}M) and diethylamine in DMSO/MeOH(2:1) at 31.3°C.

The program K22R was used to process and plot the absorbance-time data and is listed in Appendix 2.4.12.

Plots of log k_{2f} and log k_{2r} against % DMSO in the DMSO/MeOH solvent mixture are shown in figs.3.1.8 & 9 respectively, such plots enable extrapolation[26,161] to 100% methanol to be made in some cases.

Thermodynamic Parameters

Table 3.1.8 lists enthalpies and entropies of activation for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine in 2 DMSO/MeOH solvent mixtures.

Table 3.1.8 Thermodynamic parameters for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine in DMSO/MeOH solution

ΔH_f^*	ΔH_r^* kJmol^{-1}	ΔH	ΔS_f^*	ΔS_r^* Jmol^{-1} K^{-1}	ΔS
DMSO/MeOH(2:1)					
45.6	76.0	-30.4	-113	3.3	-117
DMSO/MeOH(1:1)					
45.2	-	-	-120	-	-

3.1.4 Reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO

The reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine(50 - 1600 equivalents) in DMSO has been found to obey pseudo first order forward and second order reverse kinetics according to equation (3.8) or (3.9). A straight line plot(fig.3.1.10) using equation (3.9) was obtained for the data listed in Table 3.1.9. Other straight line plots were obtained for kinetic data at three other temperatures. The values of k_{1f} derived from these

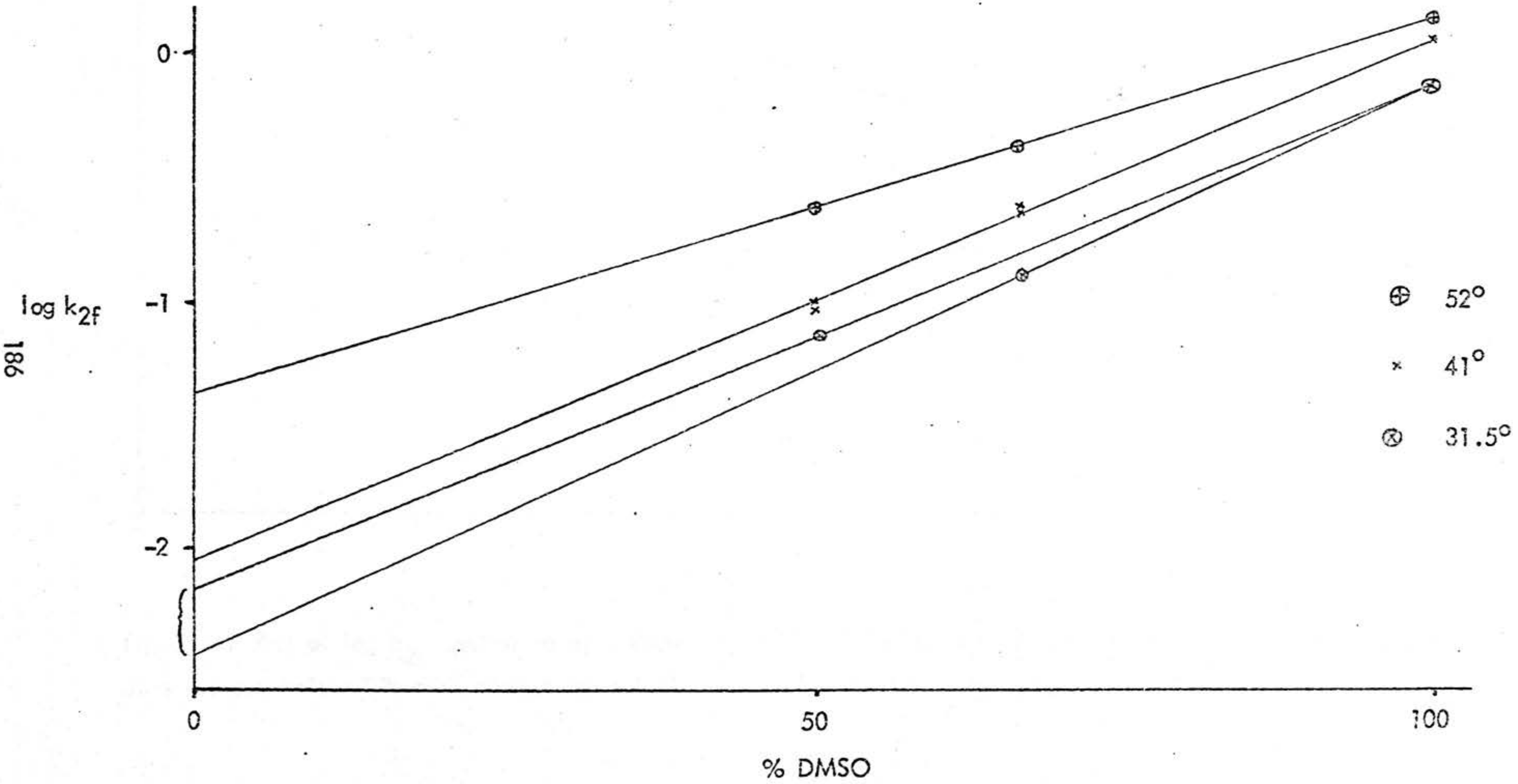


Fig.3.1.8 Plot of log k_{2f} against % by volume of DMSO in the solvent mixture for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) with diethylamine in DMSO/methanol at 3 temperatures.

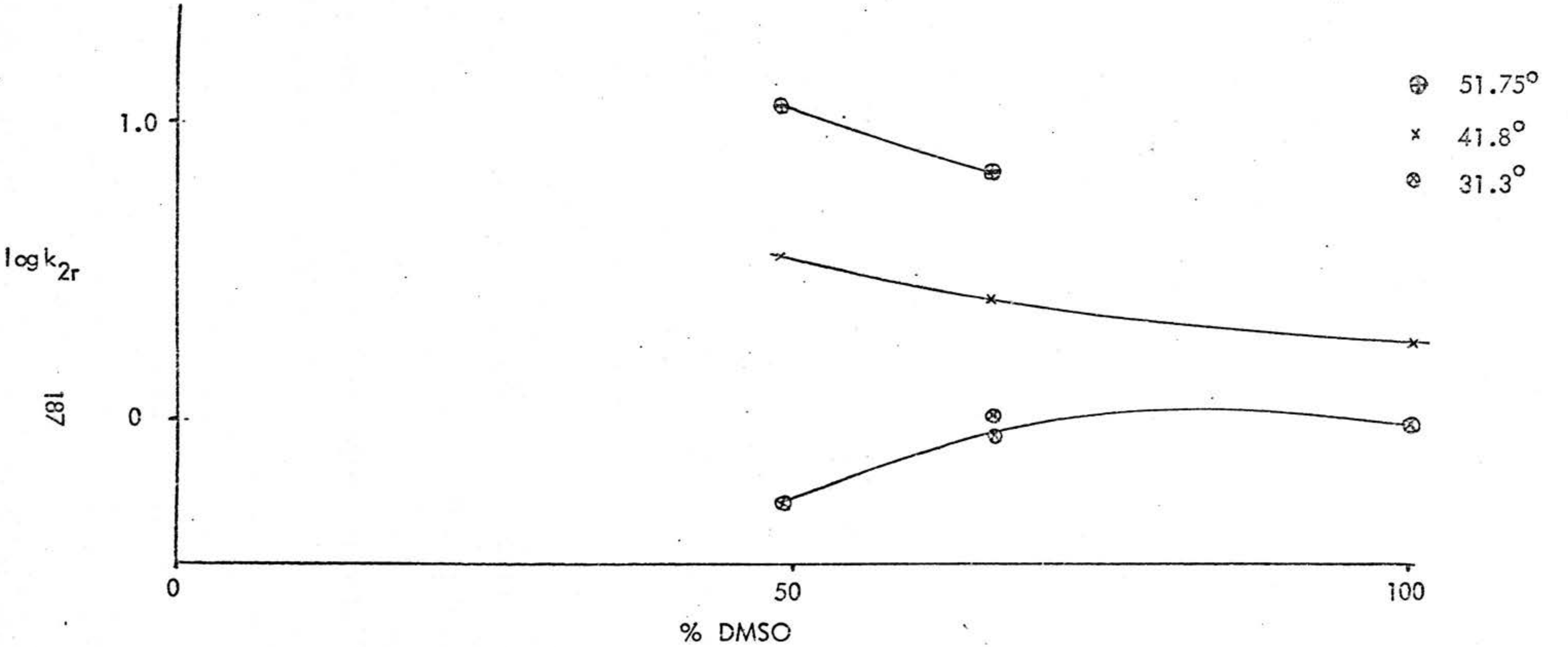


Fig.3.1.9 Plot of $\log k_{2r}$ against % by volume of DMSO in the solvent mixture for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) with diethylamine in DMSO/methanol at 3 temperatures.

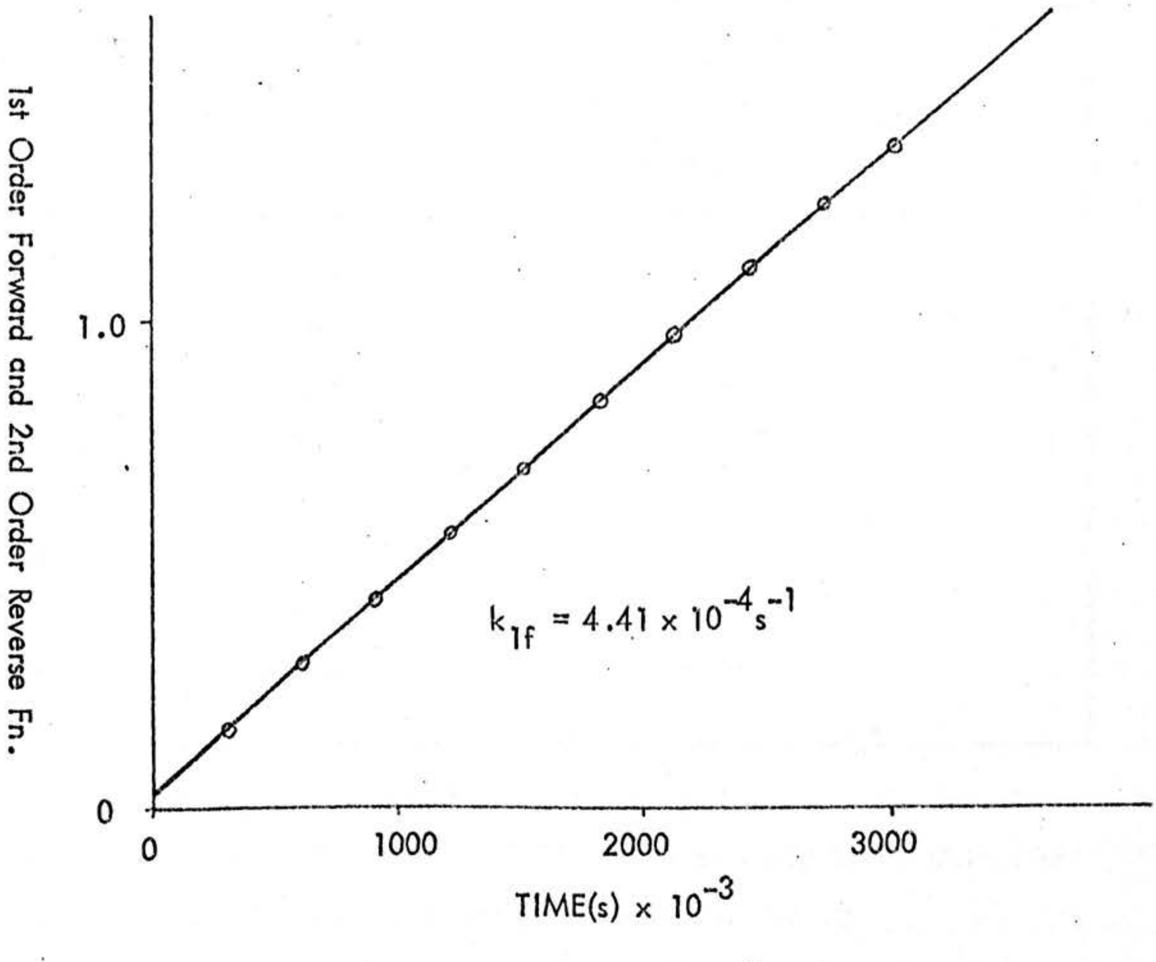


Fig.3.1.10 Kinetic plot according to equation (3.9) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93)(5.112×10^{-5}M) with 100 equivalents of triethylamine in DMSO at 30°C.

plots are listed in Table 3.1.11.

Table 3.1.9 Absorbance values of species (94) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO

$[XH]_0 = 5.112 \times 10^{-5}$M Et_3N = 100 equivalents   Temp. = 30°

Time/s	OD_t	1st order forward and 2nd order reverse function
0	0.020	0.020
300	0.153	0.164
600	0.262	0.300
900	0.353	0.431
1200	0.434	0.565
1500	0.504	0.698
1800	0.563	0.827
2100	0.613	0.953
2400	0.661	1.093
2700	0.701	1.229
3000	0.732	1.351
3600	0.788	1.623

The value of ε_{X^-} required by equation (3.9) was derived from the Benesi-Hildebrand plot according to equation (3.12) shown in fig.3.1.11. Values of ε_{X^-} and K derived from such plots are listed in Table 3.1.10.

Second order forward rate constants, k_{2f}, were determined from the slope of plots of k_{1f} against $[Et_3N]$ (fig.3.1.12). The values of k_{2f} so derived are listed in Table 3.1.11.

k_{2r} values calculated from the relationship k_{2f}/K are also given in Table 3.1.10.

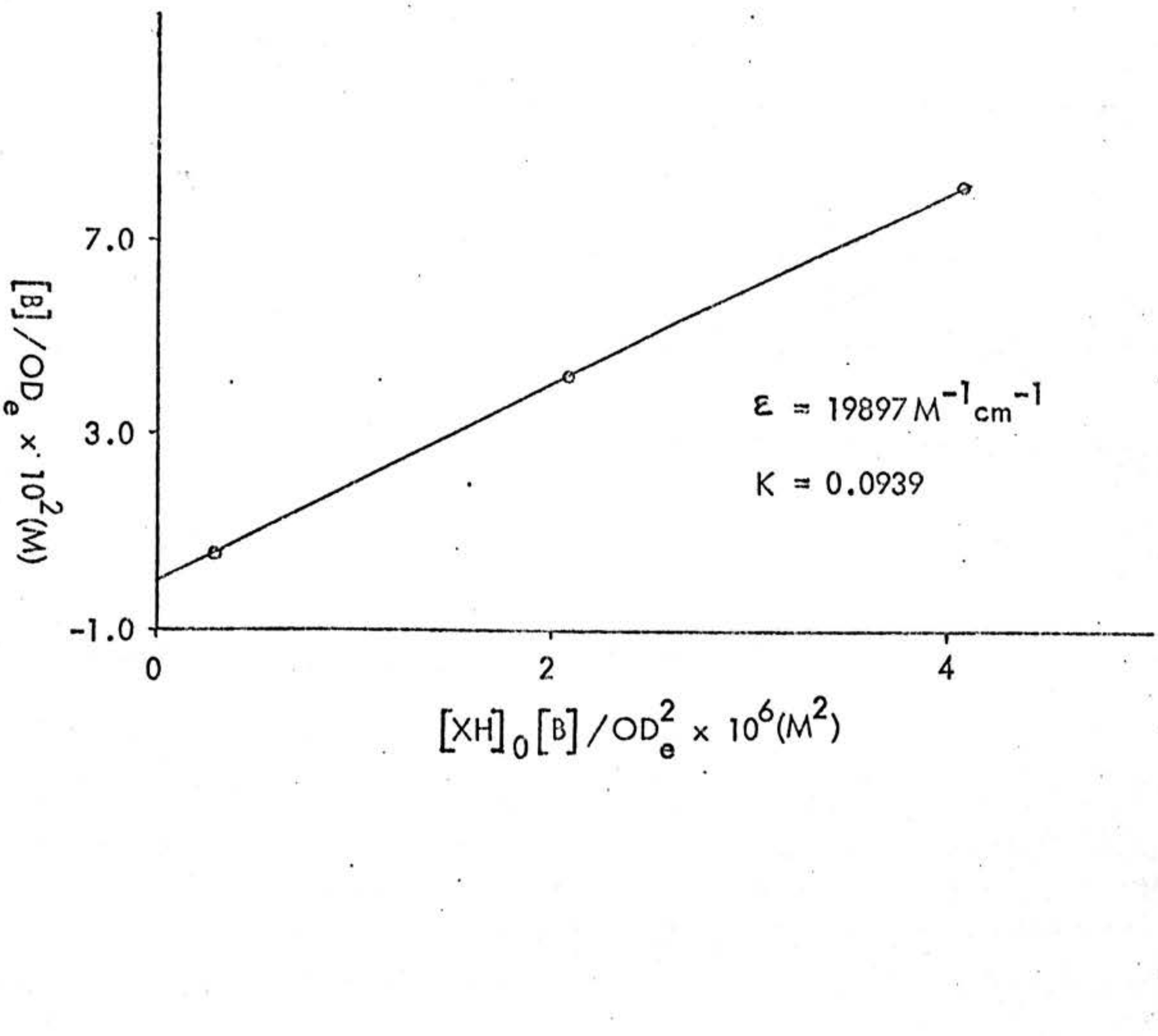


Fig.3.1.11 Benesi-Hildebrand plot according to equation (3.12) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO at 30°C.

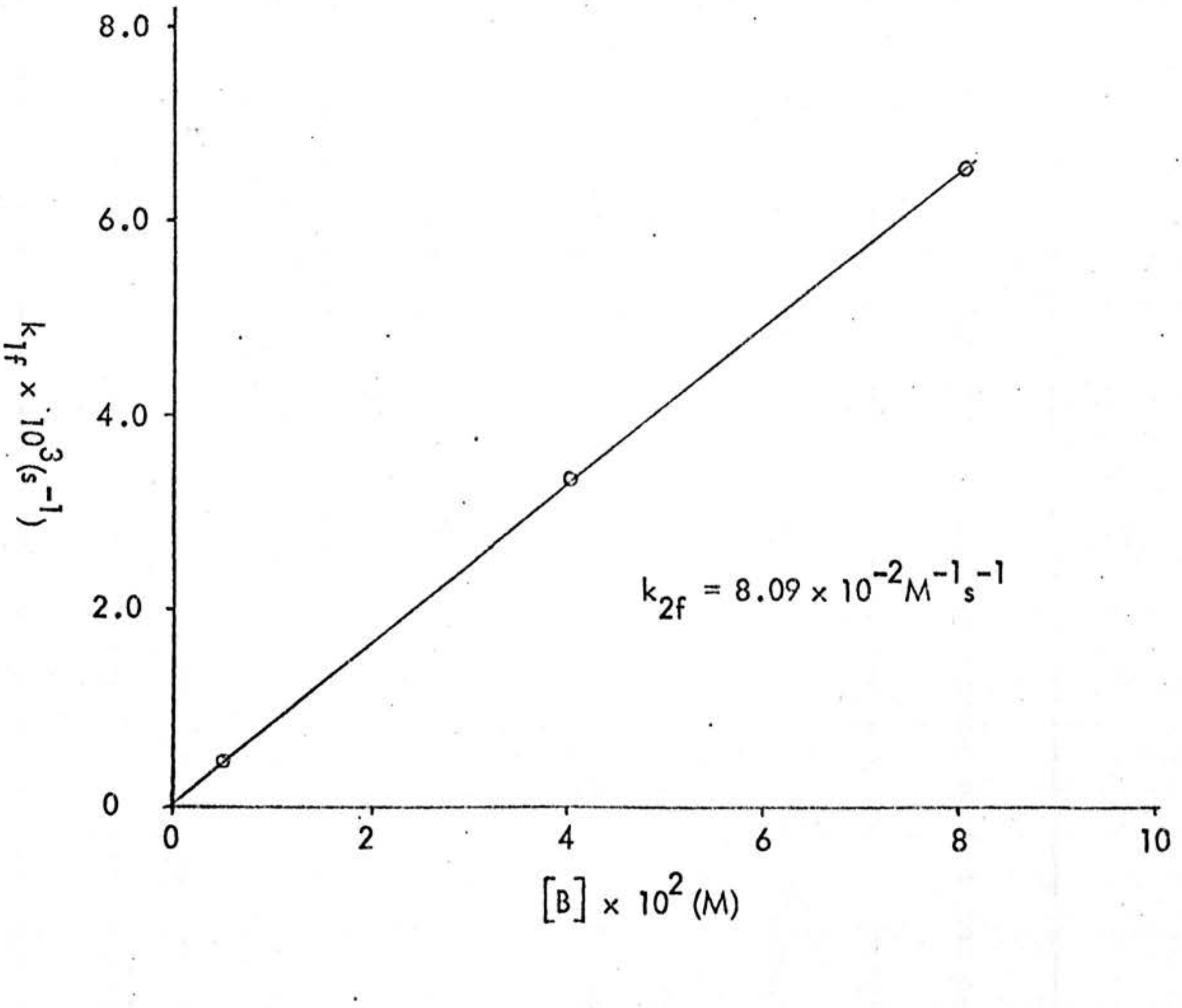


Fig.3.1.12 Plot of k_{1f} against base concentration according to equation (3.4) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) with triethylamine in DMSO at 30°C.

Table 3.1.10 Rate constants, equilibrium constants and extinction coefficients for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO

Temp.(C)	$k_{2f}/M^{-1}s^{-1}$	$k_{2r}/M^{-1}s^{-1}$ [a]	$\varepsilon_{BH}/M^{-1}cm^{-1}$ [b]	$\varepsilon_{BE}/M^{-1}cm^{-1}$ [c]	K_{BH} [d]	K_{BE} [e]	K_{spot} [f]
24.5°	-	-	(assumed 19800)		-	-	0.236
30.0°	0.0808	0.64	19800	19900	0.126	0.094	-
40.75°	0.133	1.13	19200	19400	0.133	0.102	0.154
51.25°	0.268	3.01	19100	19000	0.085	0.093	0.095
60.25°	0.449	4.93	18300	18300	0.091	0.091	0.091

a. k_{2r} calculated from k_{2f}/K_{BE}. b. ε values derived according to eqn. (3.11). c. ε values derived according to eqn. (3.12). d. K values derived from Benesi-Hildebrand eqn. (3.11).

e. K values derived according to Benesi-Hildebrand eqn. (3.12). f. K values derived according to eqn. (3.5).

Table 3.1.11 Rate constants for reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO solution

$[XH]_0 \sim 5.10 \times 10^{-5}$M

Temp.	Base equivalents	$10^3 k_{1f}/s^{-1}$	$k_{2f}/M^{-1}s^{-1}$
30.0°	100	0.441	
	800	3.34	0.0808
	1600	6.53	
40.75°	100	0.85	
	200	1.62	
	200	1.63	
	400	3.05	0.133
	800	6.12	
	1600	10.20	
	1600	11.05	
51.25°	50	0.684	
	75	1.08	
	100	1.41	
	200	2.80	0.268
	200	2.82	
	500	6.82	
60.25°	50	1.19	
	50*	2.20	
	100	2.18	0.449
	100	2.41	
	200	4.59	

* $[XH]_0 = 1.02 \times 10^{-5}$ M

Thermodynamic Parameters

Table 3.1.12 lists enthalpies and entropies of activation for the forward and reverse steps and the overall enthalpy and entropy changes for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO.

Table 3.1.12 Thermodynamic parameters for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO

ΔH_f^*	ΔH_r^* $kJmol^{-1}$	ΔH	ΔS_f^*	ΔS_r^* $Jmol^{-1}K^{-1}$	ΔS
45.9	56.4	-10.6	-115	-63	-52

3.1.5 Reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO/methanol solution

The reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine(50 - 1600 equivalents) in DMSO/methanol(9:1,4:1,2:1 and 1:1) has been found to obey pseudo first order forward and second order reverse kinetics in accord with equation (3.9). Kinetic plots using equation (3.9) of the above proton abstraction reaction are shown in figs.3.1.13 & 14.

Benesi-Hildebrand plots were used to determine ε_{X^-} required by equation (3.9) and also K values(figs.3.1.15 & 16).

Values of k_{1f} are given in Table 3.1.14 together with k_{2f} values derived from plots of k_{1f} against $[B]$ according to rquation (3.4)(figs.3.1.17 & 18).

Values of ε_{X^-} and K are listed in Table 3.1.13 as are some k_{2r} values calculated from the relationship k_{2f}/K.

Values for k_{2r} were also determined directly by reversing the reaction by addition of methanol to a DMSO solution containing an equilibrium mixture of 2,4,8-trinitro-1,5-dimethylnaphthalene and triethylamine(See section 3.1.3 for detailed explanation). The kinetic equation (3.14) was obeyed and a typical plot for reversal of the reaction is shown in fig.3.1.19.

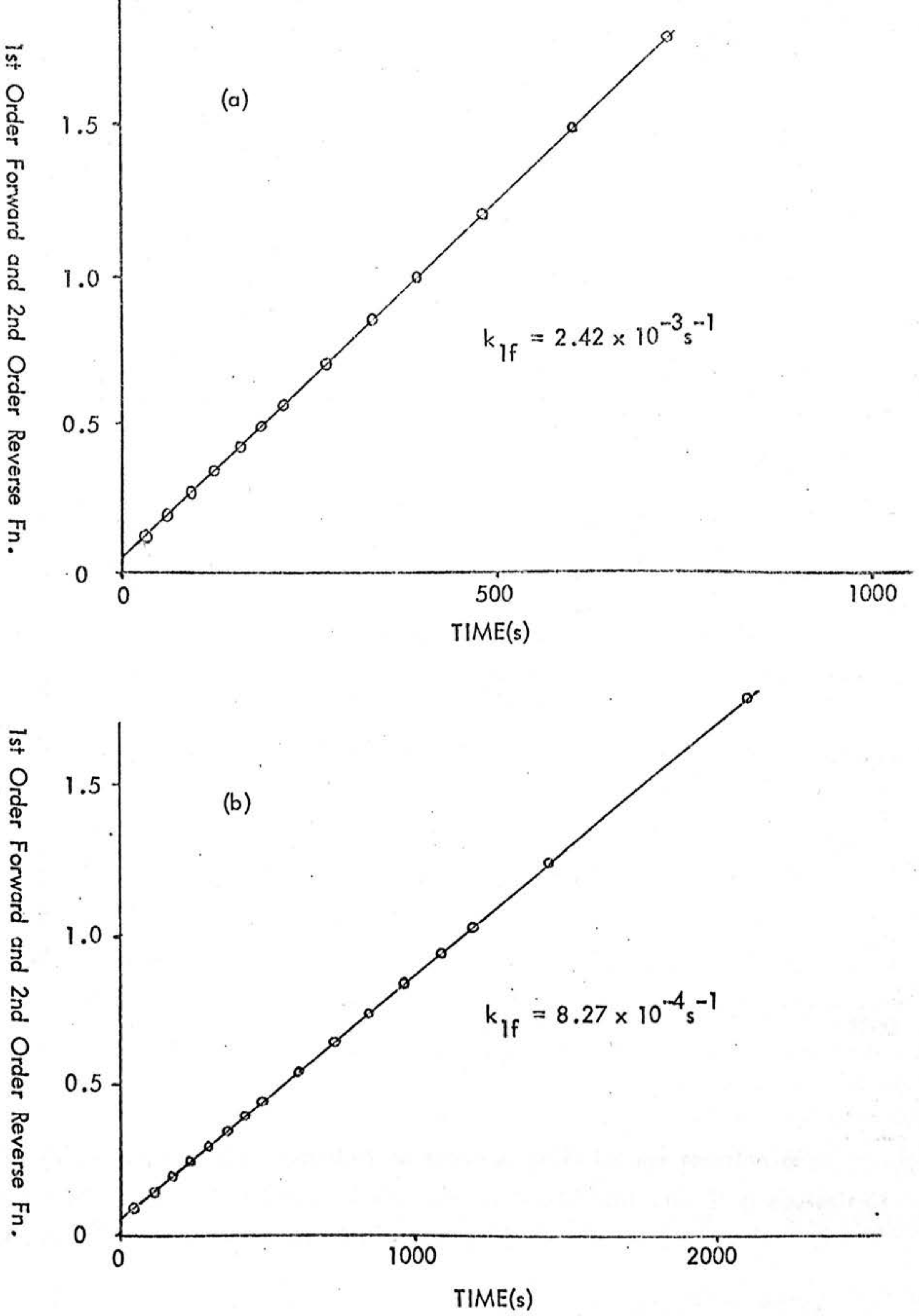


Fig.3.1.13 (a) Kinetic plot according to equation (3.9) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93)(4.581×10^{-5}M) with 800 equivalents of triethylamine in DMSO/MeOH(9:1) at 31.25°C and (b) Kinetic plot according to equation (3.9) for the reaction of compound (93)(6.794×10^{-5}M) with 400 equivalents of triethylamine in DMSO/MeOH(2:1) at 31.5°C.

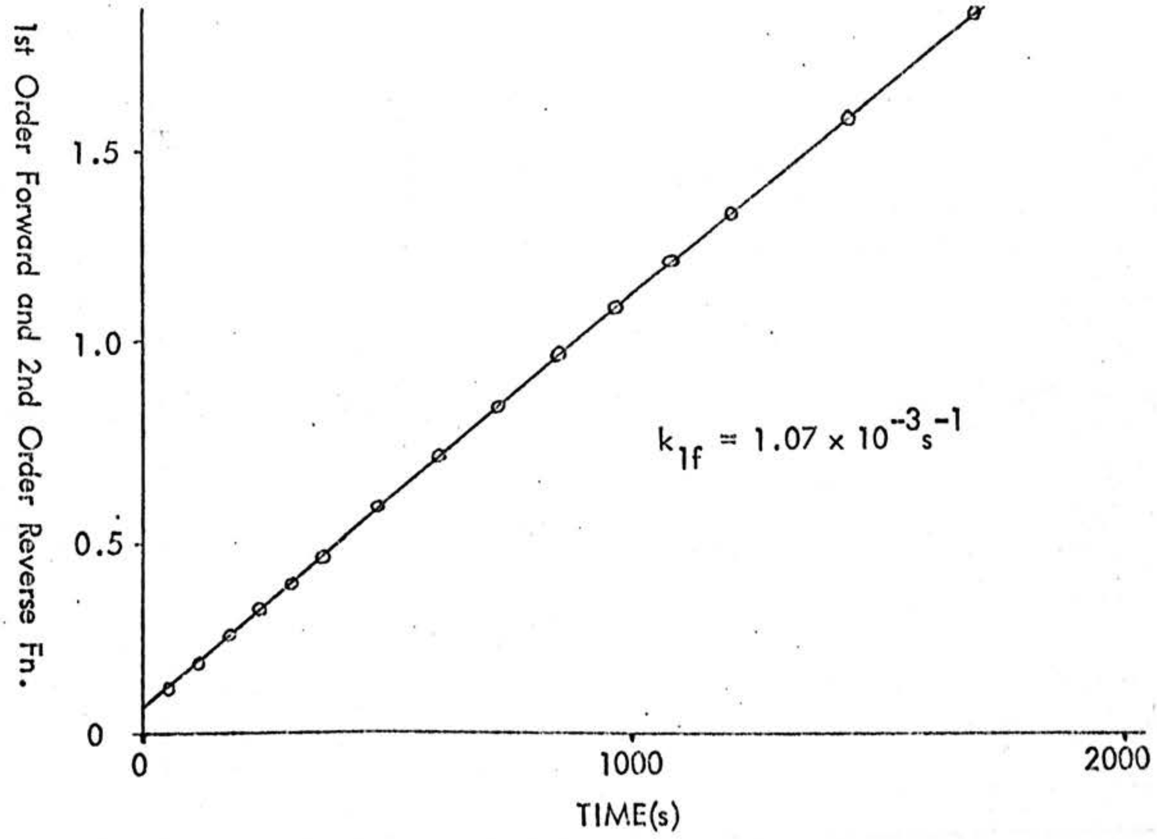


Fig. 3.1.14 Kinetic plot according to equation (3.9) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93)(5.08×10^{-5}M) with 1000 equivalents of triethylamine in DMSO/MeOH(1:1) at 32°C.

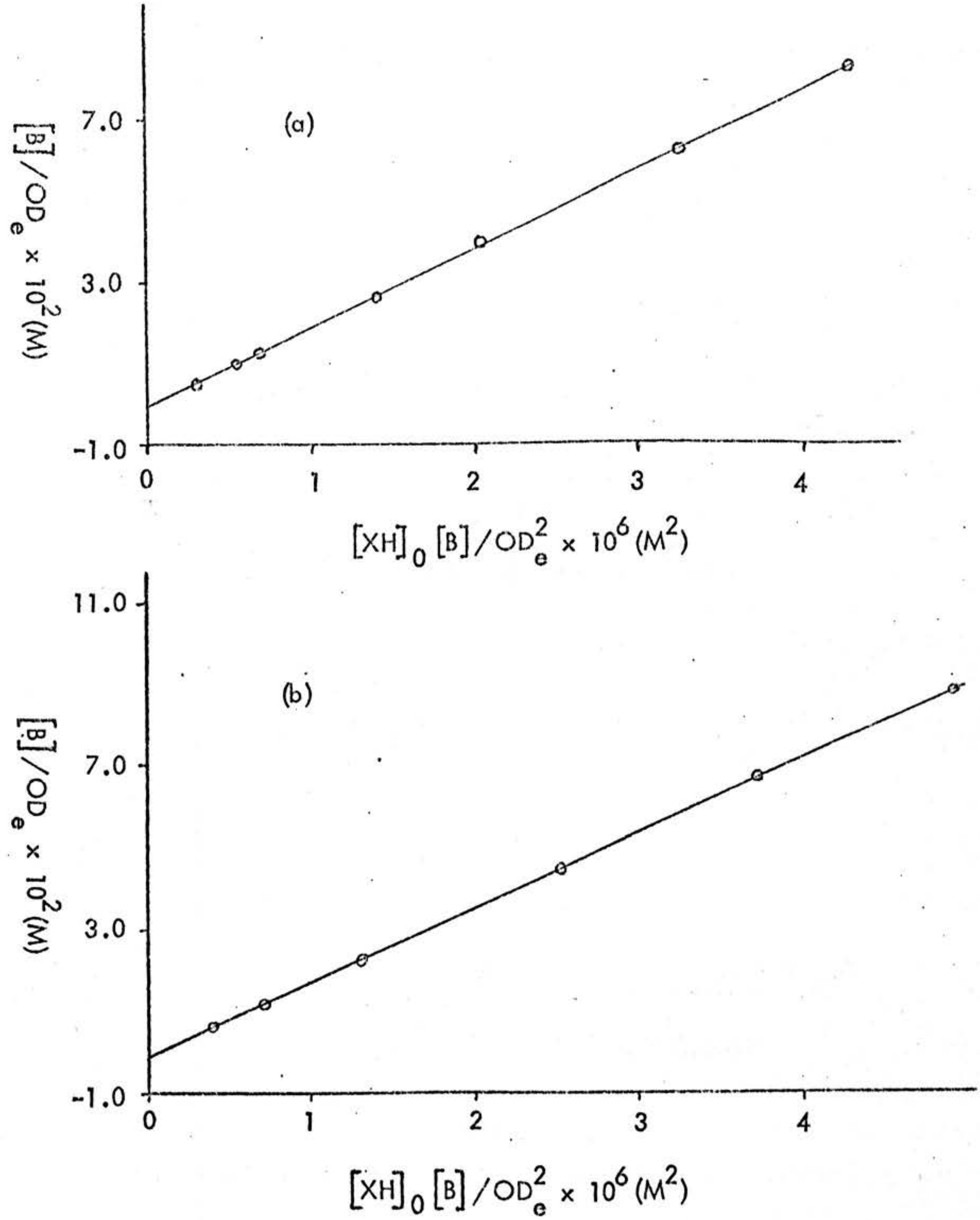


Fig.3.1.15 Benesi-Hildebrand plot according to equation (3.12) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) with triethylamine in:- (a) DMSO/MeOH(9:1) at 31.25°C and (b) DMSO/MeOH(4:1) at 31.6°C.

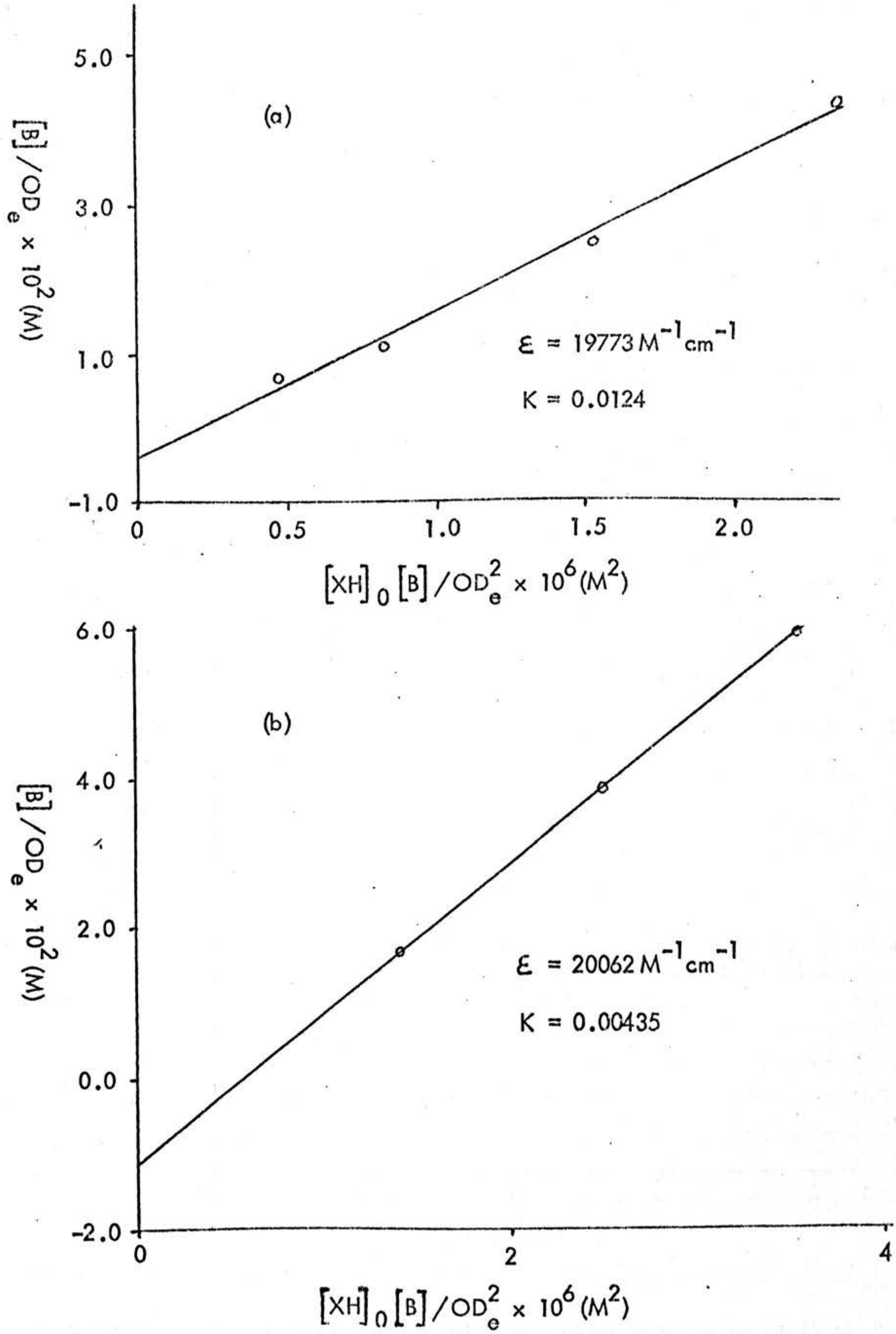


Fig.3.1.16 Benesi-Hildebrand plot according to equation (3.12) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) with triethylamine in :- (a) DMSO/MeOH(2:1) at 31.5°C and (b) DMSO/MeOH(1:1) at 32°C.

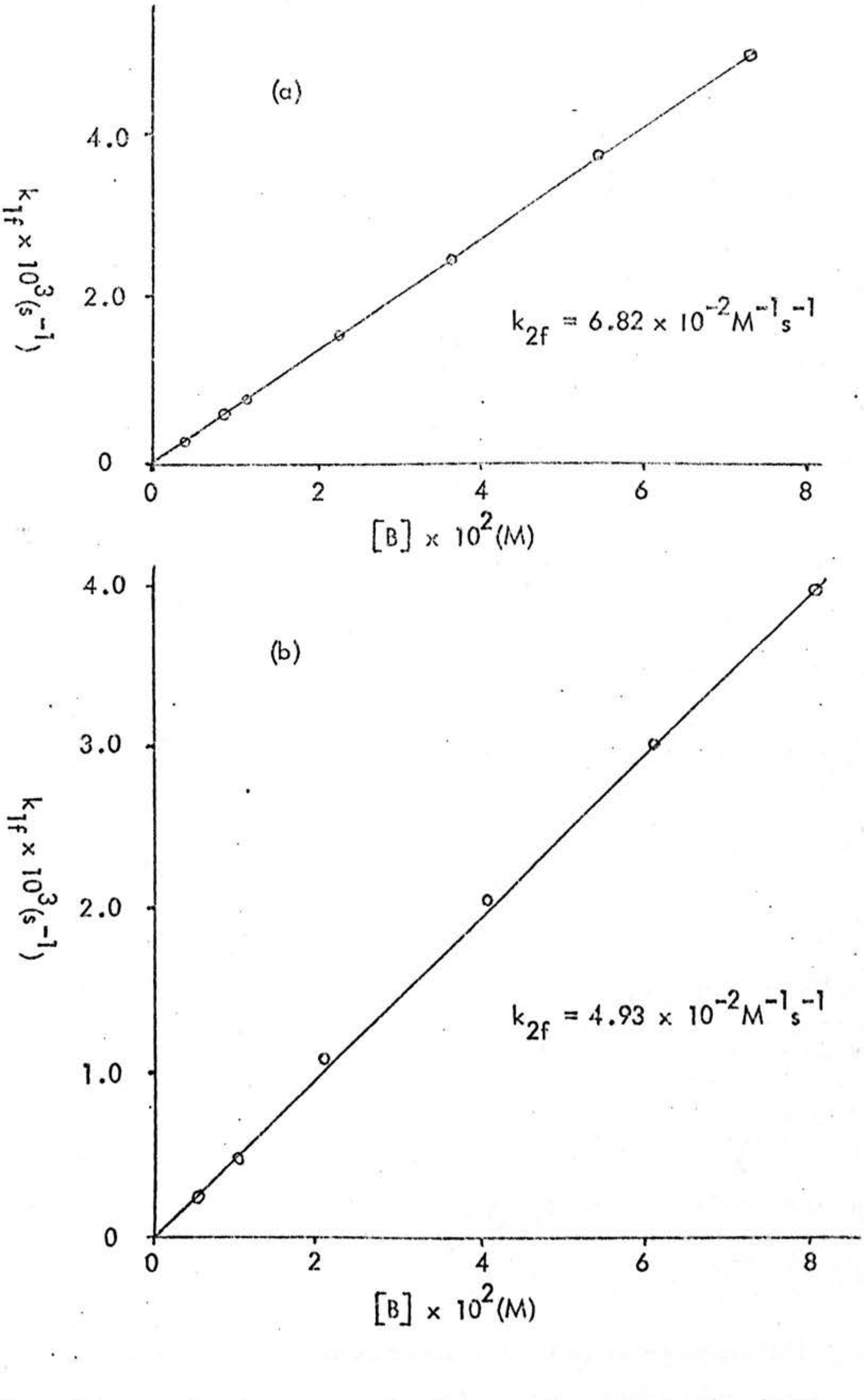


Fig.3.1.17 Plots of k_{1f} against base concentration according to equation (3.4) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) with triethylamine in:- (a) DMSO/MeOH(9:1) at 31.25°C and (b) DMSO/MeOH(4:1) at 31.6°C.

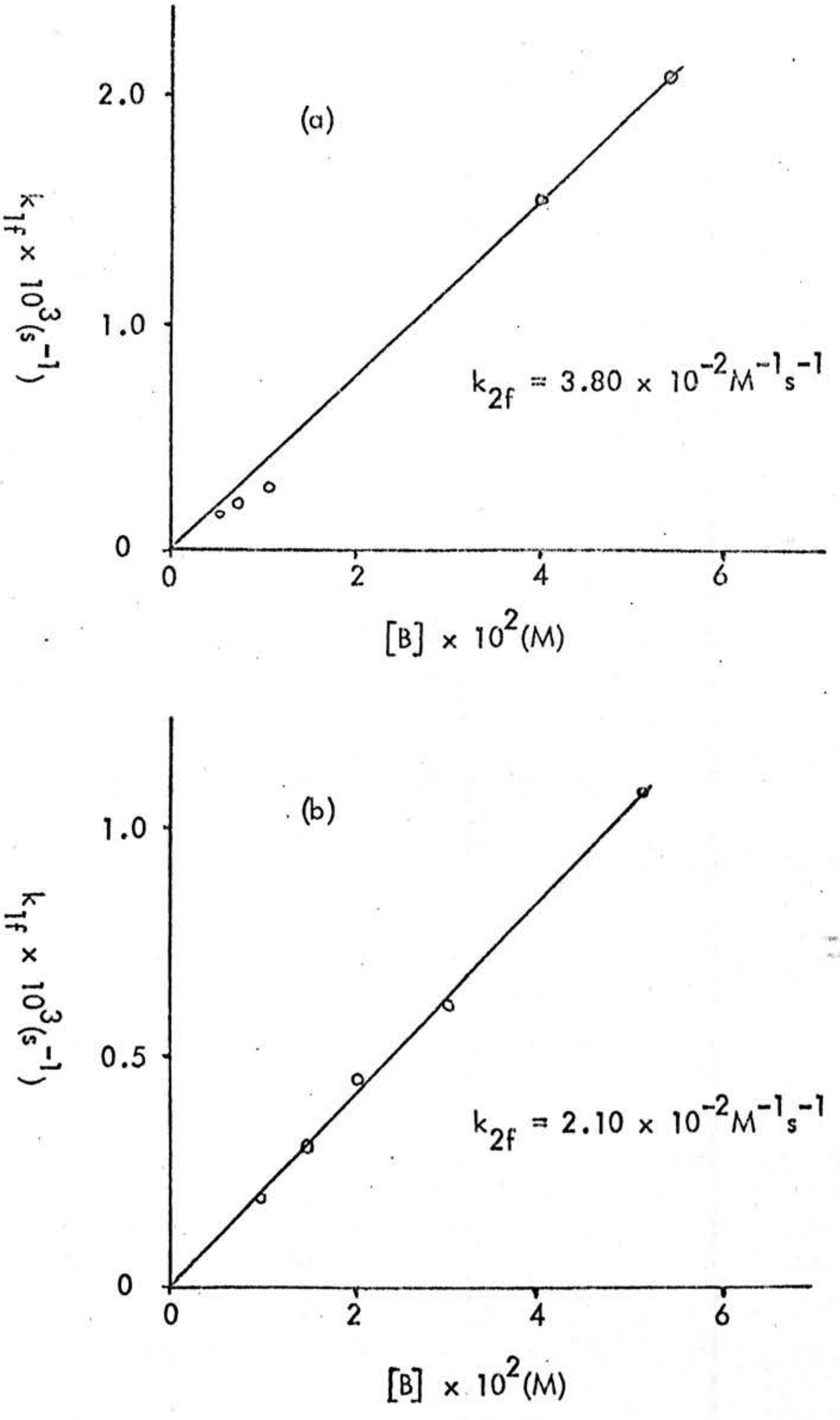


Fig.3.1.18 Plots of k_{1f} against base concentration according to equation (3.4) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) with triethylamine in:- (a) DMSO/MeOH(2:1) at 31.5°C and (b) DMSO/MeOH(1:1) at 32°C.

Table 3.1.13 Rate constants, equilibrium constants and extinction coefficients for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO/methanol solution

Temp.(C)	$k_{2f}/M^{-1}s^{-1}$	$k_{2r}/M^{-1}s^{-1}$	K^c	$\varepsilon_{BH}/M^{-1}cm^{-1\,d}$	$\varepsilon_{BE}/M^{-1}cm^{-1\,e}$	$K_{BH}{}^f$	$K_{BE}{}^g$	K_{spot}
DMSO/MeOH(9:1)								
31.25°	0.0682	-[a] 0.51[b]	-	-	19400	-	0.134	-
41.0°	0.113	- 1.30	-	18500	19000	0.085	0.076	-
52.0°	0.201	- 3.39	-	18400	18600	0.054	0.042	-
DMSO/MeOH(4:1)								
31.6°	0.0493	- 0.70	-	18200	18200	0.070	0.063	-
DMSO/MeOH(2:1)								
26.1°	-	- -	-	(assumed 19800)		-	-	0.020
31.5°	0.0380	2.28 -	0.0164	20500	19400	0.0082	0.0125	-
41.0°	0.0696	6.84 -	0.0092	19000	20600	0.0081	0.0063	-
51.5°	0.117	17.8 -	0.0059	18700	16800	0.0051	0.0095	0.0065
60.25°	-	32.3 -	-	-	-	-	-	0.0061

Table 3.1.13(contd)

Temp.(C)	$k_{2f}/M^{-1}s^{-1}$	$k_{2r}/M^{-1}s^{-1}$	K^{c}	$\varepsilon_{BH}/M^{-1}cm^{-1\,d}$	$\varepsilon_{BE}/M^{-1}cm^{-1\,e}$	$K_{BH}{}^{f}$	$K_{BE}{}^{g}$	$K_{spot}{}^{h}$
DMSO/MeOH(1:1)								
32.0°	0.0210	$-^{a}4.88^{b}$	-	20100	20100	0.0043	0.0043	-
41.0°	0.0267	- 16.1	-	-	-	-	0.0017	0.0017
52.25°	0.0695	- 25.8	-	19200	18900	0.0025	0.0027	0.0010

a. k_{2r} measured directly. b. k_{2r} calculated from k_{2f}/K_{BE}. c. K from $k_{2f}/k_{2r}{}^{a}$.

d. ε values derived according to eqn. (3.11). e. ε values derived according to eqn. (3.12).

f. K values derived from Benesi-Hildebrand eqn. (3.11). g. K values derived according to Benesi-Hildebrand eqn. (3.12).

h. K values derived according to eqn. (3.5).

Table 3.1.14 Rate constants for reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO/methanol solution

Temp.	Base equivalents	$10^3 k_{1f}/s^{-1}$	$k_{2f}/M^{-1}s^{-1}$
DMSO/MeOH(9:1)			
31.25°	100	0.275	0.0682
	200	0.621	
	250	0.782	
	500	1.59	
	800	2.42	
	1200	3.77	
	1600	4.96	
41.0°	100	0.491	0.113
	100	0.507	
	250	1.28	
	800	4.14	
52.0°	100	0.89	0.201
	100	0.88	
	250	2.41	
	800	7.91	
	1600	14.4	
DMSO/MeOH(4:1)			
31.6°	100	0.241	0.0493
	200	0.452	
	400	1.10	
	800	2.07	
	1200	3.02	
	1600	3.94	

Temp.	Base equivalents	$10^3 k_{1f}/s^{-1}$	$k_{2f}/M^{-1}s^{-1}$
DMSO/MeOH(2:1)			
31.5°	75	0.176	0.0380
	100	0.201	
	150	0.273	
	400	0.827	
	600	1.52	
	800	2.07	
41.0°	75	0.216	0.0696
	150	0.497	
	400	1.68	
	800	3.81	
51.5°	75	0.383	0.117
	150	0.815	
	400	2.47	
	800	6.56	
DMSO/MeOH(1:1)			
32.0°	200	0.182	0.0210
	300	0.300	
	400	0.455	
	600	0.611	
	1000	1.07	
41.0°	200	0.635	0.0695
	600	2.17	
	1000	3.50	

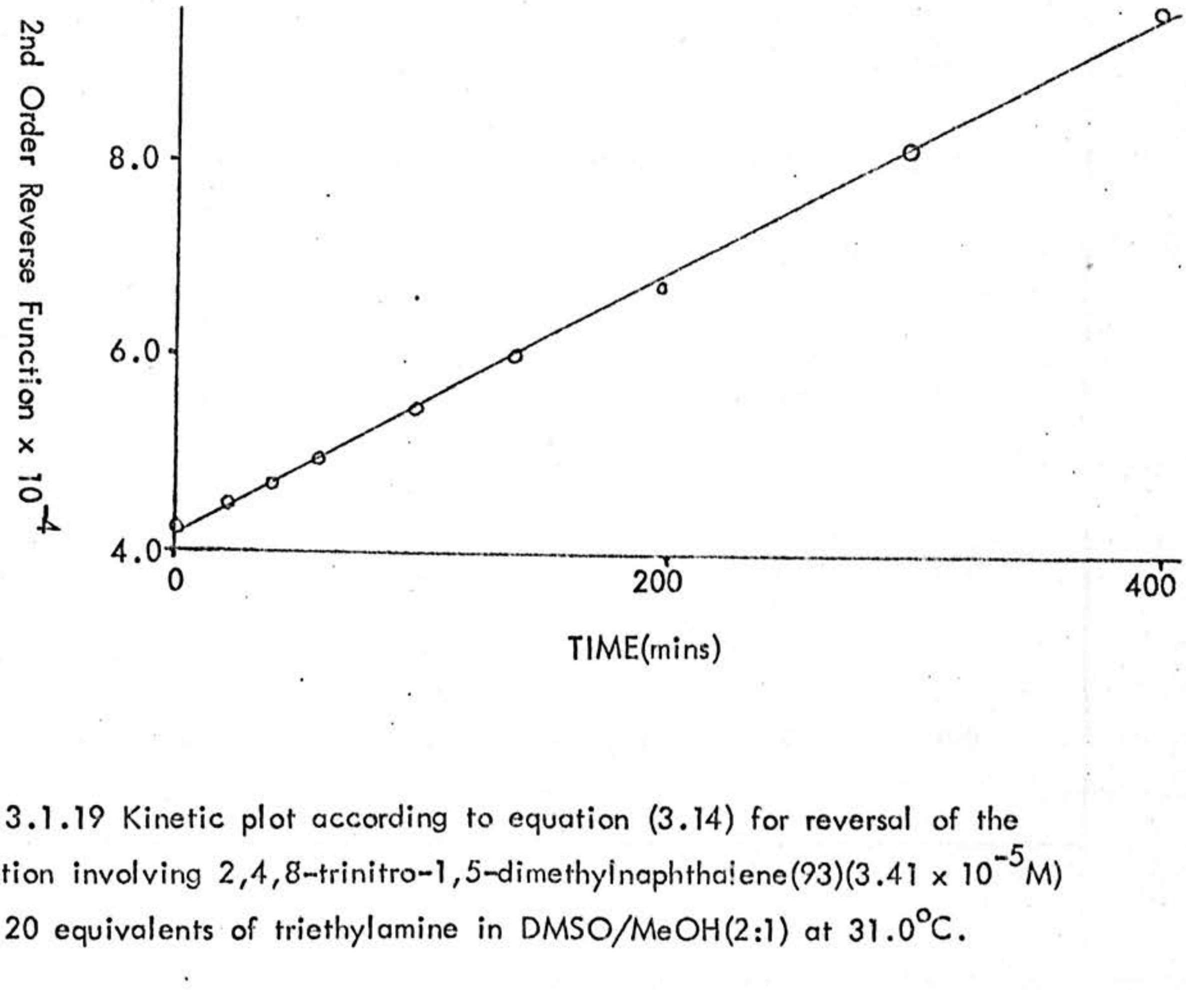


Fig.3.1.19 Kinetic plot according to equation (3.14) for reversal of the reaction involving 2,4,8-trinitro-1,5-dimethylnaphthalene(93)(3.41×10^{-5}M) and 20 equivalents of triethylamine in DMSO/MeOH(2:1) at 31.0°C.

Plots of log k_{2f} and log k_{2r} against % DMSO by volume in the solvent mixture are shown in figs.3.1.20 & 21. These plots enable extrapolation of k_{2f} and k_{2r} values to 100% methanol to be made in some cases as indicated.

Thermodynamic Parameters

Table 3.1.15 lists enthalpies and entropies of activation for the forward and reverse steps and the overall enthalpy and entropy changes for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO/methanol solution.

Table 3.1.15 Thermodynamic parameters for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO/methanol solution

ΔH_f^*	ΔH_r^*	ΔH	ΔS_f^*	ΔS_r^*	ΔS
	$kJmol^{-1}$			$Jmol^{-1}K^{-1}$	
DMSO/MeOH(9:1)					
40.4	72.6	-32.2	-135	-12	-123
DMSO/MeOH(2:1)					
43.7	81.0	-37.2	-129	28	-157
DMSO/MeOH(1:1)					
47.0	64.5	-17.5	-124	-19	-105

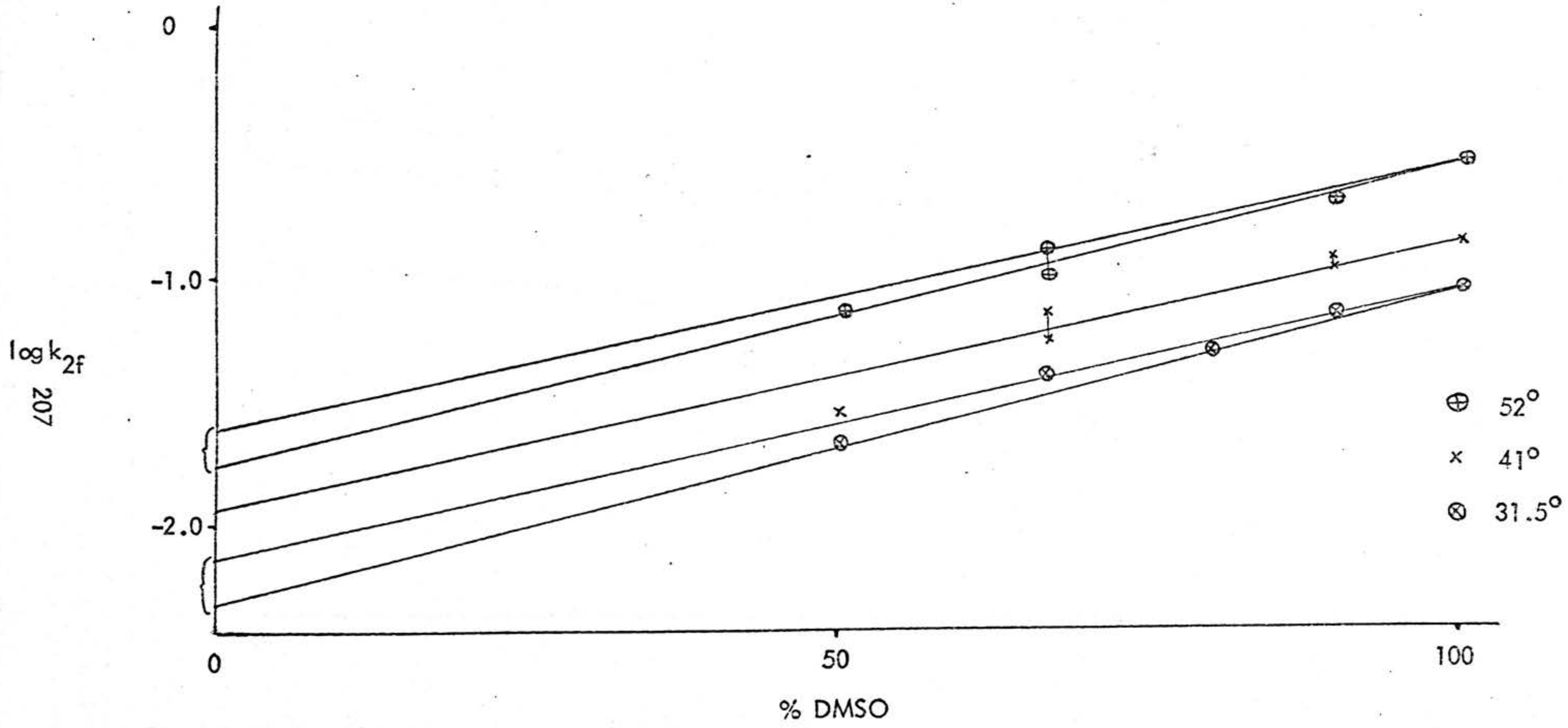


Fig.3.1.20 Plot of log k_{2f} against % by volume of DMSO in the solvent mixture for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) with triethylamine in DMSO/methanol at 3 temperatures.

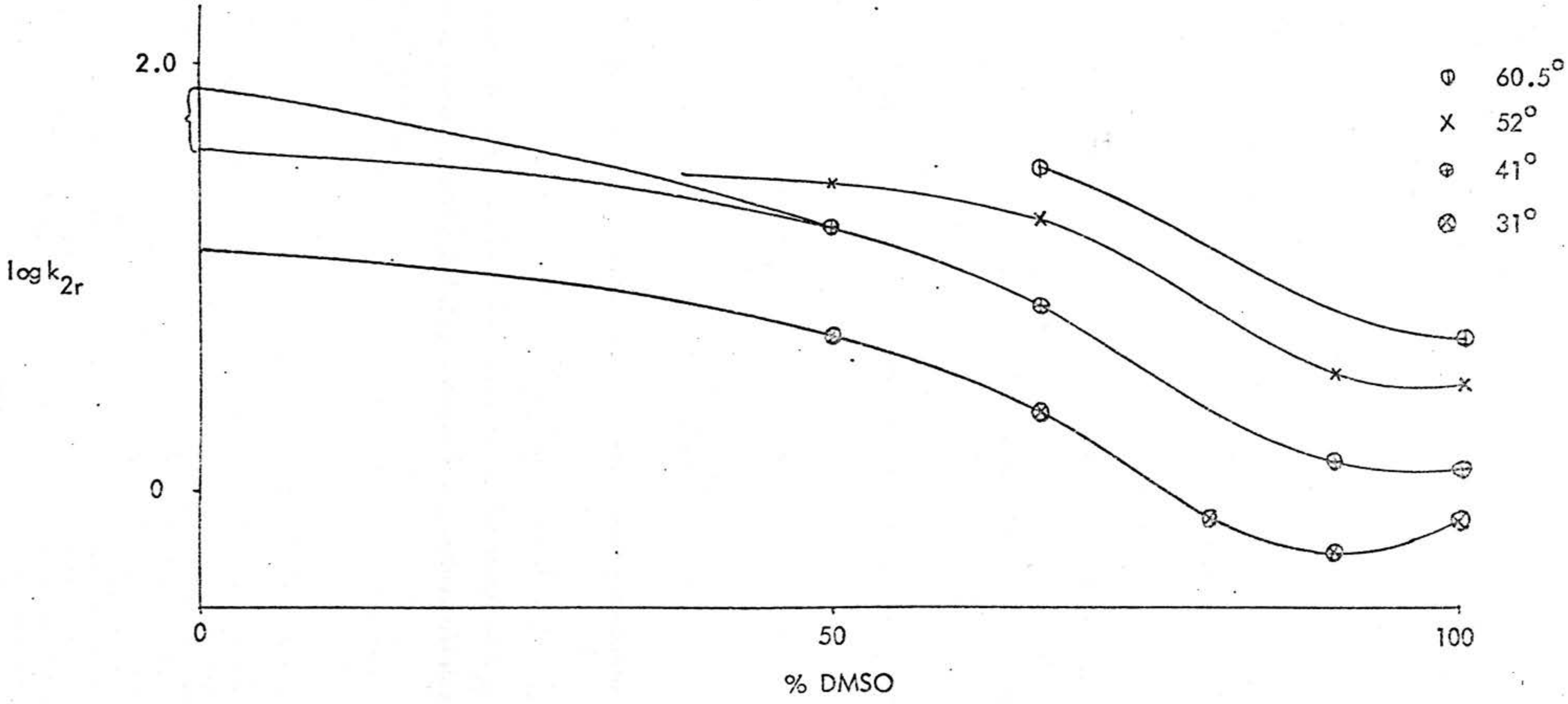


Fig.3.1.21 Plot of log k_{2r} against % DMSO by volume for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) with triethylamine in DMSO/methanol at 4 temperatures.

3.1.6 Reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO in the presence of triethylammonium chloride

The reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine(100 - 1600 equivalents) in DMSO containing 100 equivalents of triethylammonium chloride(excess conjugate acid) has been found to obey pseudo first order forward and first order reverse kinetics.

$$\mathrm{XH} \quad + \quad \mathrm{B} \quad \underset{\substack{\text{excess} \\ \mathrm{BH^{+}Cl^{-}}}}{\rightleftharpoons} \quad \mathrm{X^{-}} \quad + \quad \mathrm{BH^{+}}$$

The relevant kinetic equations are given below:-

$$-x_e \left[\ln(1 - x/x_e) \right] / a \quad = \quad k_{1f}\, t \qquad (3.16)$$

where $a = [\mathrm{XH}]_0$.

Equation (3.16) may be written in terms of the absorbance(OD) of species X^-:-

$$-OD_e \left[\ln(1 - OD_t/OD_e) \right] / \varepsilon_{X^-} l a b \quad = \quad k_{2f}\, t \qquad (3.17)$$

where l = cell path length, $b = [\mathrm{B}]$ and $k_{1f} = b k_{2f}$

or 2nd order forward and 1st order reverse function $= k_{2f}\, t$ (3.18)

A straight line plot, obtained using equation (3.17), of the data given in Table 3.1.16, is shown in fig.3.1.22. The value of k_{2f} derived from this plot is listed in Table 3.1.17, alongwith k_{2f} values obtained at different base concentrations.

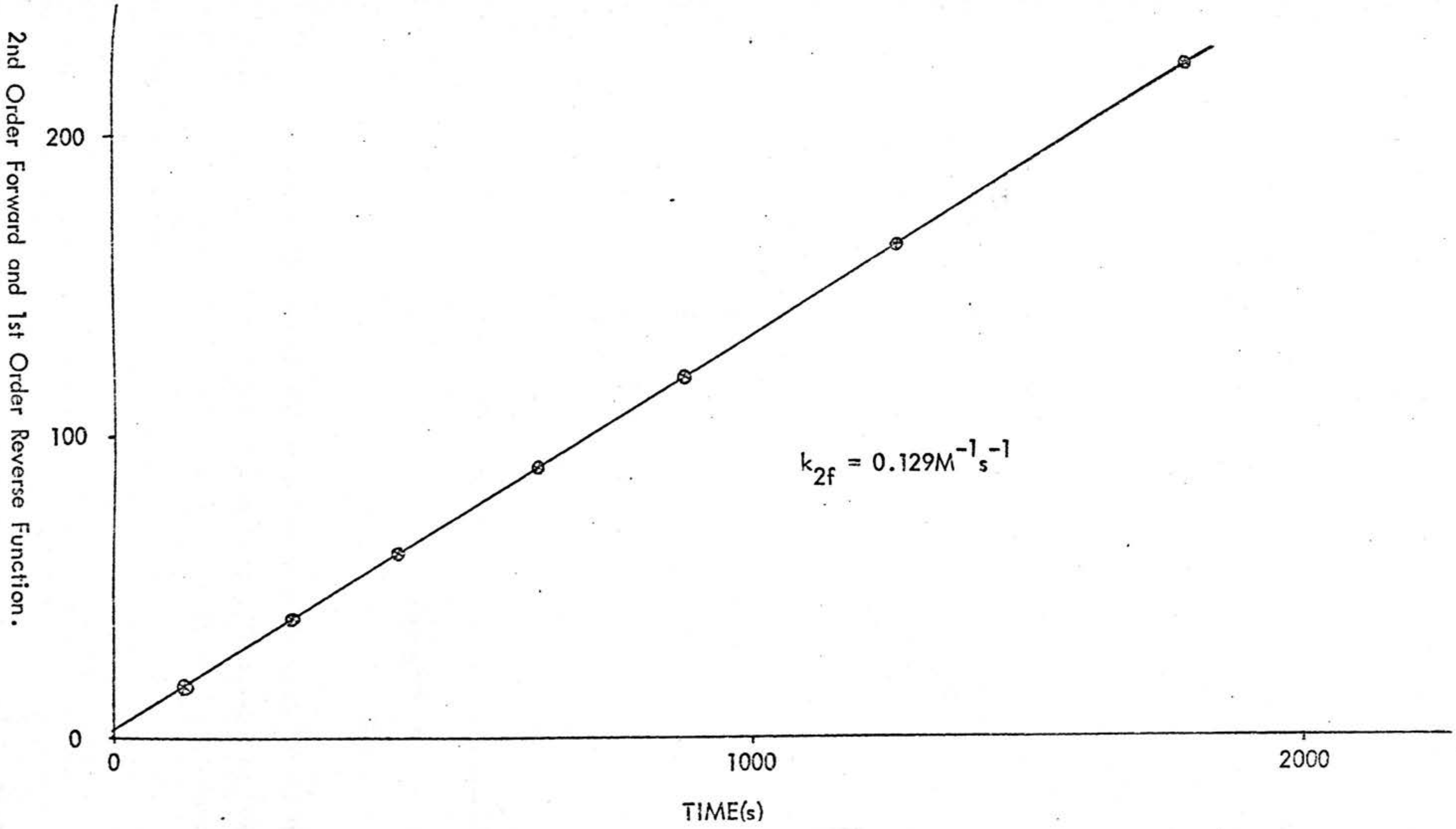


Fig.3.1.22 Kinetic plot according to equation (3.17) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93)(5.116×10^{-5}M) with 100 equivalents of triethylamine in DMSO containing 100 equivalents of triethylammonium chloride at 40.4°C.

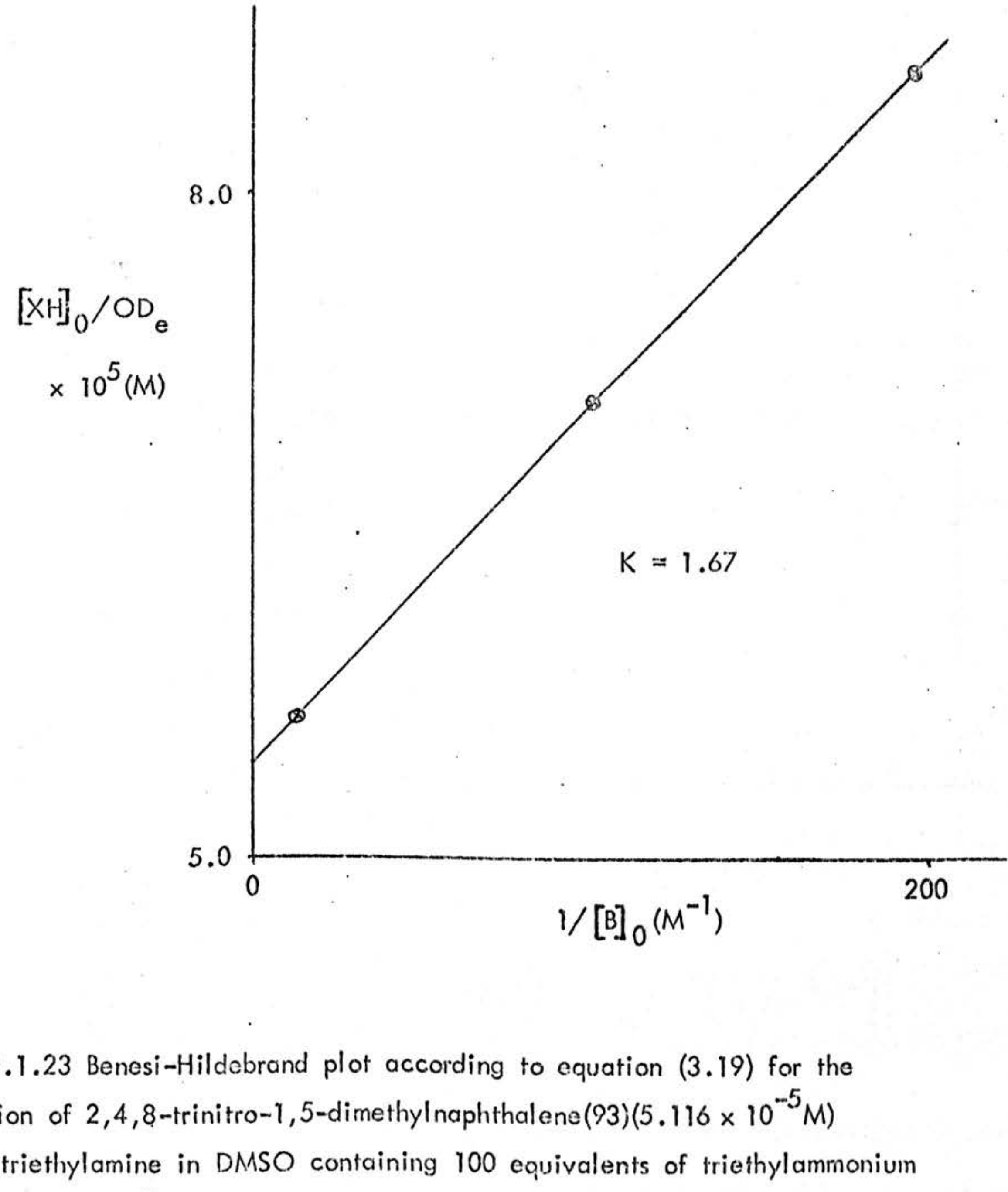


Fig.3.1.23 Benesi-Hildebrand plot according to equation (3.19) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93)(5.116 × 10^{-5}M) with triethylamine in DMSO containing 100 equivalents of triethylammonium chloride at 40.4°C.

Table 3.1.16 Absorbance values of species (94) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO containing triethylammonium chloride(100 equivalents)

$[XH]_0 = 5.116 \times 10^{-5}$ M $\quad$ Et_3N = 100 equivalents $\quad$ Temp = 40.4°

Time/s	OD_t	2nd order forward and 1st order reverse function
0	0.018	3.6
120	0.084	17.9
300	0.168	39.0
480	0.239	60.5
720	0.315	88.8
960	0.378	119.0
1320	0.445	162.9
1800	0.505	224.2
∞	0.592	∞

The value of ε_{X^-} used in the above calculation of k_{2f} was $18400 M^{-1} cm^{-1}$ and was derived from a Benesi-Hildebrand plot using equation (3.19)(fig.3.1.23). This plot also gave a value for the equilibrium constant, K = 1.67.

$$[XH]_0/OD_e = d/K\varepsilon_{X^-}lb + 1/\varepsilon_{X^-}l \qquad (3.19)$$

where intercept = $1/\varepsilon_{X^-}l$ and slope = $d/K\varepsilon_{X^-}l$ $\quad$ ($d = [Et_3NH^+Cl^-]$)

Table 3.1.17 Second order forward rate constants for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO solution containing triethylammonium chloride

Base equivalents	$k_{2f}/M^{-1}s^{-1}$
100	0.129
200	0.132
1600	0.121
	mean 0.127

From the relationship $k_{2r} = k_{2f}/K$ the value of $k_{2r} = 0.076M^{-1}s^{-1}$. Direct determination of k_{2r} is also possible by adding triethylammonium chloride in DMSO to a solution of compound (94) at equilibrium in DMSO to reverse the reaction.

$$B \quad + \quad XH \xrightleftharpoons[BH^+Cl^-]{\text{excess}} X^- \quad + \quad BH^+$$

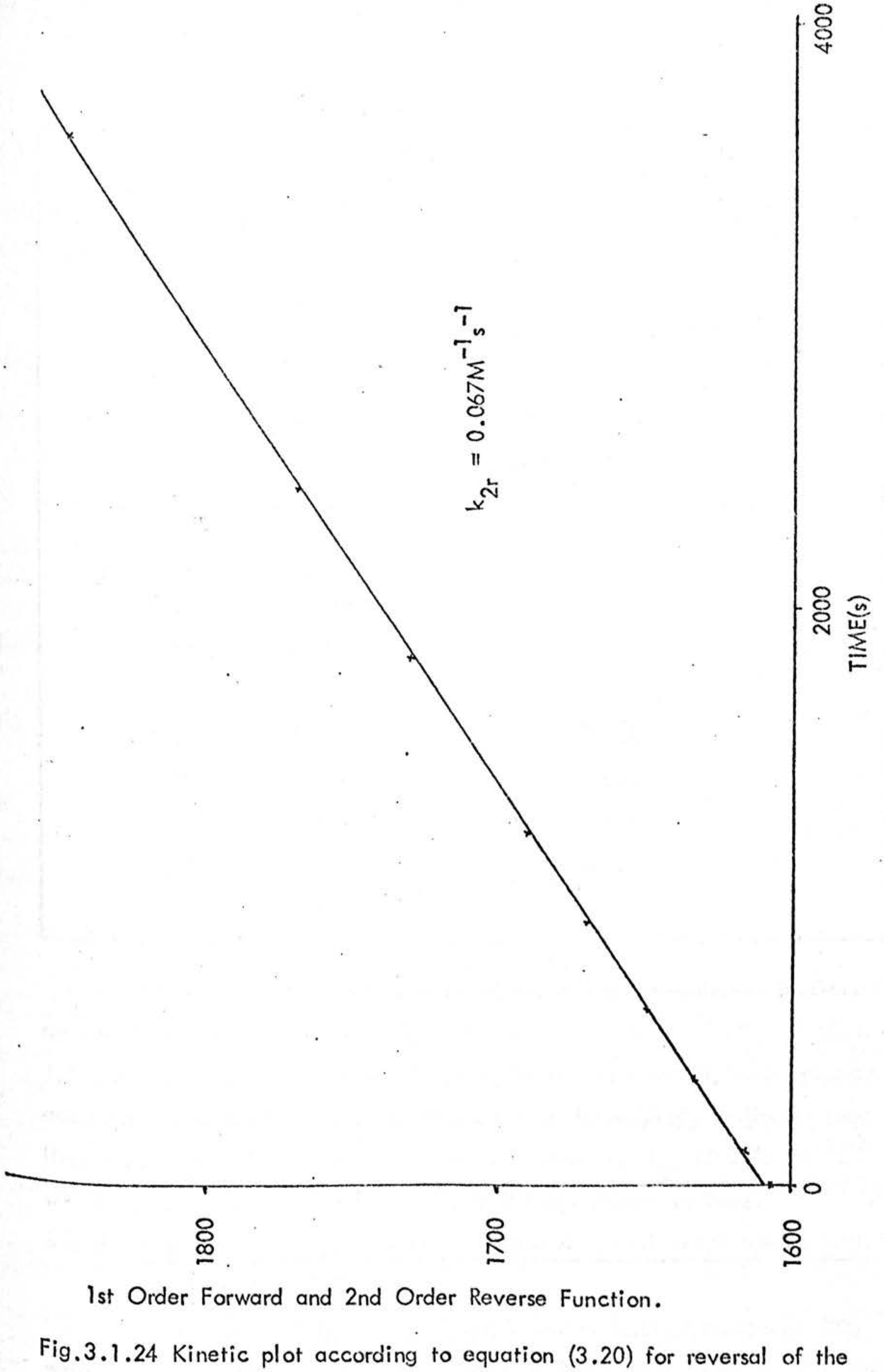
By monitoring the absorbance due to species X^- the approach to the new equilibrium position was found to obey equation (3.20) (See Appendix 2.3.6 for derivation of equation (3.20)).

$$-\ln\left[\frac{OD_t}{\varepsilon_{X^-}}(1 + OD_e/m) - a\,OD_e/m\right] / b(1 + OD_e/m) = k_{2r}\,t \qquad (3.20)$$

or 1st order forward and 2nd order reverse function = $k_{2r}\,t$ (3.21)

where $m = a\,\varepsilon_{X^-} - OD_e$ and $a = [XH]_0 + [X^-]_0$

A straight line plot(fig.3.1.24) was obtained, using equation (3.20) for the data given in Table 3.1.18. A value for k_{2r} of $0.067M^{-1}s^{-1}$ was obtained from this plot assuming $\varepsilon_{X^-} = 18400\,M^{-1}cm^{-1}$.



1st Order Forward and 2nd Order Reverse Function.

Fig.3.1.24 Kinetic plot according to equation (3.20) for reversal of the reaction involving 2,4,8-trinitro-1,5-dimethylnaphthalene(93)(5.116×10^{-5}M) and 20 equivalents of triethylamine in DMSO by the addition of 120 equivalents of triethylammonium chloride at 40.4°C.

Table 3.1.18 Absorbance values of species (94) for the reversal of the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO by the addition of excess triethylammonium chloride

$a = 5.116 \times 10^{-5}$M Et_3N = 20 equivalents   Temp. = 40.4°

$Et_3NH^+Cl^-$ = 120 equivalents

Time/s	OD_t	1st order forward and 2nd order reverse function
0	0.600	1606.2
120	0.575	1615.4
360	0.533	1632.1
600	0.495	1648.9
900	0.454	1669.5
1200	0.419	1689.4
1800	0.361	1729.6
2400	0.318	1768.0
3600	0.258	1845.5
∞	0.166	∞

Addition of 120 equivalents of triethylammonium chloride in DMSO to an equilibrium mixture of 40 equivalents of triethylamine and 2,4 8-trinitro-1,5-dimethylnaphthalene in DMSO gave kinetic data which, when plotted according to equation (3.20), produced a line increasingly divergent from linearity. Initial slope measurement gave a value for k_{2r} of $0.068M^{-1}s^{-1}$ which agrees with that determined using 20 equivalents of base.

3.1.7 Reaction of 2,4,8-trinitro-d_3-1-methyl-5-methylnaphthalene with triethylamine in DMSO

The reaction of the trideuterated-1-methyl form of compound (93) with triethylamine(100 - 1000 equivalents) in DMSO was found to obey pseudo first order forward and second order reverse kinetics according to equation (3.9).

$$XD \quad + \quad B \rightleftharpoons X^- \quad + \quad BD^+$$

A kinetic plot according to equation (3.9) for the reaction of 154 equivalents of triethylamine with 2,4,8-trinitro-d_3-1-methyl-5-methylnaphthalene in DMSO at 41° is shown in fig.3.1.25. Table 3.1.19 gives the forward rate constants at several base concentrations derived from plots such as that shown in fig.3.1.25.

Table 3.1.19 Forward rate constants for the reaction of 2,4,8-trinitro-d_3-1-methyl-5-methylnaphthalene with triethylamine in DMSO at 41°

Base equivalents	$k_{1f} \times 10^4/s^{-1}$	$k_{2f} \times 10^2/M^{-1}s^{-1}$
103	4.69	9.80
154	7.23	10.10
205	9.25	9.70
255	11.7	9.80
1026	46.0	9.66
		mean = 9.81

The value of k_{2f} for the reaction of the fully protonated form of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine at 41° in DMSO is $0.133M^{-1}s^{-1}$ (See Table 3.1.10)

$$\text{Hence,} \quad \frac{(k_{2f})_H}{(k_{2f})_D} = \frac{0.133}{9.81 \times 10^{-2}} = 1.37$$

This ratio shows the existence of a small kinetic isotope effect. Ratios as large as 7 - 8 have been observed for the reaction of alkoxides with TNT-d_3.[125, 126]

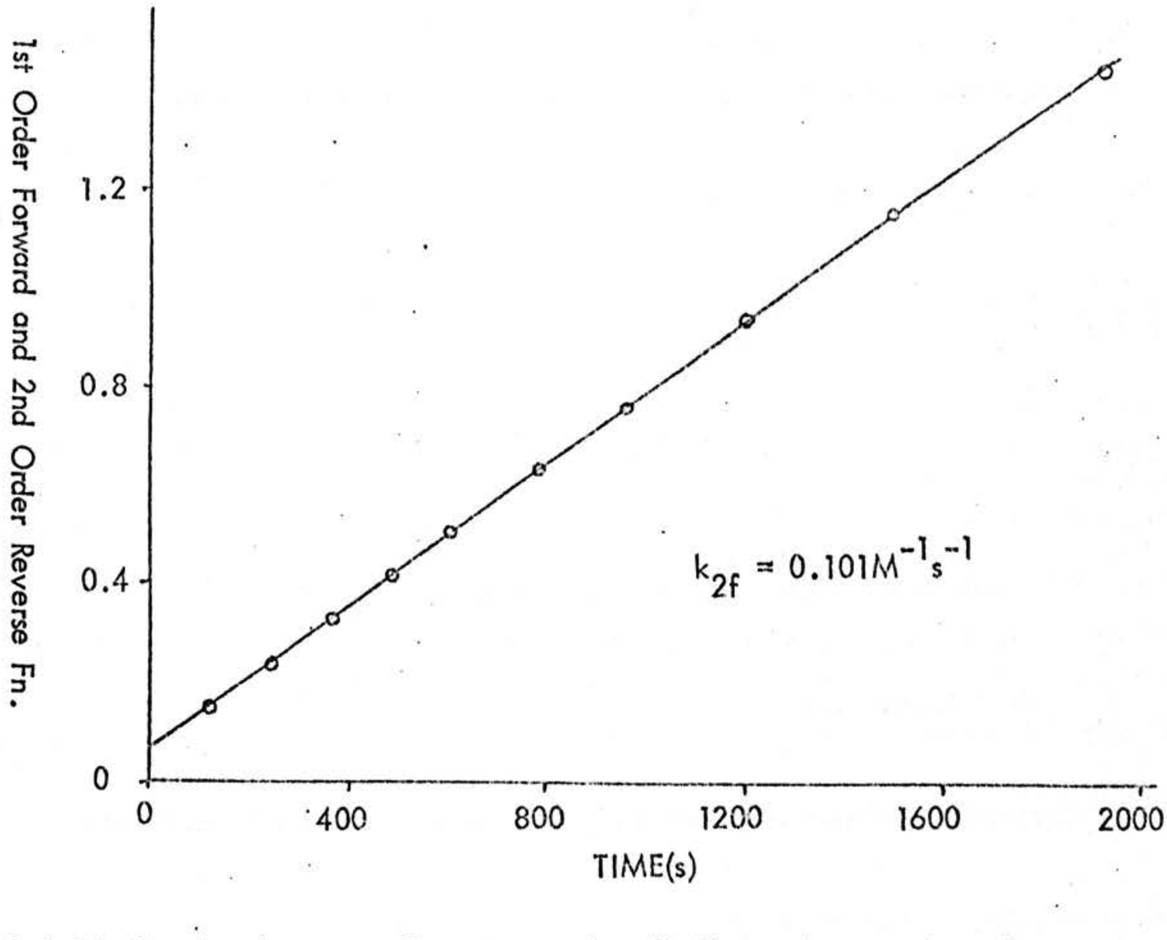


Fig.3.1.25 Kinetic plot according to equation (3.9) for the reaction of d_3-2,4,8-trinitro-1,5-dimethylnaphthalene(4.665×10^{-5}M) with 154 equivalents of triethylamine in DMSO at 41°C.

3.1.9 Reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with sodium hydroxide(< 1 equivalent) in aqueous DMSO

The reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with less than 1 equivalent of sodium hydroxide in DMSO/H_2O(9:1) proceeded via at least 2 different processes, namely a fast step corresponding to formation of an addition complex and a slow step corresponding to proton abstraction from the nitroaromatic(See Section 2.2.1(A)). The proton abstraction step may be represented as below:-

$$XH \quad + \quad OH^- \rightleftharpoons X^- \quad + \quad \underset{\text{excess}}{H_2O}$$

Kinetic analysis of the slower reaction using equation (3.21) for second order forward and pseudo first order reverse kinetics was carried out by means of program KD21(See Appendix 2.3.4 for derivation of equation (3.21)).

$$\ln\left[\frac{x - ab/x_e}{x - x_e}\right] \Big/ \left[ab/x_e - x_e\right] \quad + \quad \text{constant} \quad = \quad k_{2f}\,t \qquad (3.21)$$

or 2nd order forward and 1st order reverse function = $k_{2f}\,t$ (3.22)

where $a = [XH]_0$ and $b = [B]_0$.

Equation (3.21) is derived in Appendix 2.3.3. The kinetic plot assuming equation (3.21) to hold for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with 0.6 equivalent of base in aqueous DMSO is shown in fig.3.1.26.

Table 3.1.20 lists the values of k_{2f} for the slow step at different base concentrations.

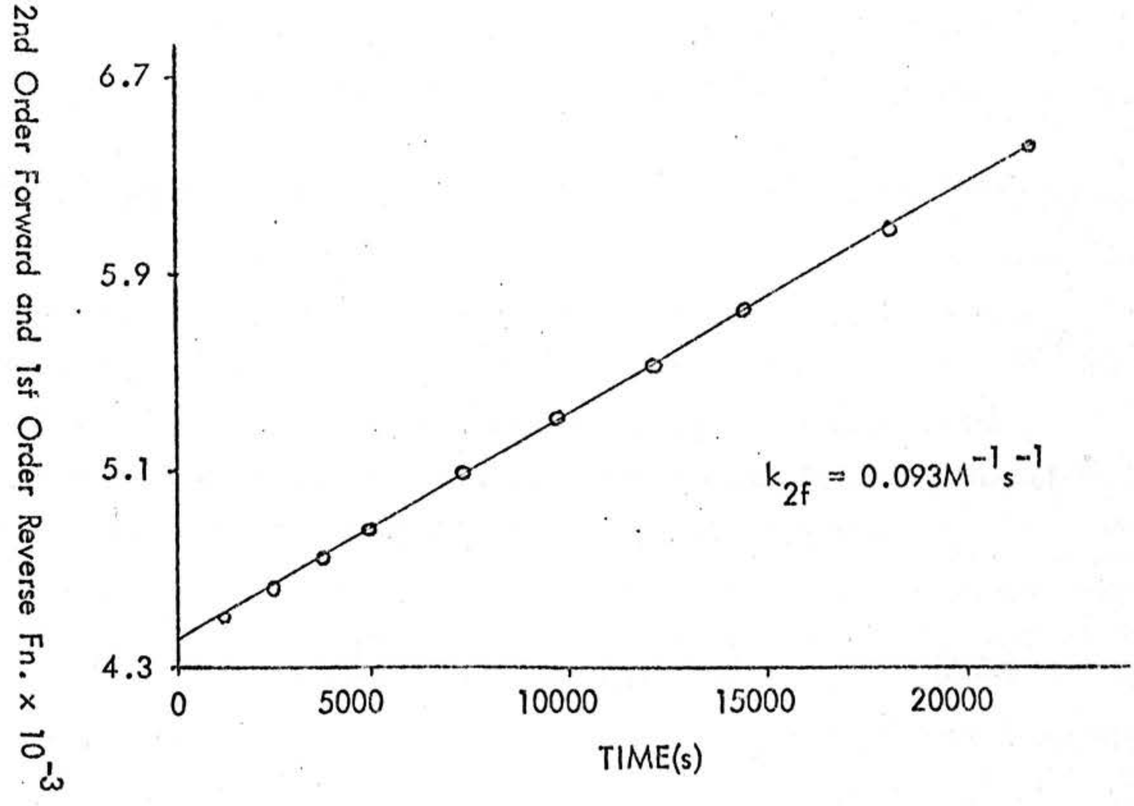


Fig.3.1.26 Kinetic plot according to equation (3.21) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93)(2.558×10^{-4}M) with 0.6 equivalent of sodium hydroxide in DMSO/H_2O(9:1) at 40.75°C.

Table 3.1.20 Rate constants for the proton abstraction step and initial and final absorbance changes produced on reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with less than 1 equivalent of sodium hydroxide in aqueous DMSO

$[XH]_0 \simeq 2.558 \times 10^{-4}$M ε_{X^-} assumed = 19300 $M^{-1}cm^{-1}$ Temp = 41°

Base equivalents	$k_{2f}/M^{-1}s^{-1}$	$OD_{initial}$	OD_{final}
0.5	0.071	0.135	0.648
0.6	0.083	0.135	0.925
0.7	0.103	0.253	1.262
0.8	0.103	0.253	1.487
0.9	0.134	0.276	1.783

where $OD_{initial}$ = absorbance of solution immediately after base added.

Clearly, the k_{2f} values for proton abstraction are only approximate due to interference by the first step($[XH]_0$ assumed constant = 2.558×10^{-4}M).

A set of runs at 51° has been used to determine the approximate equilibrium constant for formation of the addition complex by substitution of data into equation (3.23) below(Derivation in Appendix 2.2.1).

$$K = 1/(\varepsilon_{X^-} N [XH]_0^2/OD_e - [XH]_0(1 + N)) \qquad (3.23)$$

Table 3.1.21 Rate constants for the formation of 'benzyl-type' anion (94); initial absorbance changes and equilibrium constants of the addition complex produced on reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with less than 1 equivalent of sodium hydroxide in aqueous DMSO

$[XH]_0 \simeq 2.558 \times 10^{-4}$ M ε_{X^-} assumed = 20000$M^{-1}cm^{-1}$ Temp. = 51°

Base equivalents	$k_{2f}/M^{-1}s^{-1}$ for formation of (94)	$OD_{initial}$	$K_{addition}/M^{-1}$
0.4	0.145	0.107	220
0.5	0.163	0.130	215
0.6	0.198	0.183	257
0.7	0.228	0.227	277
0.8	0.283	0.272	294
0.9	0.297	0.352	348

3.1.10 Reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with excess sodium hydroxide in aqueous DMSO

The rapid reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with hydroxide ion(50 - 200 equivalents) in DMSO/H_2O(9:1) to give an addition complex appears to obey pseudo first order forward and first order reverse kinetics:-

$$XH + OH^- \rightleftharpoons [XH.OH]^-$$

The kinetic equation (3.24) given below was used to process and plot the stopped-flow voltage-time data given in Table 3.1.22(using program SF11).

$$-\ln(\ln((V_t + V_{IN})/V_{IN}))/\ln(10) = (k_{1f} + k_{1r})t \qquad (3.24)$$

where $V_{IN} = V_\infty$ = infinity voltage and V_t = voltage at time t.

$$\text{or} \quad \text{1st order forward and reverse function} = (k_{1f} + k_{1r})t \qquad (3.25)$$

Table 3.1.22 Voltage-time data for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with sodium hydroxide in aqueous DMSO(1:9)

$[XH]_0 = 2.558 \times 10^{-5}M$ NaOH = 122.2 equivalents   Temp = 26.8°

Time/ms	Trace voltage/V	1st order forward and reverse function
0	11.15	1.055
50	10.11	1.185
100	9.32	1.308
150	8.68	1.428
200	8.17	1.545
250	7.73	1.664
350	7.04	1.908
∞	5.00	∞

The data in Table 3.1.22 is plotted according to equation (3.25) in fig.3.1.27. The value for k_{1f} of $2.42s^{-1}$ derived from this plot is based on the assumption that k_{1r} is negligibly small. Table 3.1.23 lists values for the pseudo first order rate constant, k_{1f} at various base concentrations.

Table 3.1.23 Pseudo first order rate constants for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with excess sodium hydroxide in aqueous DMSO(1:9)

Temp. = 26.8°

Base equivalents	k_{ψ}^{*}/s^{-1}	$k_{2f}/M^{-1}s^{-1}$
48.9	0.957	
73.3	1.33	
97.7	1.92	884
122.2	2.43	
195.5	4.52	

* mean of at least 6 traces

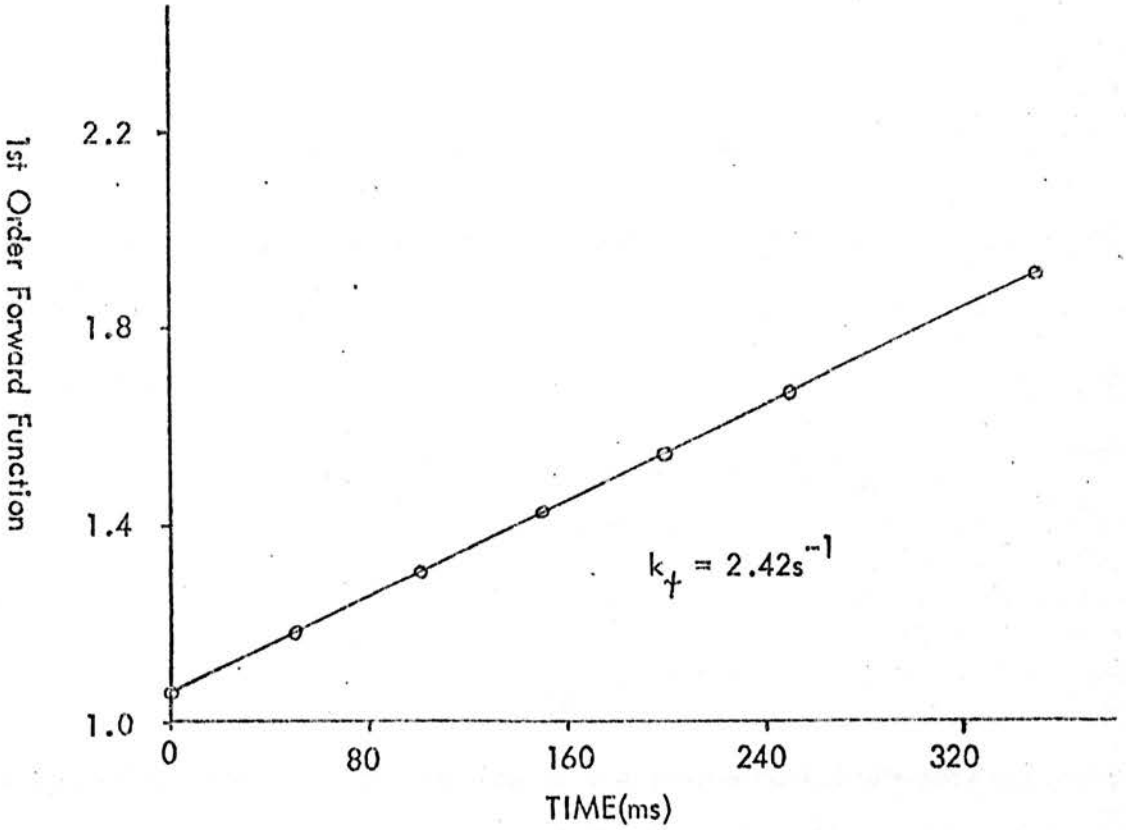


Fig.3.1.27 Kinetic plot according to equation (3.25) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93)(2.558×10^{-5}M) with 122.2 equivalents of sodium hydroxide in DMSO/H_2O(9:1) at 26.8°C.

A plot of k_{ψ} against $[OH^-]$ is shown in fig.3.1.28, where $k_{\psi} = k_{2f}[B] + k_{1r}$. It will be noted that the intercept occurs at a negative value of the ordinate, probably due to the existence of a second very fast reaction.

For the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with 391 equivalents of hydroxide ion in aqueous DMSO at 25.9°C, a decrease in absorbance at the monitoring wavelength was observed to follow the formation of addition complex. This decrease in absorbance gives a linear first order plot(fig.3.1.29) in accord with equation (3.26). The slope of this plot gives a value for k_{ψ} ($\simeq k_{1f}$) of $0.0247s^{-1}$. Since $k_{1f} = k_{2f}[B]$, the value of k_{2f} is $2.48M^{-1}s^{-1}$. This process may correspond to loss of nitrite ion from the addition complex.[26]

$$-\ln(\ln(V_{IN}/(V_t + V_{IN})))/\ln(10) = k_{\psi}\, t \qquad (3.26)$$

where $V_{IN} = V_{\infty}$ = infinity voltage and V_t = voltage at time t.

3.1.11 Reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with alkoxides in alcohols

Stopped-flow studies of the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with sodium alkoxides in the corresponding alcohols have been carried out but the products have not been identified.

The reaction may be represented simply as:-

$$XH \quad + \quad OR^- \underset{ROH}{\rightleftharpoons} \text{Products}$$

Stopped-flow traces for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with several alkoxides in the corresponding alcohols are shown in fig.3.1.30. Table 3.1.24 lists the forward rate constants obtained for the reactions on the basis that pseudo first order kinetics are obeyed according to equation (3.24). In the case of the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with sodium t-butoxide in t-butanol, the reaction with increasing absorbance is analysed using equation (3.24)(fig.3.1.30(c)). The slower reaction with decreasing absorbance is also analysed in fig.3.1.30(d) using equation (3.26).

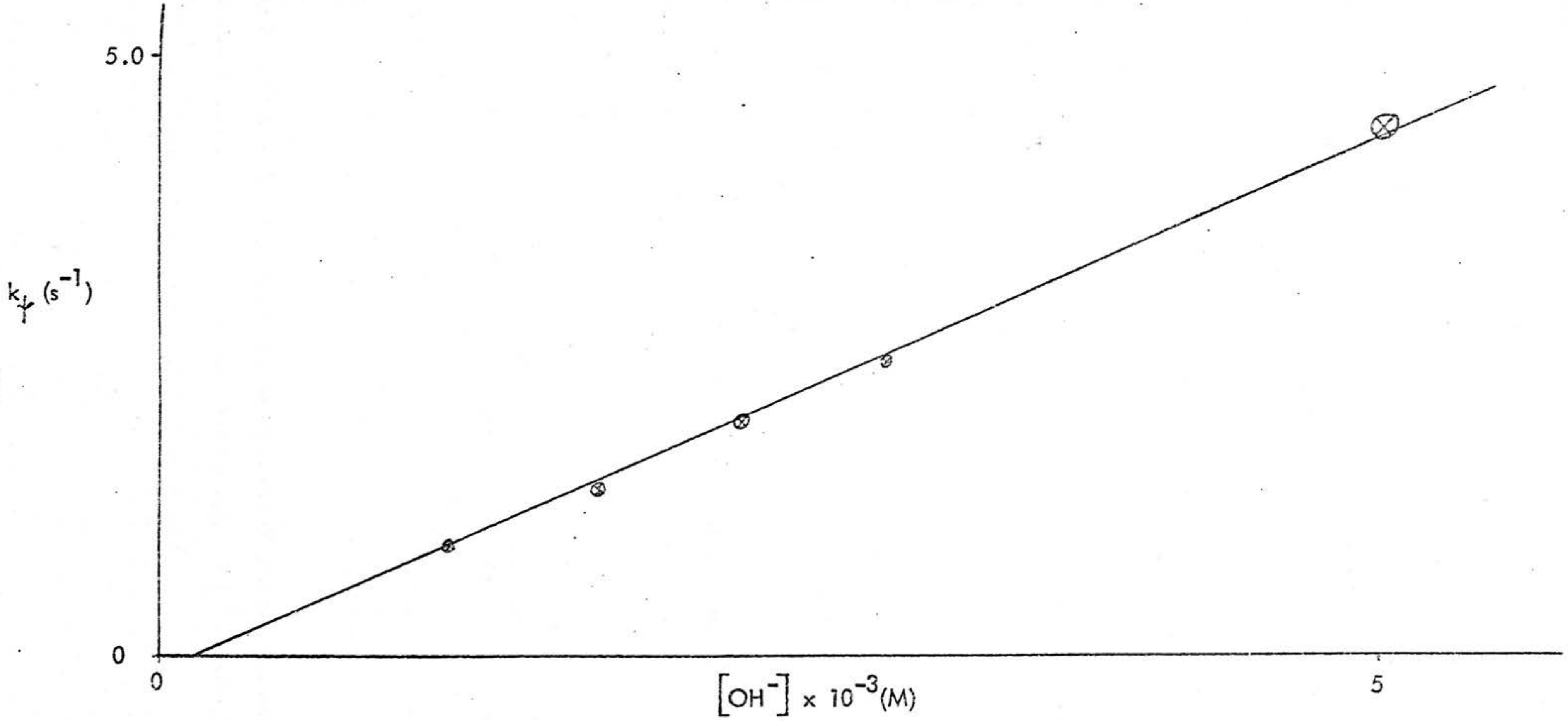


Fig.3.1.28 Plot of k_{ψ} against $[OH^-]$ for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93)(2.558×10^{-5}M) with sodium hydroxide in DMSO/H_2O(9:1) at 26.8°C.

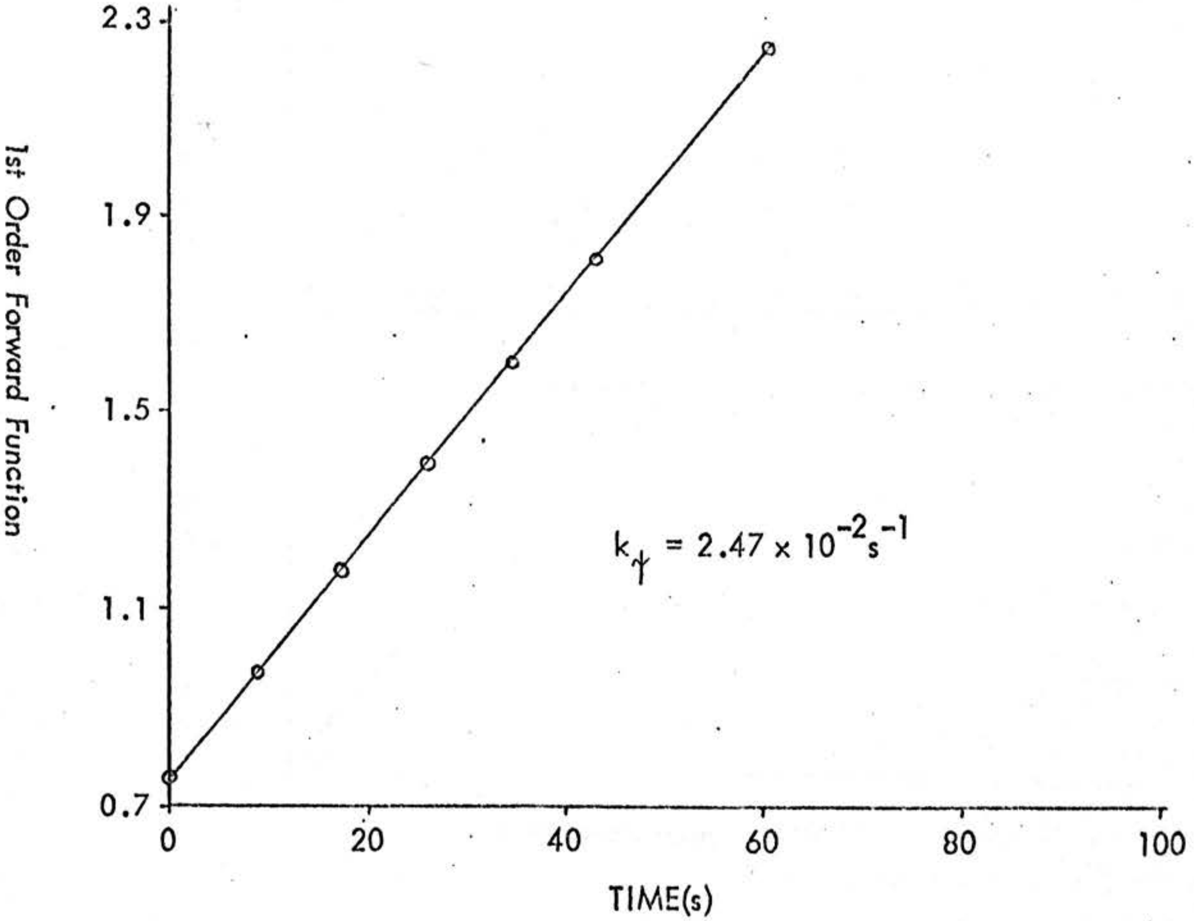


Fig.3.1.29 Kinetic plot according to equation (3.26) for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93)(2.558×10^{-5}M) with 391 equivalents of sodium hydroxide in DMSO/H_2O(9:1) at 25.9°C.

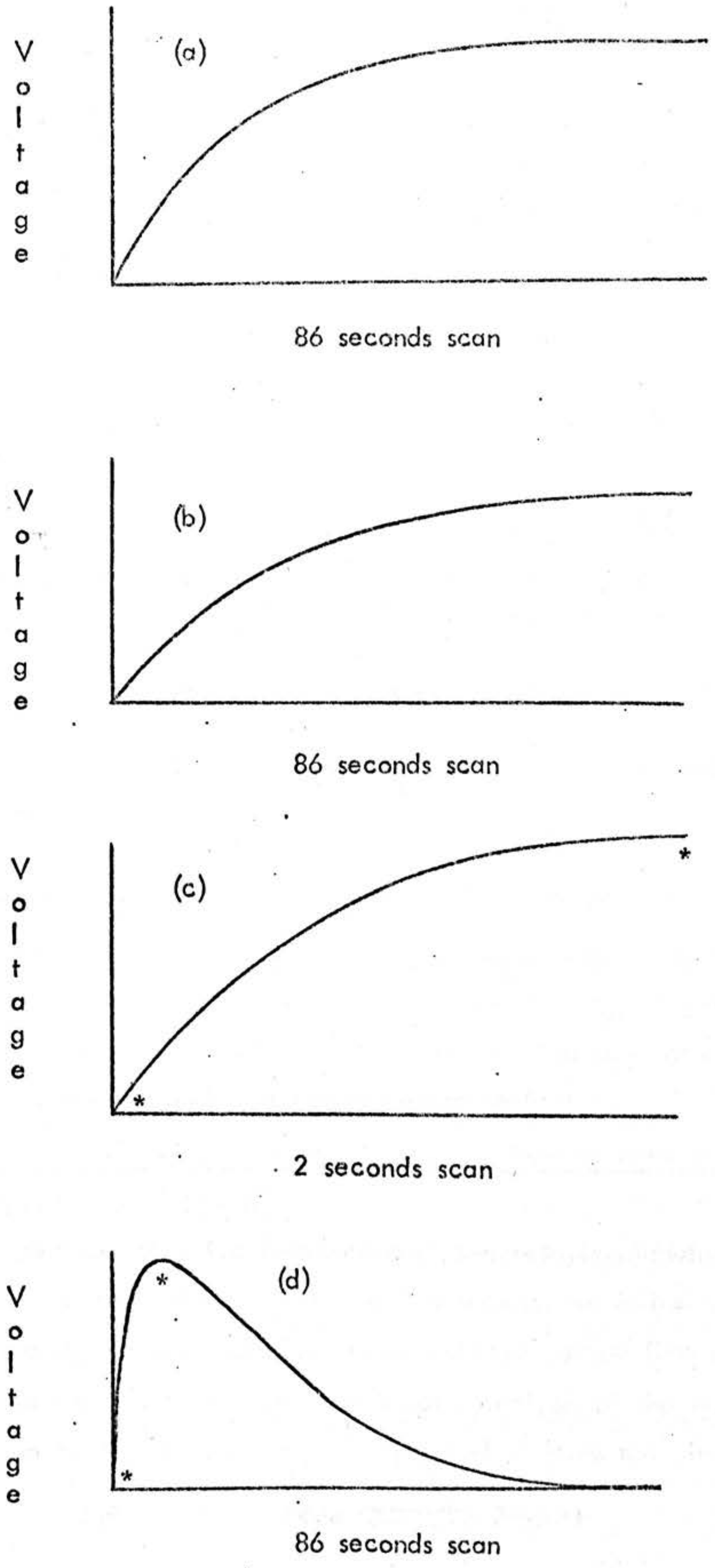


Fig.3.1.30 Stopped-flow traces for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene(93)(2.5×10^{-5}M) with:- (a) 2000 equivalents sodium methoxide in methanol; (b) 200 equivalents sodium ethoxide in ethanol; (c) and (d) 200 equivalents sodium tert-butoxide in tert-butanol.

Program SF11 was used to process and plot the kinetic data.

Table 3.1.24 Rate constants for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with alkoxide ions in the corresponding alcohols

Temp. = 27.0°

	Base equivalents	k_ψ/s^{-1}	approx $k_{2f}/M^{-1}s^{-1}$
MeO^-/methanol	2000	0.0579	0.6
EtO^-/ethanol	200	0.0258	2.6
Bu^tO^-/t-butanol/ DMSO(1:1)	20	2.40	2400
Bu^tO^-/t-butanol	200	0.341	34
" " "	199	0.0623*	6.2(NO_2^- loss)

*pseudo 1st order rate constant for nitrite loss

The second order forward rate constant, k_{2f}, is given by $k_\psi/[B]$ and as can be seen from Table 3.1.24 there is a trend in k_{2f} on passing from methoxide to t-butoxide ion(See chapter 4 for a fuller discussion).

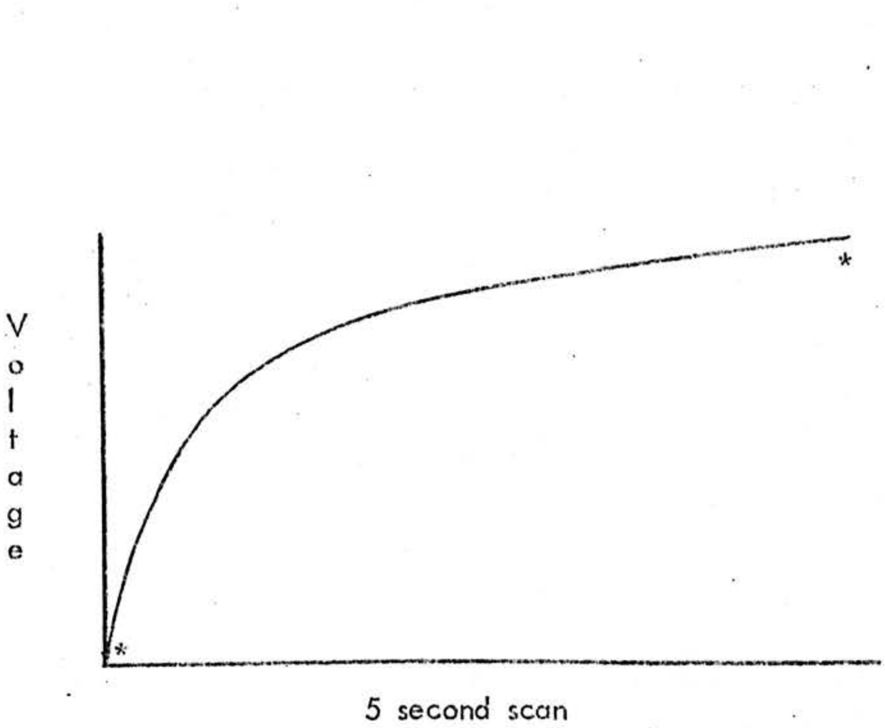
3.2 2,4,6,8-Tetranitro-1,5-dimethylnaphthalene(98)

3.2.1 Reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with sodium methoxide in methanol

The reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with methoxide ion in methanol occurred via 2 processes, an initial rapid step followed by a slower step. Both processes followed pseudo first order forward kinetics. Equation (3.24) was used for kinetic analysis of the stopped-flow data. Program SF11 was used for processing and plotting the kinetic data.

$$XH \quad + \quad {}^-OMe \rightleftharpoons \text{Products}$$

The stopped-flow trace for the initial rapid step is shown in fig.3.2.1(a) and the relevant kinetic plot in fig.3.2.2(a). A value for $k_{2f} = 144M^{-1}s^{-1}$



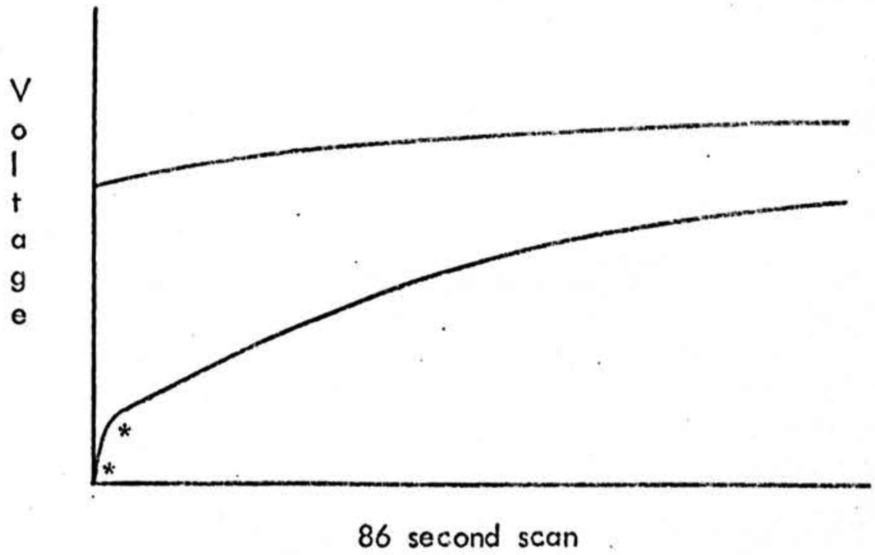


Fig.3.2.1 Stopped-flow traces for the reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene(98)(2×10^{-5}M) with 500 equivalents of sodium methoxide in methanol:- (a) showing initial rapid reaction and (b) showing both initial rapid step(limits denoted by *) and subsequent slower reaction for which 2 consecutive scans are shown.

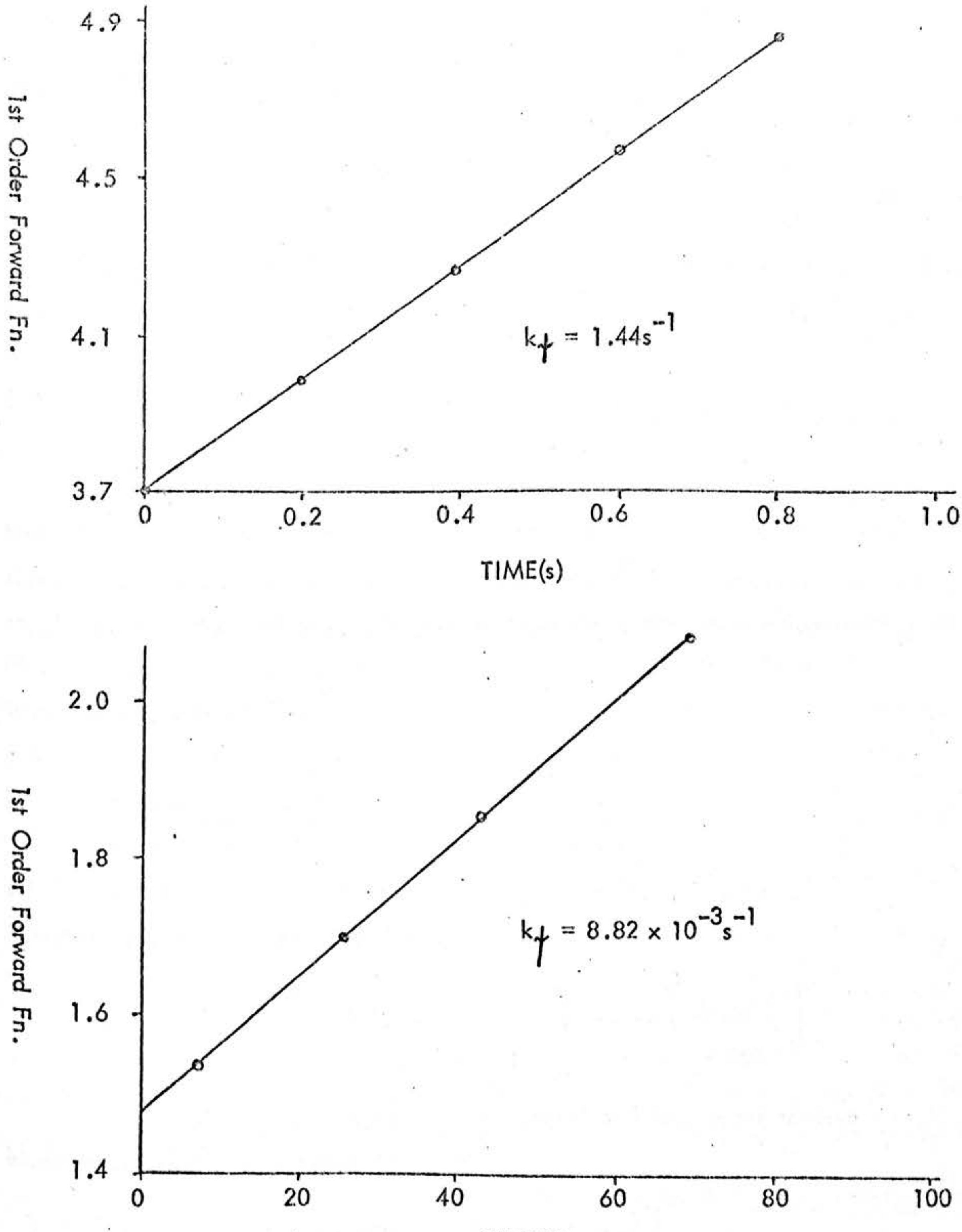


Fig.3.2.2 Kinetic plots according to equation (3.24) for the reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene(98)(2×10^{-5}M) with 500 equivalents of sodium methoxide in methanol:- (a) fast step(at 28.7°C) and (b) slower step (at 28.5°C).

was obtained at 28.6°(where $k_{2f} \sim k_{\psi} / [B]$).

The stopped-flow trace for the subsequent slower step is shown in fig.3.2.1(b) and the relevant kinetic plot in fig 3.2.2(b). A value for $k_{2f} = 0.88M^{-1}s^{-1}$ at 28.6° was obtained.

It is probable that the rapid step corresponds to proton abstraction and/or addition(possibly at C-3). The slower reaction may correspond to decomposition by loss of nitrite ion.

3.2.2 Reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with sodium hydroxide in aqueous DMSO

The reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with hydroxide ion(11 equivalents) in DMSO/H_2O(9:1) obeyed pseudo first order forward and reverse kinetics according to equation (3.24). Reaction was very rapid with $k \sim 25s^{-1}$ at 27.7°, which leads to an approximate value for k_{2f} of $25000M^{-1}s^{-1}$. The magnitude of k_{2f} probably points to the reaction involving addition at C-3.

3.2.3 Reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with sodium sulphite in aqueous DMSO

The reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with sulphite ion in aqueous DMSO(2:3) probably gives the C-3 addition complex (105) (See section 2.2.2(F)).

$$XH \quad + \quad SO_3^{2-} \rightleftharpoons \underset{(105)}{\left[XH.SO_3^{2-}\right]}$$

The reaction obeyed second order forward and first order reverse kinetics according to equation (3.27):-

$$\frac{1}{s^{\frac{1}{2}}} \ln \left[\frac{2\,OD_t/\varepsilon l - (ab\,\varepsilon l/OD_e + OD_e/\varepsilon l) - s^{\frac{1}{2}}}{2\,OD_t/\varepsilon l - (ab\,\varepsilon l/OD_e + OD_e/\varepsilon l) + s^{\frac{1}{2}}} \right] = k_{2f}t + \text{const.} \quad (3.27)$$

or 2nd order forward and 1st order reverse function = $k_{2f}t$ + const. (3.28)

where $s^{\frac{1}{2}} = ab\,\varepsilon l/OD_e - OD_e/\varepsilon l$; $x = OD_t/\varepsilon l$; $x_e = OD_e/\varepsilon l$; $a = [XH]_0$

and b = $[B]$. ε = extinction coefficient of compound (105) and is assumed to be $\sim 19000M^{-1}cm^{-1}$(See Appendix 2.3.4 for derivation of equation (3.27)).

Table 3.2.1 lists the stopped-flow voltage-time data for the reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with sulphite ion in aqueous DMSO where $OD_t = \log(V_0/V_t)$.

Table 3.2.1 Voltage-time and absorbance-time data for the reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with sulphite ion in DMSO/H_2O(3:2)

$[XH]_0 = 6.3 \times 10^{-5}M$ SO_3^{2-} = 9.5 equivalents   Temp. = 27.0°

Time/s	V_t	OD_t	2nd order forward and 1st order reverse function
0	15.955	0.052	1369
0.05	15.656	0.061	1389
0.1	15.394	0.068	1408
0.15	15.068	0.074	1426
0.25	14.784	0.085	1462
0.35	14.479	0.095	1498
0.55	15.034	0.108	1567
0.75	13.729	0.118	1636
∞	13.04	0.140	∞

where V_0 = 18.00V = 0 - 100% voltage change(See Appendix 2.3.9).

The kinetic plot of the above data according to equation (3.27) is shown in fig.3.2.3. The value of k_{2f} derived from the plot is $354M^{-1}s^{-1}$. Unfortunately, due to the instability of sodium sulphite in aqueous DMSO solution consistent results for the value of k_{2f} were not obtained as shown by the data in Table 3.2.2.

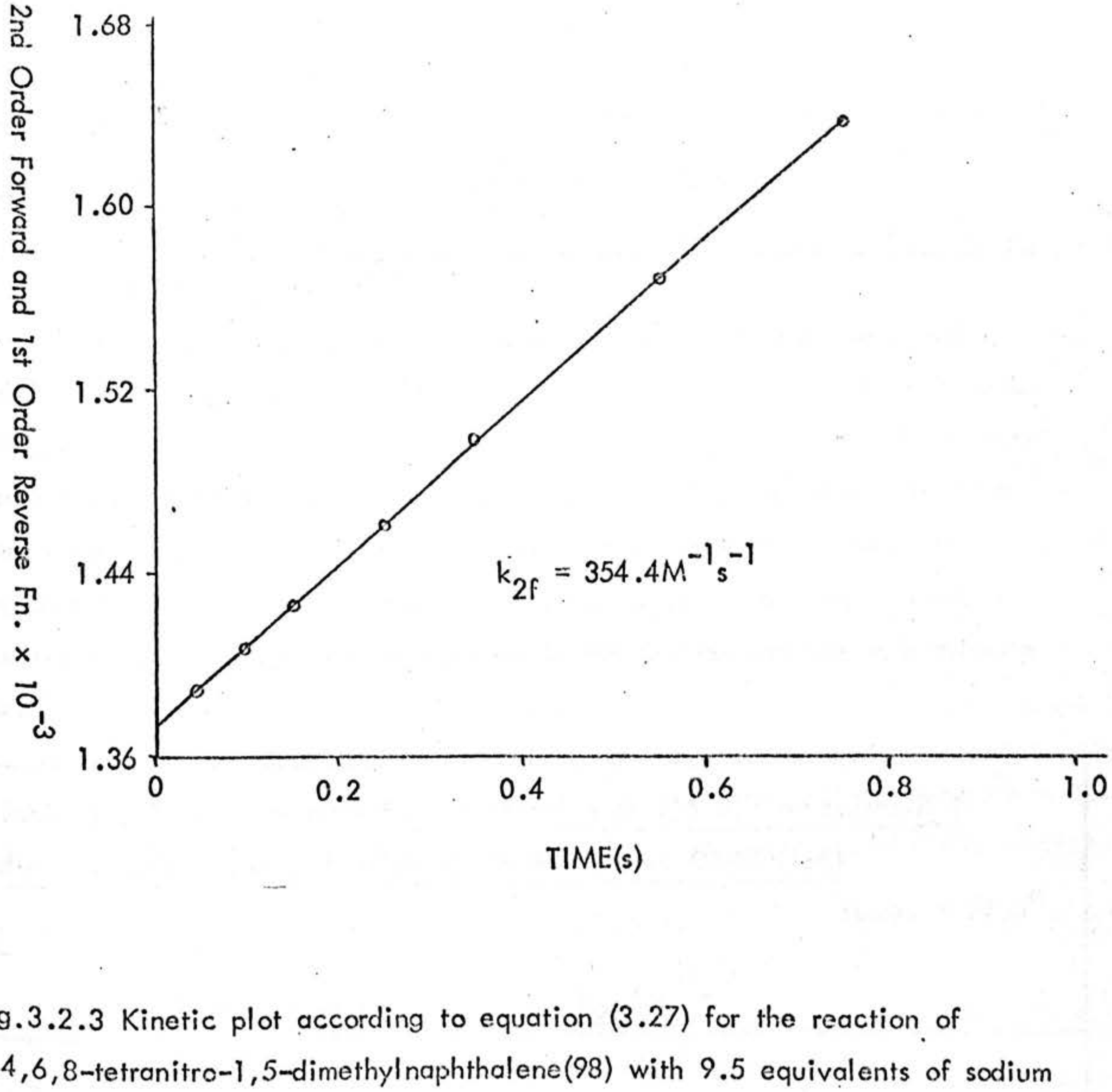


Fig.3.2.3 Kinetic plot according to equation (3.27) for the reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene(98) with 9.5 equivalents of sodium sulphite in DMSO/H_2O(3:2) at 27°C.

Table 3.2.2 Rate constants for the reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with sulphite ion in aqueous DMSO(2:3)

Temp. = 27.0°

Base equivalents	$k_{2f}/M^{-1}s^{-1}$
5.0	460 - 500
6.5	743 - 772
9.5	348 - 367

3.3 1,4,5,7-Tetranitro-2,3-dimethylnaphthalene(161)

3.3.1 Reaction of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene with sodium sulphite in aqueous DMSO

The reaction of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene with sulphite ion in aqueous DMSO(2:3) probably gives the C-8 addition complex (60)(See Section 2.4.2(B)). The reaction obeyed first order forward and first order reverse kinetics in accord with equation (3.24). The kinetic plot for the reaction of 10 equivalents of sodium sulphite at 27.5° is shown in fig.3.3.1. Table 3.3.1 lists rate constants for several base concentrations for the reaction of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene with sulphite ion.

Table 3.3.1 Rate constants for the reaction of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene with sulphite ion in aqueous DMSO(1:4)

Temp. = 27.5°

Base equivalents	$k_{2f}/M^{-1}s^{-1}$
7.5	237000 ± 2000
10*	106000 ± 1000
10*	132000 ± 3000
12.5*	72000 ± 2000
12.5*	131000 ± 4000

*Separately prepared soln's (Under N_2)

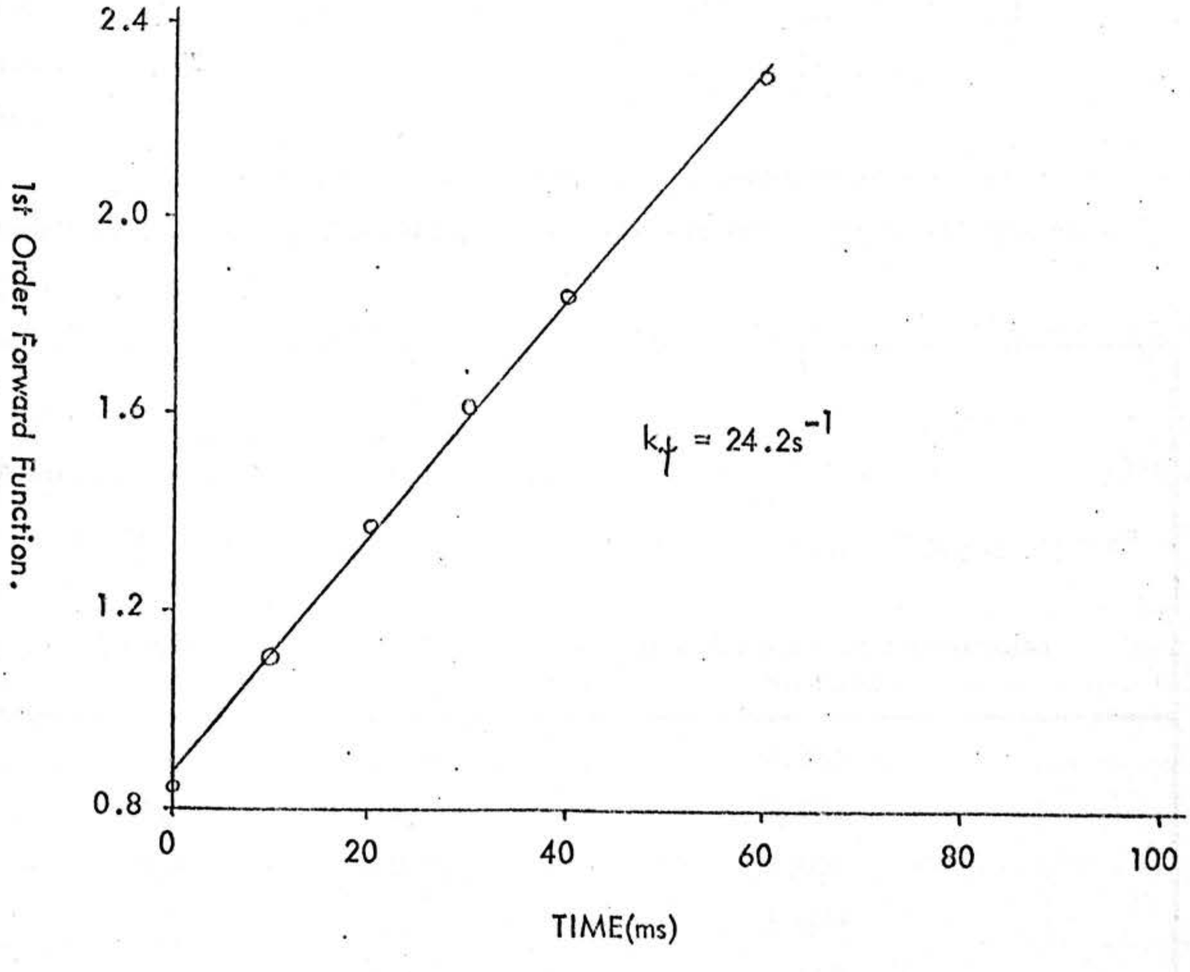


Fig.3.3.1 Kinetic plot according to equation (3.24) for the reaction of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene(161) with 10 equivalents of sodium sulphite in DMSO/H_2O(4:1) at 27.5°C.

The instability of sodium slphite in aqueous DMSO solution probably accounts for the lack of consistency in the results shown in Table 3.3.1.

3.4 1,3,5-Trinitro-2,6-dimethylnaphthalene(162)

3.4.1 Reaction of 1,3,5-trinitro-2,6-dimethylnaphthalene with sodium hydroxide in aqueous DMSO

The rapid reaction of 1,3,5-trinitro-2,6-dimethylnaphthalene with excess hydroxide ion in DMSO/H_2O(7:3,4:1 or 9:1) to probably form the C-4 addition complex (163) has been studied using the stopped-flow technique. Pseudo first order forward and first order reverse kinetics were apparently obeyed. Program SF11 was used for processing and plotting the data according to equation (3.24).

The kinetic data for the reaction of 1,3,5-trinitro-2,6-dimethylnaphthalene with 272.7 equivalents of hydroxide ion in DMSO/H_2O(4:1) is given in Table 3.4.1.

Table 3.4.1 Voltage-time data for the reaction of 1,3,5-trinitro-2,6-dimethylnaphthalene with hydroxide ion in DMSO/H_2O(4:1)

$[XH]_0 = 5 \times 10^{-5}$M OH^- = 272.7 equivalents   Temp. = 27.5°

Time/ms	Voltage/V	1st order forward and reverse function
0	5.389	0.833
250	4.901	0.932
500	4.590	1.007
750	4.331	1.079
1250	3.901	1.222
1750	3.566	1.364
2250	3.310	1.500
3250	2.916	1.783

The value of k_{1f} derived from the above data = $0.283 s^{-1}$ and the kinetic plot is shown in fig.3.4.1.

Rate constants for the reaction of 1,3,5-trinitro-2,6-dimethylnaphthalene with hydroxide ion in DMSO/H_2O(4:1) at 3 temperatures are given in Table 3.4.2.

Table 3.4.2 Rate constants for the reaction of 1,3,5-trinitro-2,6-dimethylnaphthalene with hydroxide ion in DMSO/H_2O(4:1)

Temp.	Base equivalents	k_{ψ}/s^{-1}	$k_{2f}/M^{-1}s^{-1}$	k_{1r}/s^{-1}
27.4°	90.9	0.0912	37.8	< 0.005
	181.8	0.181		
	272.7	0.284		
	363.6	0.375		
36.0°	90.9	0.210	76.8	< 0.005
	181.8	0.384		
	272.7	0.555		
	363.6	0.773		
46.0°	100	0.397	160.8	< 0.005
	200	0.744		
	300	1.201		
	400	1.632		

Plots, according to equation (3.29), are shown in fig.3.4.2.

$$k_{\psi} = k_{2f}\left[OH^{-}\right] + k_{1r} \qquad (3.29)$$

The values of k_{2f} and k_{1r} derived from the slope and intercept respectively of these plots are given in Table 3.4.2.

Rate constants for the reaction of 1,3,5-trinitro-2,6-dimethylnaphthalene with hydroxide ion in other solvent mixtures are given in Table 3.4.3.

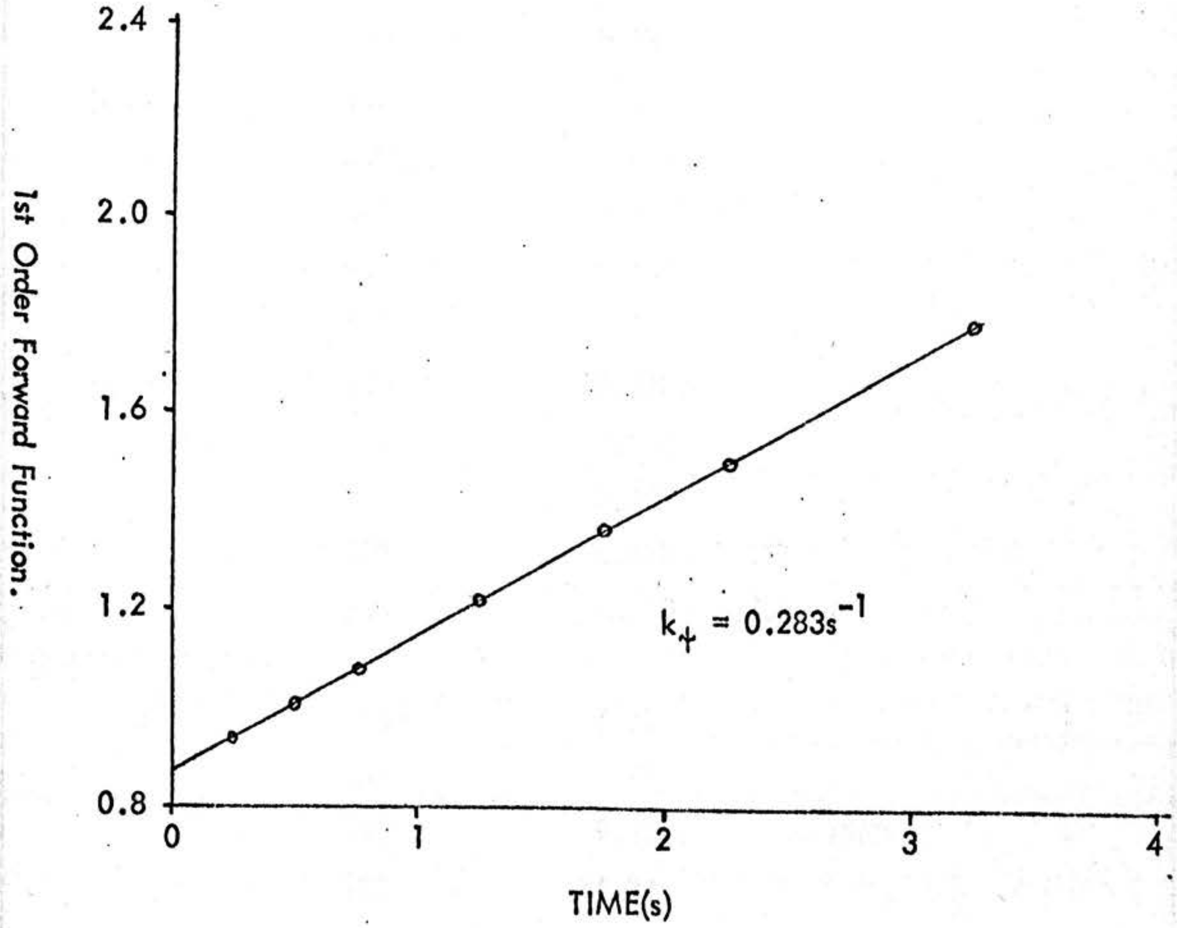


Fig.3.4.1 Kinetic plot according to equation (3.24) for the reaction of 1,3,5-trinitro-2,6-dimethylnaphthalene(162) with 272.7 equivalents of sodium hydroxide in DMSO/H_2O(4:1) at 27.5°C.

Table 3.4.3 Approximate rate constants for the reaction of 1,3,5-trinitro-2,6-dimethylnaphthalene with hydroxide ion in DMSO/H_2O(7:3 and 9:1)

Temp.	Base equivalents	k_{ψ}/s^{-1}	$k_{2f}/M^{-1}s^{-1}$	k_{1r}/s^{-1}
DMSO/H_2O(7:3)				
27.8°	100	0.0113	-	0.002
	200	0.0209		
	300	0.0611		
	400	0.0841		
	500	0.104		
	600	0.120		
36.0°	100	0.0097	-	-
	200	0.0270		
	300	0.0972		
	400	0.187		
	500	0.226		
46.0°	100	0.0187	-	-
	200	0.0509		
	300	0.192		
	400	0.288 - 0.352		
	500	0.510 - 0.538		
DMSO/H_2O(9:1)				
27.4°	80	1.83	~ 1960	-
	160	5.75		
	240	9.33		
	320	14.21		
	400	17.48		
36.0°	40	0.241	-	-
	80	2.10		
	120	5.26		
	160	7.77		
	200	9.58		

Mean of at least 2 runs used throughout

Non-linear plots of k_ψ against $[OH^-]$ were obtained for the reactions carried out in solvent mixtures containing 10 and 30% water(figs.3.4.3 & 4). This suggests the existence of at least 2 reaction steps. Only one reaction step appears to occur on reaction of 1,3,5-trinitro-2,6-dimethylnaphthalene with hydroxide ion in DMSO/H_2O(4:1), namely the formation of the addition complex (163).

Application of the Benesi-Hildebrand equation (3.30) to the equilibrium absorbance, OD_e in DMSO/H_2O(4:1) gives an approximate K value for the formation of compound (163) and ε value for compound (163).

$$\frac{[X]_0 l}{OD_e} = \frac{1}{K\varepsilon[B]} + \frac{1}{\varepsilon} \qquad (3.30)$$

Plots of $[X]_0 l/OD_e$ against $1/[B]$ are shown in fig.3.4.5(See Appendix 2.1.1 for derivation of equation (3.30)).

Table 3.4.4 gives the Benesi-Hildebrand K and ε values and also k_{1r} values calculated from k_{2f}/K.

Table 3.4.4 Equilibrium constants, extinction coefficients and first order reverse rate constants for the reaction of 1,3,5-trinitro-2,6-dimethylnaphthalene with hydroxide ion in DMSO/H_2O(4:1)

Temp.(°C)	K/M^{-1}	$\varepsilon/M^{-1}cm^{-1}$	k_{1r}/s^{-1}
27.4	7340	18490	0.005
36.0	3440	17750	0.022
46.0	2240-2550	17400	0.067

Thermodynamic Parameters

Using equation (3.6) the enthalpy of activation for the formation of compound (163) from 1,3,5-trinitro-2,6-dimethylnaphthalene and hydroxide ion in DMSO/H_2O(4:1) is calculated to be 61.8kJmol^{-1}. The entropy of

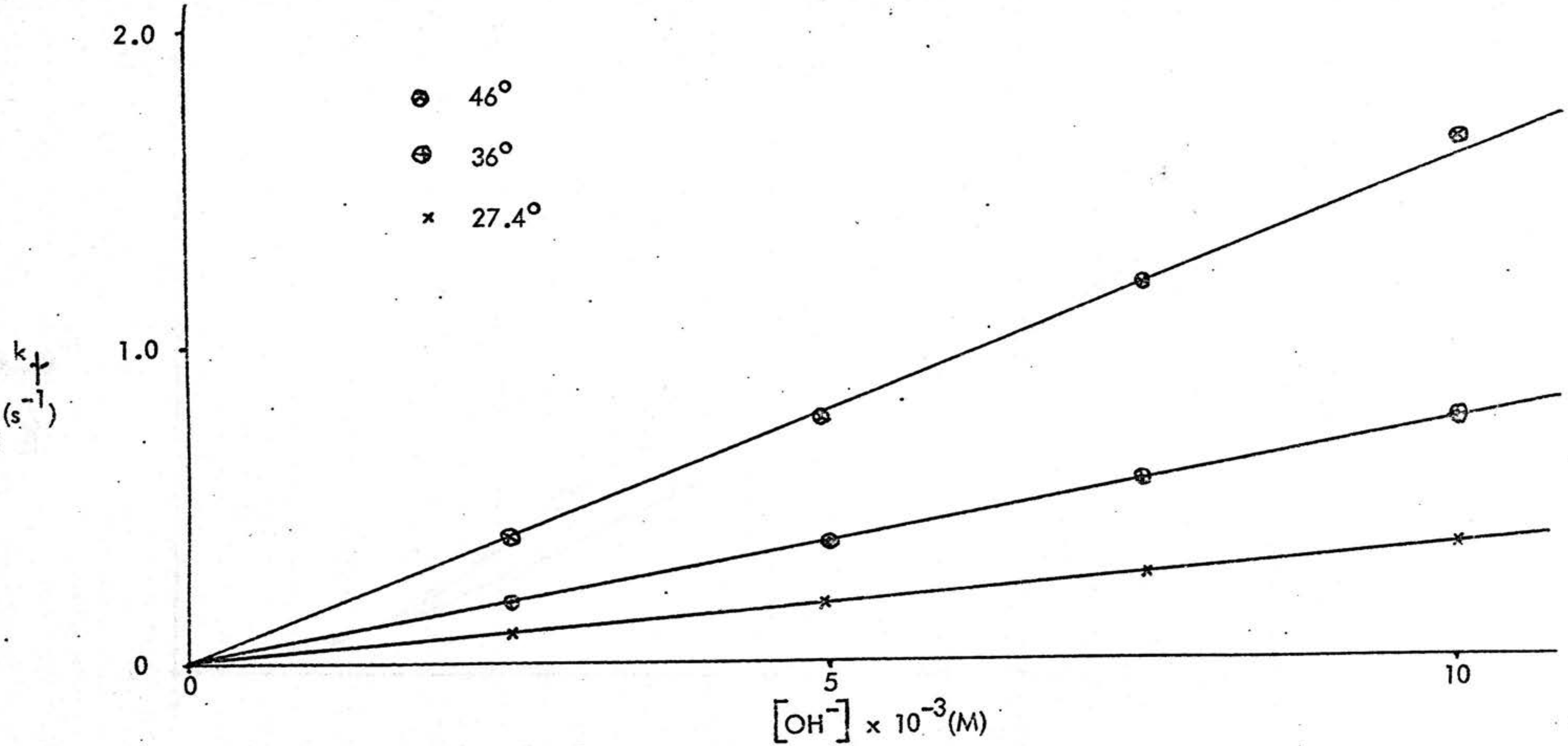


Fig.3.4.2 Plot of k_{ψ} against $[OH^-]$ according to equation (3.29) for the reaction of 1,3,5-trinitro-2,6-dimethylnaphthalene (162) with sodium hydroxide in DMSO/H_2O(4:1) at 3 temperatures.

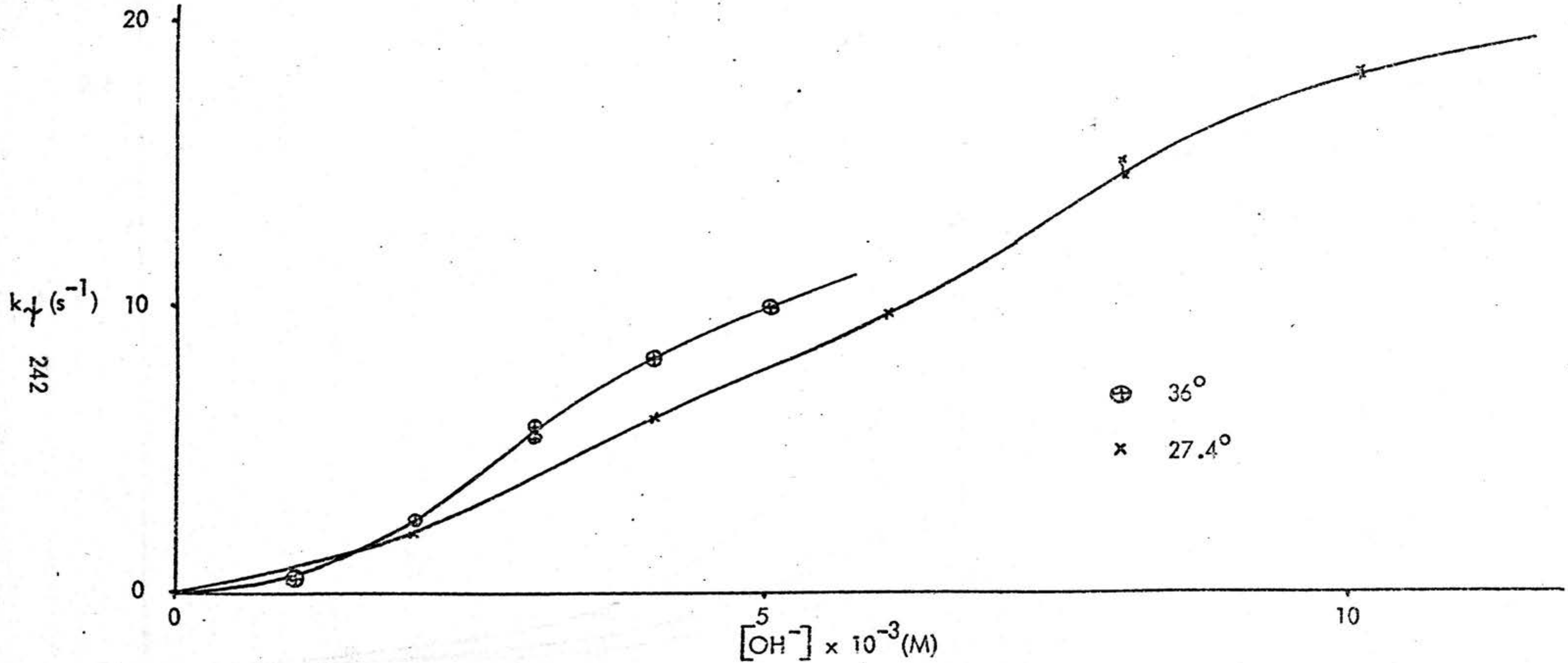


Fig.3.4.3 Plot of k_{ψ} against $[OH^-]$ according to equation (3.29) for the reaction of 1,3,5-trinitro-2.6-dimethylnaphthalene (162) with sodium hydroxide in DMSO/H_2O(9:1) at 2 temperatures.

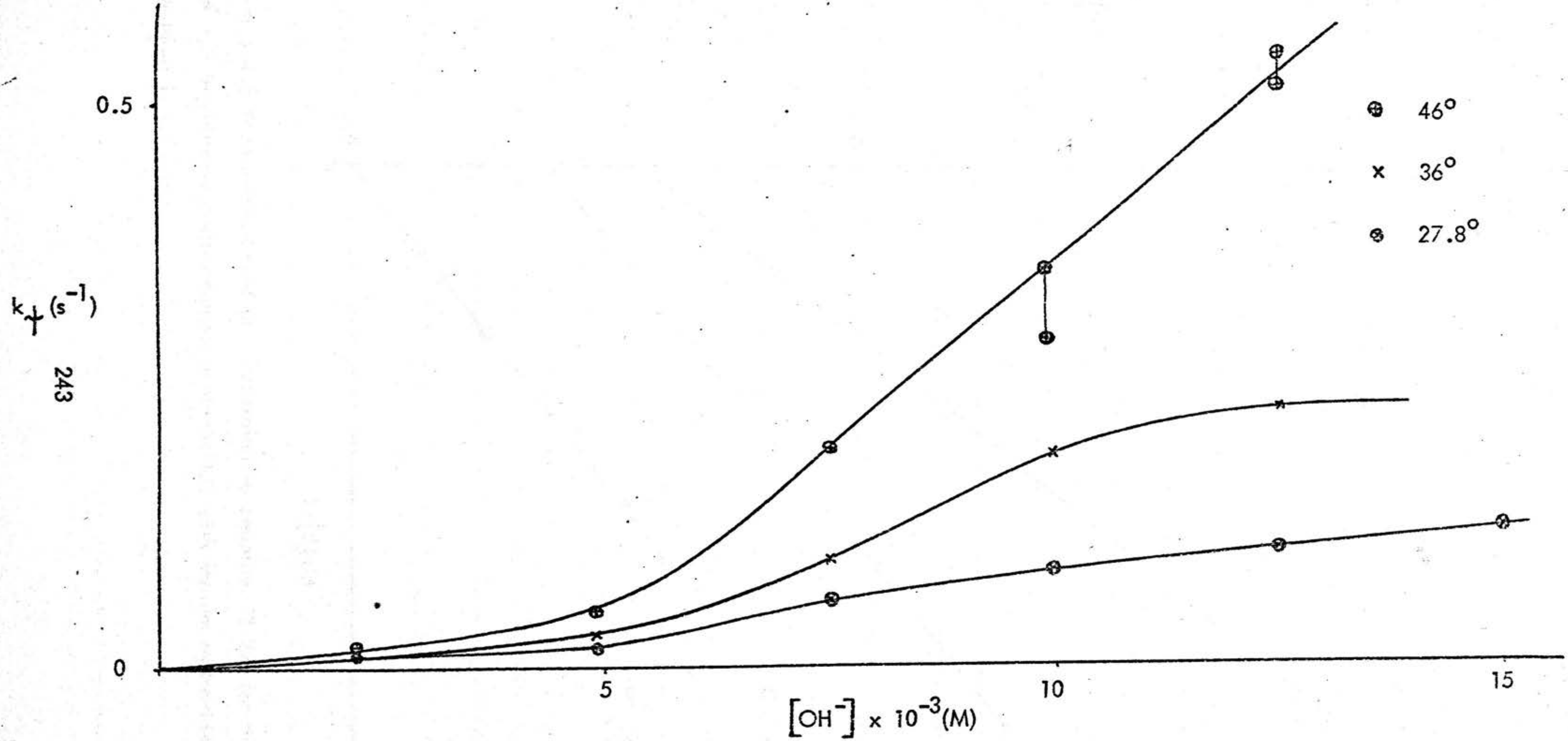


Fig.3.4.4 Plot of $k_{\dagger}$ against $[OH^-]$ according to equation (3.29) for the reaction of 1,3,5-trinitro-2,6-dimethylnaphthalene (162) with sodium hydroxide in DMSO/H_2O(7:3) at 3 temperatures.

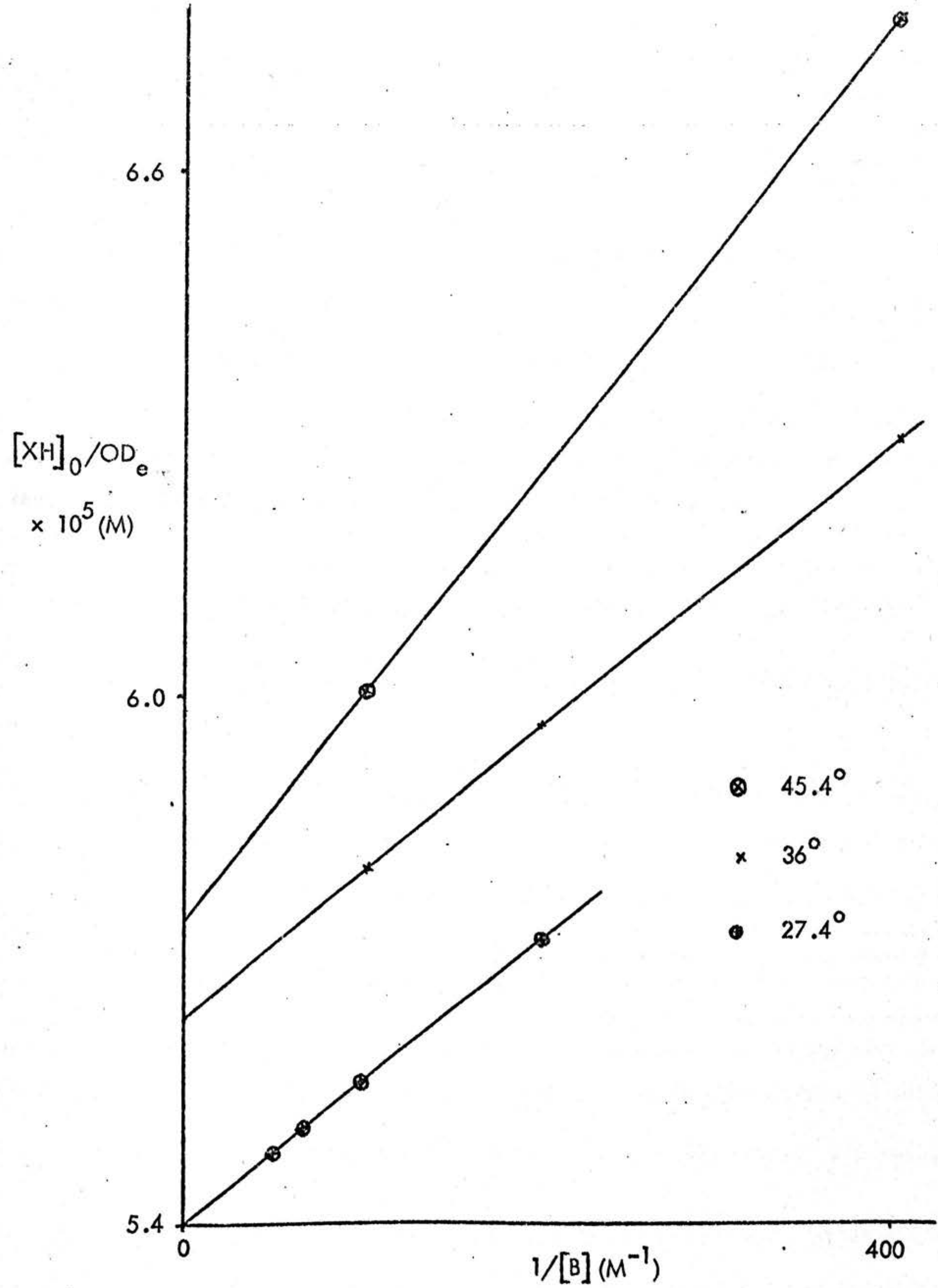


Fig.3.4.5 Benesi-Hildebrand plot according to equation (3.29) for the reaction of 1,3,5-trinitro-2,6-dimethylnaphthalene(162) with sodium hydroxide in aqueous DMSO(1:4).

activation is $-16.4\mathrm{Jmol^{-1}K^{-1}}$. The thermodynamic plot according to equation (3.6) is shown in fig.3.4.6.

From the relationship $\Delta G^0 = -RT\ln K$, ΔG^0 for the above reaction is approximately $11.2\mathrm{kJmol^{-1}}$.

Using equation (3.31) a plot of ln K against 1/T should give a straight line with slope, $-\Delta H/R$.

$$\ln K = -\Delta H/RT + \text{constant} \qquad (3.31)$$

Hence $\Delta H \simeq -34\mathrm{kJmol^{-1}}$($\Delta H$ may be as high as $-15\mathrm{kJmol^{-1}}$). From the relationship $\Delta S = (\Delta H - \Delta G)/T$, the total entropy change for the reaction, $\Delta S \simeq (-53) \rightarrow -77\mathrm{Jmol^{-1}K^{-1}}$.

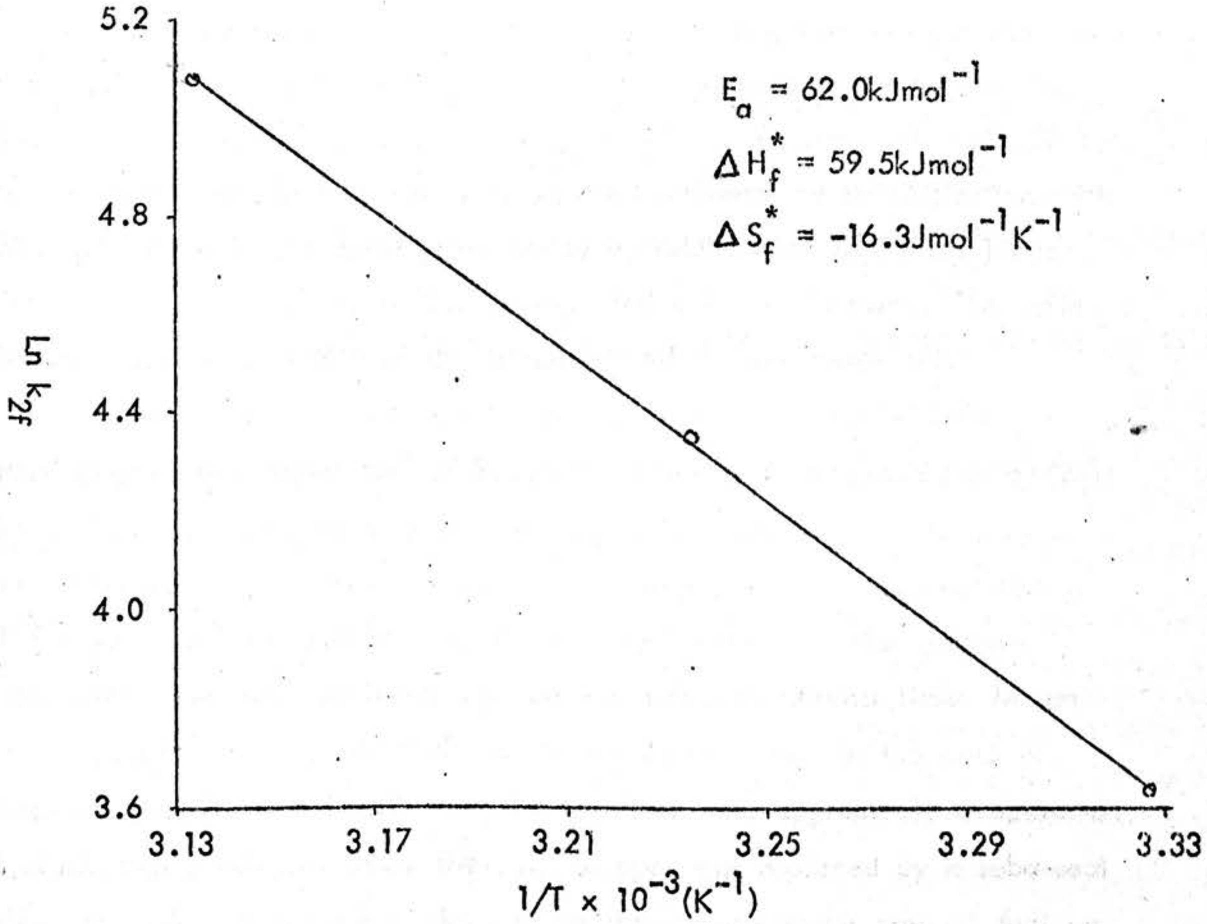


Fig.3.4.6 Arrhenius plot according to equation (3.6) for the reaction of 1,3,5-trinitro-2,6-dimethylnaphthalene(162) with sodium hydroxide in DMSO/ H_2O(4:1).

Experimental Section

The DMSO used was Hopkin and Williams laboratory reagent grade and the methanol used was BDH analar reagent. Diethylamine and triethylamine were distilled using a Fischer Spaltrohr 60 theoretical plate column; middle fractions selected. Triethylammonium chloride was made by addition of concentrated hydrochloric acid to stirred triethylamine at 0°C. The white crystals that appeared on complete neutralisation were filtered off and twice recrystallised from absolute ethanol before drying in vacuo.

Nitroaromatic compounds were synthesised as given in Appendix 1.1. Deuteriation of the 1-Me- of 2,4,8-trinitro-1,5-dimethylnaphthalene was accomplished by treating 0.23g of it in 10cm^3 DMSO with 5M NaOD(0.16cm^3) for 5 minutes(away from strong light sources) followed by neutralisation with 6M DCl(0.25cm^3). The solid precipitated by addition of D_2O(5cm^3) was filtered off and the above procedure repeated a further 6 times. The solid obtained contained ~94% of the trideuteriated 1-Me- compound.

Slow kinetic runs were performed on a Perkin Elmer SP 1700 spectrophotometer. Three cm^3 of 2,4,8-trinitro-1,5-dimethylnaphthalene(93) (5 x 10^{-5}M) in DMSO in a quartz optical cell(in thermostat jacket) were treated with the neat amine from a micro-syringe, the cell capped with a PTFE stopper and thoroughly shaken before replacement in the spectrophotometer. The increase in absorbance was followed against time. Mixed solvent solutions were treated similar to the above case. In the case of compound (93) in neat DMSO solution to check that appreciable evaporation of diethylamine did not occur the PTFE stopper was replaced by a suba-seal rubber cap. Injection through the cap by the micro-syringe ensured that no base escaped from the cell. Identical results were obtained for each method.

Reversal of the reaction involving compound (93) and amine base was achieved by removing 1 cm^3 of the DMSO solution of compound (94) from the cell and adding 1 cm^3 of methanol(thermostatted). The cell was rapidly shaken and replaced in the spectrophotometer with minimum exposure to light. The decrease in optical density was then followed against time.

Kinetics of the reaction of compound (93) with triethylamine in DMSO containing 100 equivalents of triethylammonium chloride were performed by adding neat amine from a micro-syringe to 3 cm^3 of nitroaromatic solution (5.116×10^{-5}M) which contained 70.1 mg $Et_3NH^+ Cl^-/100cm^3$ stock solution.

Reversal of the reaction for the formation of compound (94) was achieved by adding $0.5cm^3$ of triethylammonium chloride (0.0307M) in DMSO to $2.5cm^3$ of compound (93) (5.116×10^{-5}M) and triethylamine (20 or 40 equivalents).

Reaction of sodium hydroxide with compound (93) in excess was followed using a Perkin Elmer SP 1700 spectrophotometer. Three cm^3 of compound (93) (2.558×10^{-4}M) in DMSO/H_2O(9:1) were treated with 0.1M aqueous NaOH.

Fast reaction of sodium hydroxide (50-200 equivalents) with compound (93) was observed by 1:1 mixing of base and 5.116×10^{-5}M solutions of compound (93) in an Applied Photophysics stopped-flow apparatus(λ = 525nm). The trace was displayed on a Telequipment DM64 storage oscilloscope and then photographed using Polaroid film.

Alkoxides were reacted with solutions of compound (93) (5×10^{-5}M) in the corresponding alcohols. Kinetic measurements were made on the stopped-flow apparatus(λ = 530-550nm).

2,4,6,8-tetranitro-1,5-dimethylnaphthalene(98) (2×10^{-5}M) in methanol was reacted with 0.01M sodium methoxide(λ = 570nm); and compound (98) (1.83×10^{-4}M) with 0.002M NaOH in DMSO/H_2O(9:1) (λ = 540nm).

Compound (98) (6×10^{-5}M) in DMSO/H_2O(3:2) was reacted with freshly made aqueous DMSO solutions of sodium sulphite(λ = 510nm).

1,4,5,7-Tetranitro-2,3-dimethylnaphthalene(161) (5×10^{-5}M) was reacted with aqueous DMSO solutions of sodium sulphite(λ = 525nm). The solutions were freshly made and kept under an atmosphere of nitrogen before loading into the stock syringes of the stopped-flow apparatus.

1,3,5-trinitro-2,6-dimethylnaphthalene(162) (5.0-5.5×10^{-5}M) in DMSO/H_2O(7:3; 4:1 and 9:1) was reacted with sodium hydroxide(0.005-0.02M) in aqueous DMSO.

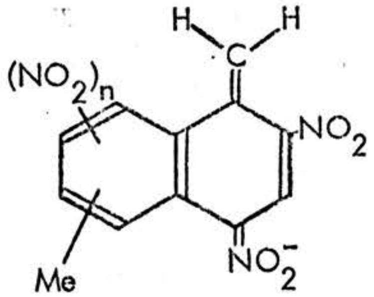
CHAPTER FOUR

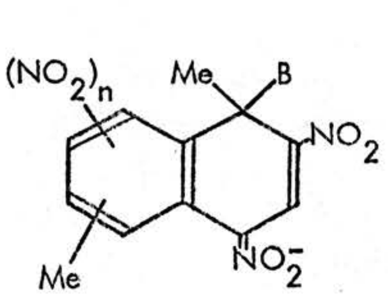
DISCUSSION OF SPECTROSCOPIC AND KINETIC DATA

4.1 Summary of spectroscopic results

Table 4.1.1 shows the product types obtained for the reaction of base with polynitrodimethylnaphthalenes as evidenced by PMR spectroscopy. These products result from addition at the C-1 position and proton abstraction or from addition at the C-3,4 or 8 positions. In the case of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene subsequent intramolecular reaction occurs to give yet another product.

n = 1 or 2





However, it is clear that polynitro-α- dimethylnaphthalenes differ from polynitro-β-dimethylnaphthalenes in the types of product given.

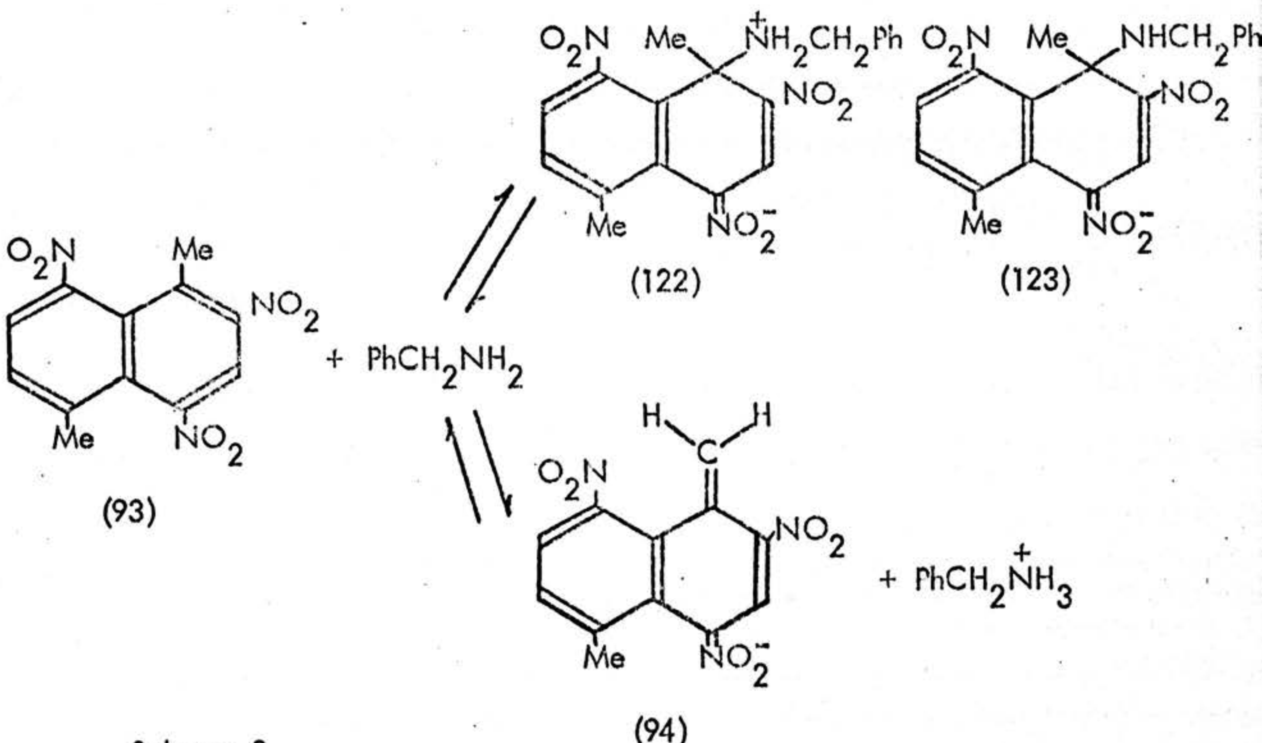
Polynitro-1,5- and 1,8-dimethylnaphthalenes

Tri- and tetra-nitro-1,5- and 1,8-dimethylnaphthalenes mainly undergo proton abstraction from one α-methyl group on reaction with one equivalent of the strong bases hydroxide or methoxide ion($pK_a \sim 16$) in DMSO[132]. Excess of methoxide ion gives the proton abstracted C-3 addition complex with the trinitro-isomers only. Reaction of excess of methoxide ion with 2,4,6-TNT has also been noted to give a proton abstacted addition complex.[17]

The effect of an additional nitro group on going from tri- to tetranitro-1,5-dimethylnaphthalene is that the 'benzyl-type' anion(100) is not stable and undergoes intramolecular reaction to form the bridged compound (101).

Sulphite ion, being a weak base, does not proton abstract from α-methyl groups, but instead adds at the C-3 position for 2,4,6,8-tetranitro-1,5- and 2,4,5-trinitro-1,8-dimethylnaphthalenes.

The aliphatic amines diethylamine($pK_a = 11.09$) and triethylamine ($pK_a = 10.78$), even in large excess, only abstract a proton from one of the α-methyl groups. However, the weaker bases benzylamine($pK_a = 9.33$) and hydrazine hydrate($pK_a = 8.23$) add at the C-1 position and this is paralleled by the slower proton abstraction reaction which results in the C-1 addition complex being converted to the more thermodynamically stable abstraction product via the equilibrium concentration of unreacted polynitroaromatic (e.g. See Scheme 2).



Scheme 2

The tendency of aliphatic amines to proton abstract rather than form addition complexes on reaction with nitroaromatic compounds has been noted previously.[103,181]

Polynitro-2,3-dimethylnaphthalenes

1,5,7-trinitro- and 1,4,5,7-tetranitro-2,3-dimethylnaphthalenes only give well defined products in the case of reaction with sulphite ion in aqueous DMSO. The position of addition is C-8 which may be constrasted with the positions of attack by alkoxide ion(a stronger base) on 1,4,5,7-tetranitronaphthalene, which is at C-3[26].

Proton abstraction is not apparently observed with alkoxides, where addition decomposition products are formed.

Polynitro-2,6-dimethylnaphthalenes

1,3,5-trinitro-; 1,4,5-trinitro-trinitro-; 1,3,5,7-tetranitro- and 1,3,5,8-tetranitro-2,6-dimethylnaphthalenes react with sulphite ion in aqueous DMSO to give stable C-4 addition products, except the 1,4,5-trinitro-compound which adds at C-3. The position of addition of sulphite ion in this latter compound is the same for alkoxide addition to 1,4,5-trinitronaphthalene[26].

The reaction of alkoxide ions with tri- and tetranitro-2,6-dimethylnaphthalenes produces unstable addition complexes and free radicals. The reaction of aliphatic amines with these nitroaromatic compounds also seems to produce unstable addition complexes and in some cases free radicals.

Table 4.1.1 Products of reaction of polynitrodimethylnaphthalenes with base in DMSO as indicated by PMR.

Base / Nitroaromatic	OH^-	OMe^-	Et_2NH	Et_3N	HMDS	$PhCH_2NH_2$	$NH_2NH_2 \cdot H_2O$	SO_3^{2-}
2,4,8-TN- 1,5-DMN	1 eq HABS^{n} 1 eq HABS^{d} C-3 adduct	1 eq HABS^{n} 1 eq HABS^{d} C-3 adduct	HABS^{n} only	HABS^{n} only	HABS^{n} only	C-1 add^{n} & HABS^{n}	C-1 add^{n} & HABS^{n}	C-3 & C-6 or 7 add^{n}
2,4,6,8-TETN- 1,5-DMN	HABS^{n} & intramolec rearrang†	HABS^{n} & intramolec rearrang†	HABS^{n} & intramolec rearrang†	HABS^{n} & intramolec rearrang†	C-1 add^{n} & HABS^{n}	C-1 add^{n} MAINLY	C-1 add^{n} & HABS^{n} & intramolec rearrang†	C-3 add^{n}
2,4,5-TN- 1,8-DMN	1 eq HABS^{n} & C-1 add^{n} 1 eq HABS^{d} C-3 adduct	1 eq HABS^{n} & C-1 add^{n} 1 eq HABS^{d} C-3 adduct	HABS^{n} only	HABS^{n} only	HABS^{n} only	HABS^{n} & C-1 add^{n}	C-1 add^{n}	C-3 add^{n}
2,4,5,7-TETN- 1,8-DMN	HABS^{n} only	HABS^{n} & C-1 add^{n}	HABS^{n} only	HABS^{n} only	HABS^{n} only	C-1 add^{n} & HABS^{n}	1 eq HABS^{n} 5 eq C-1 add^{n}	Unknown product
1,5,7-TN- 2,3-DMN	Unknown product	C-8 add^{n} ?	Unknown product	-	-	-	-	C-8 add^{n}
1,4,5,7-TETN- 2,3-DMN	Radicals ?	C-6 & C-8 add^{n} *	Radicals ?	Radicals ?	Radicals ?	Radicals ?	-	C-8 add^{n}

Table 4.1.1(contd)

Base Nitroaromatic	OH^-	OMe^-	Et_2NH	Et_3N	HMDS	$PhCH_2NH_2$	$NH_2NH_2 \cdot H_2O$	SO_3^{2-}
1,3,5-TN-2,6-DMN	C-4 add^n & unknown product	C-4 add^n & radicals	C-4 add^n ?	-	-	Unknown product	Unknown product	C-4 add^n
1,4,5-TN-2,6-DMN	Unknown product	C-3 add^n	Unknown product	-	-	Unknown product	Unknown product	C-3 add^n
1,3,5,7-TETN-2,6-DMN	C-4 add^n & unknown product	C-4 add^n & radicals ?	Unknown product	-	Unknown product	Unknown product	-	C-4 add^n
1,3,5,8-TETN-2,6-DMN	Unknown product	Unknown product	Unknown product	-	-	Radicals ?	C-2 or C-6 add^n ?	C-4 & C-7 add^n
1,4,5,8-TETN-2,6-DMN	Unknown product	C-3 add^n or H ABS^n ?	⊛ Unknown product	-	-	⊛ Unknown product	Unknown product	Unknown product

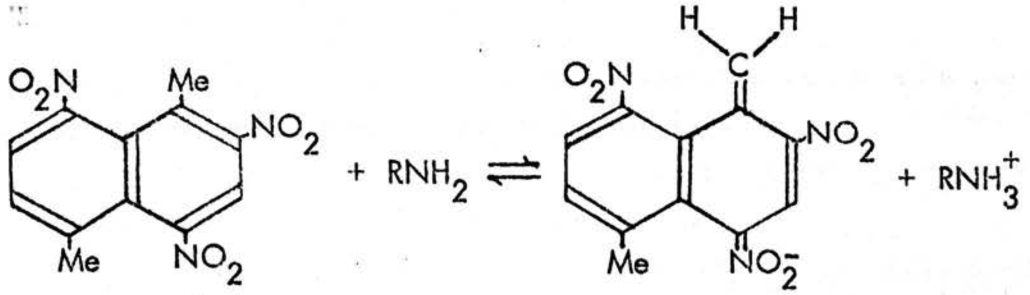
* ref. 109. ⊛ in DMA solvent. TN = trinitro-; TETN- = tetranitro-; DMN = dimethylnaphthalene; H ABS^n = proton abstraction; add^n = addition and intramolec rearrang† = intramolecular rearrangement.

4.2-5 Discussion of kinetic results

4.2.1 Reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine and triethylamine

The results presented in Chapter 3 show that the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine and triethylamine in different solvent mixtures results in formation of the 'benzyl-type' anion (94) as shown below.

$$XH \quad + \quad B \rightleftharpoons X^- \quad + \quad BH^+$$



(93) (94)

Kinetics for this reaction have been studied. The rate constants for the forward process for the reaction at 52°C are tabulated below in Table 4.2.1.

Table 4.2.1 Forward rate constants for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine and triethylamine in DMSO and methanol at 52°C.

Solvent / Base	Et_2NH	Et_3N	
DMSO	1.70	0.279	$k_{2f}/M^{-1}s^{-1}$
Methanol	0.038*	0.0158-0.0225*	

* by extrapolation

In neat DMSO the reaction of diethylamine proceeds 7 times faster than triethylamine with compound (93) at 52°C. Diethylamine is a stronger base than triethylamine as indicated by the respective pK_a values of 11.09

and 10.78, and this difference is resposible for the change in rates. The difference in rates for the reactions in DMSO and methanol solvent is considered in thermodynamic terms later.

Virtually no literature exists on the subject of proton abstraction from alkylated polynitroaromatics by amines. However, abstraction from the alkylamino group of substituted polynitroaromatics and their zwitterions has been observed[103,183]. The only related comparisons that may be made are the reaction of methoxide ion in methanol with 2,4,6-trinitrotoluene(TNT) ($k_{2f} = 13.3 M^{-1} s^{-1}$ at 25°C); and the reaction of methoxide ion with compound (93) in methanol ($k_{2f} \sim 0.6 M^{-1} s^{-1}$ at 27°C).

It is possible that in these systems the amine base could react with the methanol solvent to give the methoxide ion, according to:-

$$MeOH + B \rightleftharpoons MeO^- + BH^+$$

If this reaction occured, then it would be expected that the equilibrium constant, K, for the reaction

$$XH + B \rightleftharpoons X^- + BH^+$$

would vary as the base concentration $[B]$ changed. The equilibrium constants for the reactions at various base concentrations and temperatures were measured and these are listed in Table 4.1.2. It can be seen from this table that the values of K are reasonably constant for each temperature suggesting that the reaction of base with methanol was not significant.

Equilibrium constant values calculated according to equation (4.1) are tabulated in Table 4.2.2.

$$K = [X^-][BH^+]/[XH][B] \qquad \text{equation (4.1)}$$

Table 4.2.2 Equilibrium constants for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in various DMSO/methanol solvent.

Temp.	Solvent	Base equivalents	10^2K
60.25°	DMSO	50	9.16
		100	9.18
		200	9.13
52.0°	DMSO/MeOH(9:1)	100	4.10
		200	3.53
		600	2.41
		1200	1.66
51.5°	DMSO/MeOH(2:1)	75	0.326
		150	0.355
		400	0.304
		800	0.347
32.0°	DMSO/MeOH(1:1)	200	0.432
		300	0.377
		400	0.503
		600	0.436
		1000	0.429

The results given in Table 4.1.2 show that the equilibrium constant, K, decreases with increasing methanol content for mixed solvents. This results from a decrease in the forward and an increase in the reverse rate constants (See Table 4.2.3 below). This behaviour is frequently observed for reactions involving Meisenheimer complexes[161].

The increase in the second order reverse rate constant, k_{2r}, is greater than the decrease in k_{2f} for the triethylamine reaction on increasing the methanol concentration relative to DMSO(See Table 4.2.3). This behaviour is best explained in thermodynamic terms(See later).

Table 4.2.3 Rate and equilibrium constants for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine and triethylamine in DMSO and DMSO/MeOH(2:1).

Temp. = 41°C

Solvent/Base	Et_2NH			Et_3N		
	$k_{2f}/M^{-1}s^{-1}$	$k_{2r}/M^{-1}s^{-1}$	K	$k_{2f}/M^{-1}s^{-1}$	$k_{2r}/M^{-1}s^{-1}$	K
DMSO	0.97	1.72	0.577	0.133	1.13	0.118
DMSO/MeOH(2:1)	0.21	2.35	0.092	0.070	6.84	0.009

The molar decadic absorbtivities(extinction coefficients) of the 'benzyl-type' anion (94) tend to decrease with increase in temperature(See Table 4.2.4). A similar effect has been noted by Foster for charge-transfer complexes[203].

Table 4.2.4 Extinction coefficients for the 'benzyl-type' anion (94) in DMSO produced by the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine and triethylamine.

	$\varepsilon\ M^{-1}cm^{-1}$	
Temp./Base	Et_2NH	Et_3N
30°	19600	19900
41°	19300	19400
51.5°	19000	19000

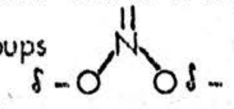
Part of Table 3.1.4 is reproduced below in Table 4.2.5 to facilitate discussion of the thermodynamic parameters for the reaction of compound (93) with amines in DMSO and mixed solvent.

Table 4.2.5 Thermodynamic parameters for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with diethylamine and triethylamine in DMSO and DMSO/MeOH(2:1).

Base	% DMSO	ΔH_f^*	ΔH_r^* $kJmol^{-1}$	ΔH	ΔS_f^*	ΔS_r^* $Jmol^{-1}K^{-1}$	ΔS
Et_3N	100	45.9	56.4	-10.6	-115	-63	-52
	67	43.7	81.0	-37.2	-129	28	-157
Et_2NH	100	34.9	48.4	-13.5	-135	-87	-48
	67	45.6	76.0	-30.4	-113	3.3	-117

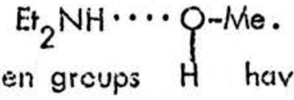
From the data presented in Table 4.2.5 two postulates may be made:-

(1) That there is greater solvation of the products and transition state in DMSO/MeOH mixed solvent system than in DMSO solvent. This is likely to arise because of hydrogen bonding between the nitro groups



and the hydrogen atom of R-OH molecules. This effect has been previously noted[204-5].

(2) That triethylamine molecules are less solvated than diethylamine molecules in DMSO/MeOH solvent system. In the case of diethylamine, hydrogen bonds between the amine hydrogen and alcohol oxygen are possible i.e.



$Et_2NH\cdots\cdots\underset{\displaystyle H}{\underset{|}{O}}\text{-}Me$. Hydrogen bonds between amine proton and nitro oxygen groups have previously been reported[53].

Each thermodynamic parameter is considered in detail below. All mixed solvent values refer to the DMSO/MeOH(2:1) mixtures.

Overall enthalpy change, ΔH

It can be seen from Table 4.2.5 that the overall enthalpy change for the reactions is more negative in DMSO/MeOH systems than in pure DMSO solvent systems. For example, for the reaction of diethylamine ΔH is -37.2 $kJmol^{-1}$ in DMSO/MeOH and -10.6 in pure DMSO. The difference is probably due to assumption (1), in that more energy is released when bonds are formed involving solvated products in the DMSO/MeOH system compared to non-solvated products in DMSO.

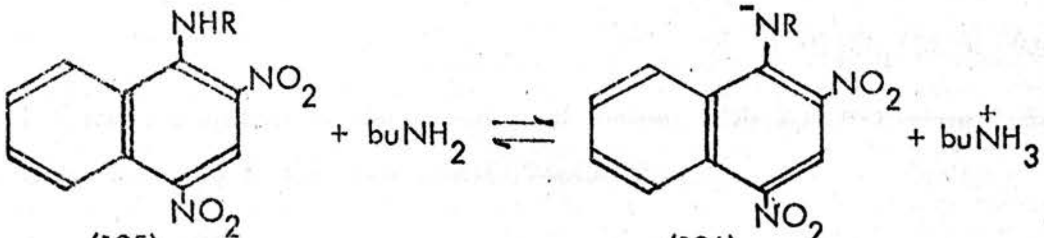
Overall entropy change, ΔS

It can be seen from Table 4.2.5 that the overall entropy change for the reaction is much more negative in DMSO/MeOH than for the reaction in DMSO. For example in the reaction with triethylamine the value in the former case is -157 Jmol^{-1}K^{-1} whereas in the latter case it is -52 Jmol^{-1}K^{-1}. This difference may be explained in terms of effect (1) where a more ordered system results(hence more negative ΔS) for the mixed solvent system due to hydrogen bonding between product and methanol solvent molecules.

In DMSO/MeOH the overall entropy change for the triethylamine reaction is more negative than for the diethylamine reaction. The values for ΔS are -157 and -117 Jmol^{-1}K^{-1} respectively for the above mentioned cases. This difference may be explained in terms of effect (2) where the reactants would be less solvated in the case of triethylamine which does not possess an amino proton and hence the overall decrease in entropy on forming products would be larger than for the triethylamine reaction.

An entropy diagram is shown in fig.4.2.1, where the relative levels of the reactants are arbitrary and show only the postulated qualitative differences.

By comparison ΔS for the proton abstraction from n-butylamino-2,4-dinitronaphthalene(195) by n-butylamine in DMSO is -126 Jmol^{-1}K^{-1} which is in the more negative range of values encountered for the reaction of amines with compound (93) and certainly more negative(by ~ 76 Jmol^{-1}K^{-1}) than the ΔS values in pure DMSO solvent[103]. These values are in reasonable agreement and demonstrate that both processes are probably similar in nature and involve proton abstraction.



(195) (196)

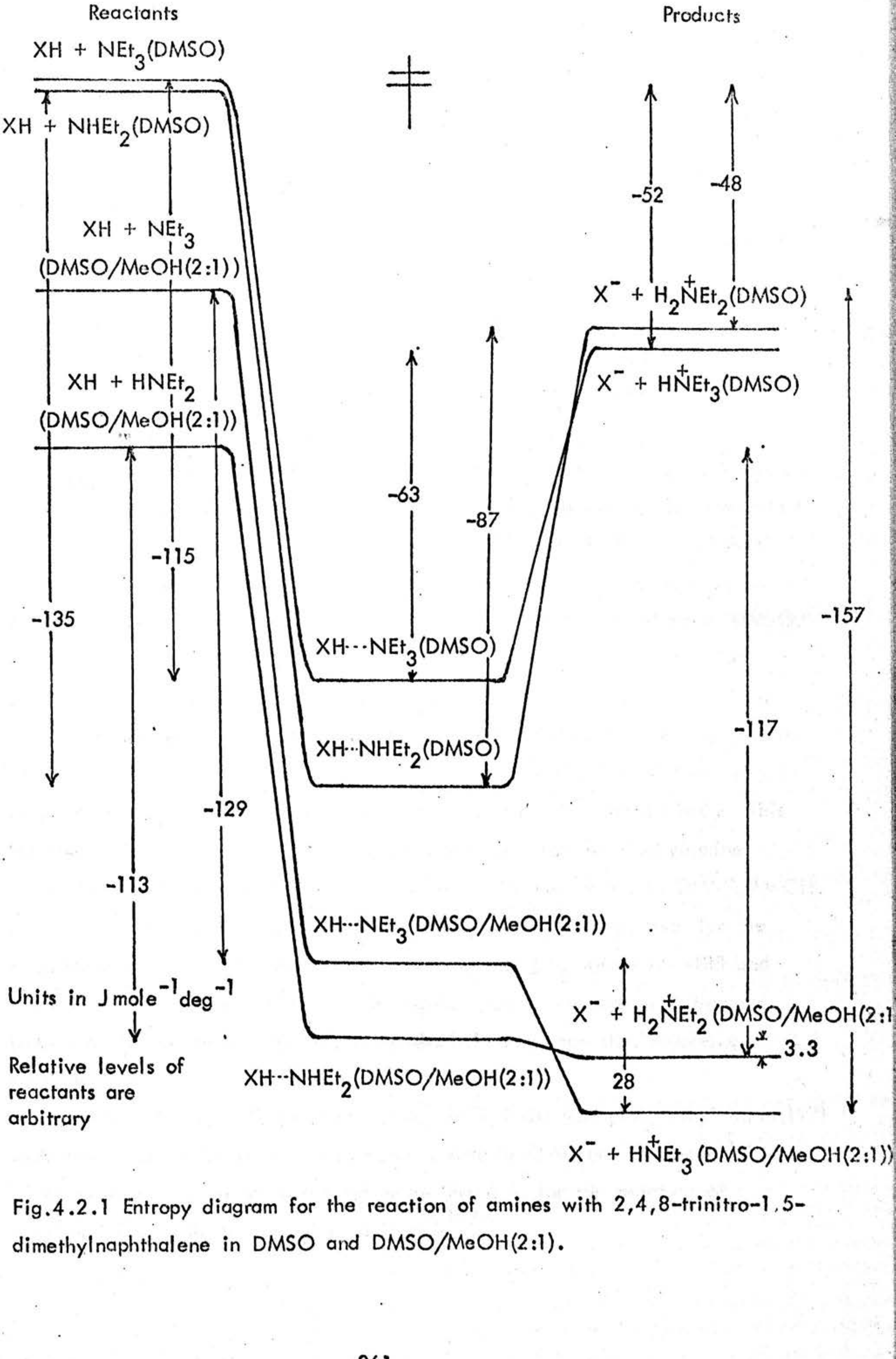


Fig.4.2.1 Entropy diagram for the reaction of amines with 2,4,8-trinitro-1,5-dimethylnaphthalene in DMSO and DMSO/MeOH(2:1).

Entropy of activation for the forward reaction, ΔS_f^*

The entropy of activation for the forward reaction is large and negative for both reactions due to the more ordered state produced on forming the solvated transition complex.

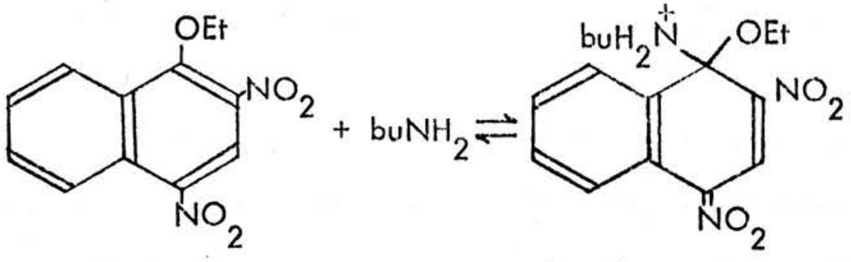
Although the ΔS_f^* values for the two reactions in the two solvents are not greatly different, the difference could be explained as follows.

For the triethylamine reaction ΔS_f^* is more negative in DMSO/MeOH than DMSO solvent, as shown by the respective values of -129 and -115 $Jmol^{-1}K^{-1}$. This could be due to effect (1) where the solvation of the transition state is greater in DMSO/MeOH mixed solvent.

However, for the diethylamine reaction ΔS_f^* is more negative in DMSO than is DMSO/MeOH solvent, as shown by the ΔS_f^* values of -135 and -113 $Jmol^{-1}K^{-1}$ respectively. Here it would appear that effect (2) (i.e. weaker solvation of diethylamine in DMSO than in DMSO/MeOH) compensates for effect (1). This could be due to the lower entropy of the reactants in DMSO/MeOH compensating for the increased solvation on forming the transition state in this medium relative to that in DMSO.

The entropy of activation for the forward reaction is more negative in DMSO/MeOH for the triethylamine reaction than for the diethylamine reaction as shown by the ΔS_f^* values of -129 and -113 $Jmol^{-1}K^{-1}$ respectively. This may be explained by effect (2) where the reactants for the diethylamine system have a lower entropy than for the triethylamine system in DMSO/MeOH. However, ΔS_f^* is more negative for the diethylamine reaction than for the triethylamine reaction in DMSO, as shown by the ΔS_f^* values of -135 and -115 $Jmol^{-1}K^{-1}$ respectively. This is possibly due to stronger solvation by DMSO of the transition state involving diethylamine than that involving triethylamine.

Interestingly, ΔS_f^* for the reaction of 2,4-dinitronaphthylethyl ether(197) with n-butylamine in DMSO to form the zwitterion(198) is -134 $Jmol^{-1}K^{-1}$ which is almost identical to the value for the ΔS_f^* for the reaction of compound (93) with diethylamine in DMSO[103].



(197) (198)

Entropy of activation for the reverse reaction, ΔS_r^*

The entropy of activation for the reverse reaction, ΔS_r^*, is more positive for the reaction of both amines in DMSO/MeOH than in DMSO, as shown by the ΔS_r^* values of 28(Et_3N) and 3.3(Et_2NH); and -63(Et_3N) and -87(Et_2NH) $Jmol^{-1}K^{-1}$ for triethylamine and diethylamine in each solvent system respectively. This is probably due to effect (1), where there would be a larger increase in entropy when solvated molecules are released on forming the transition transition state in DMSO/MeOH than in DMSO solvent.

Summary of thermodynamic parameters

Overall the thermodynamic parameters listed in Table 4.2.5 are typical of those observed for proton abstraction involving two neutral molecules.

For the reaction of 2,4-dinitronaphthylethyl ether with n-butylamine in DMSO to form the zwitterion (198), values for ΔS_f^* -134$Jmol^{-1}K^{-1}$ and for ΔH_f^* of 24.3$kJmol^{-1}$ have been obtained[103]. Although separate free ions are not formed these thermodynamic parameters are very similar to those for the reaction of compound (93) with diethylamine in DMSO to give 'benzyl-type' anion (94) and conjugate acid($Et_2NH_2^+$) viz. $\Delta S_f^* = -135Jmol^{-1}K^{-1}$ and $\Delta H_f^* = 34.9kJmol^{-1}$.

For the deprotonation of n-butylamino-2,4-dinitronaphthalene by n-butylamine in DMSO, values for ΔS^0 of -126$Jmol^{-1}K^{-1}$ and for ΔH^0 of -38.5$kJmol^{-1}$ have been found. These values are not too dissimilar from those for the reaction of compound (93) with triethylamine or diethylamine in DMSO/MeOH(2:1) solvent. The values of ΔH and ΔS are -37.2$kJmol^{-1}$ and -157 $Jmol^{-1}K^{-1}$ for the triethylamine reaction and -30.4$kJmol^{-1}$ and -117$Jmol^{-1}K^{-1}$

respectively for the diethylamine reaction in DMSO/MeOH(2:1) solvent.

The decrease in the forward rate constant, k_{2f}, on increasing the methanol content of the solvent for the reaction of triethylamine with compound (93) appears to be due to the decrease in ΔS_f^*. The small decrease in ΔH_f^* for this reaction on increasing the methanol content would tend to increase k_{2f}, so the effect of ΔS_f^* is dominant. On the other hand for the reaction with diethylamine, the decrease of k_{2f} with increasing methanol content appears to be due to an increase in ΔH_f^* outweighing a decrease in ΔS_f^*.

The increase in the reverse rate constant, k_{2r}, with increasing methanol content of the solvent for the reaction of triethylamine or diethylamine is due to the large increase in ΔS_r^* outweighing an increase in ΔH_r^*.

Effect of conjugate acid on reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO

The forward rate constant for reaction of compound (93) with triethylamine is virtually unchanged when triethylammonium chloride is added to the reaction mixture(See Table 4.2.6).

The value of k_{2f} obtained from the product of k_{2r} and K is in agreement with the value of k_{2f} determined directly.

The values of k_{2r} and K for the system containing excess triethylammonium chloride, however, differ from those values obtained for the pure DMSO system. The enhanced value of the equilibrium constant, K and reduced value for k_{2r} may be accounted for by stabilisation of the 'benzyl-type' anion (94) by association with triethylammonium cations. Indeed, stabilisation of the methoxide addition complexes of substituted dinitroanisoles by ion association has been noted to be due mainly to apparent decrease in the rate constant for the reverse reaction[164].

Table 4.2.6 Rate and equilibrium constants for the reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with triethylamine in DMSO, with and without triethylammonium chloride.

Temp. = 41°C	$k_{2f}/M^{-1}s^{-1}$	$k_{2r}/M^{-1}s^{-1}$	K
DMSO	0.133	1.1	0.12
DMSO/$Et_3NH^+Cl^-$	0.131(0.127*)	0.076	1.67

* from product of k_{2r} and K.

Effect of deuteration of 1-Me group of 2,4,8-trinitro-1,5-dimethylnaphthalene(93)

Proton abstraction by triethylamine from the trideuterated form of compound (93) showed the existence of a small kinetic isotope effect. The ratio of k_{2f} for the fully protonated and part deuterated compounds is 1.37 at 41°C. However, values as large as 7 or 8 have been observed for proton abstraction by alkoxide from TNT-d_3.[125, 126] It must be stated that doubts existed as to the purity of the trideuterated compound used due to the unavoidable inclusion of the decomposition products of compound (94).

4.2.2 Reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with benzylamine

The kinetics of the reaction of less than one equivalent and excess of benzylamine with compound (93) in DMSO were studied, but the data obtained were difficult to interpret due to the occurrence of two simultaneous reactions.

4.2.3 Reaction of 2,4,8-trinitro-1,5-dimethylnaphthalene with hydroxide and alkoxide ions

The reaction of less than one equivalent(0.5-0.9) of hydroxide ion with compound (93) in DMSO/H_2O(9:1) proceeded via at least two different processes:-

(1) This is a fast addition step accounting for 15-20% of the nitroaromatic(If the assumption that $\varepsilon_{ADD^n} = \varepsilon_{(94)}$ is valid).

(2) This step would appear to be due to proton abstraction with an approximate second order forward rate constant, k_{2f} in the range $0.07-0.14M^{-1}s^{-1}$ at 41°C.

The reaction of excess(50-200 equivalents) sodium hydroxide with compound (93) in DMSO/H_2O(9:1) indicated that probably only one step occurred to produce an unstable species as shown by stopped-flow spectrophotometry. The second order forward rate constant,k_{2f} is approximately 884$M^{-1}s^{-1}$ at 26.3°C and although the spectrum of products present at the infinity position(i.e. complete reaction) shows a broad absorbtion maximum peaking at 560nm(rather than 525nm), it is likely that both this latter step involving reaction with excess base and step (1) above are due to addition of hydroxide ion at C-3 of compound (93). The magnitude of k_{2f} would seem to support this conclusion, as similar values of k_{2f} have been measured for other nitroaromatic systems[26,145].

A slow decomposition of the products formed above occurs with a rate constant,k_{2f}=2.5$M^{-1}s^{-1}$. As was suggested for the reaction of methoxide ion and 1,5-dinitronaphthalene this may correspond with loss of nitrite ion[26].

The rate constant,k_{2f} for the reaction of methoxide ion with compound (93) in methanol(0.6$M^{-1}s^{-1}$ at 27°C) is similar in magnitude to that for the C-1 addition of methoxide ion to 2,4-dinitro-1-methoxy-naphthalene[101](0.9 $M^{-1}s^{-1}$ at 25°C).

Increasing the base strength by using ethoxide ion in ethanol and t-butoxide ion in t-butanol increases the forward rate constant by factors of 4 and 60 respectively relative to that obtained for the reaction of methoxide ion with compound (93) in methanol(See Table 3.1.24). This increase in rate on increasing base strength has been observed previously for 2,4,6-TNT[18,126]. Adding 50% of DMSO(by volume) to the t-butanol solvent increases the rate constant,k_{2f}(=2400$M^{-1}s^{-1}$), by a factor of 70. This was as expected for the addition of a dipolar aprotic solvent[163]. It is difficult to distinguish whether addition or proton abstraction is the dominant process for the reaction of compound (93) with alkoxides. However, for 2,4,6-TNT the rate of proton abstraction increases faster than addition at C-3 as the base strength of the attacking base is increased from methoxide to t-butoxide ion(See Tables 1.4.6 and 1.4.9).

4.3.1 Reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene(98) with hydroxide and methoxide ions

Methoxide ion reacts with 2,4,6,8-tetranitro-1,5-dimethylnaphthalene in methanol at 26.8°C via two steps:-

(1) This step has a second order forward rate constant, k_{2f} of $144M^{-1}s^{-1}$ and is possibly due to addition of methoxide ion at C-3.

(2) This has a value for the rate constant, k_{2f} of $0.88M^{-1}s^{-1}$ and is almost certainly due to proton abstraction to give compound (100).

Comparison of the above values for k_{2f} with k_{2f} for the reaction of the trinitro compound (93) with methoxide in methanol($k_{2f} = 0.6M^{-1}s^{-1}$) indicates that either the rate of (C-3) addition to compound (93) differs by a factor of 240 from that for compound (98), or that proton abstraction from compound (93) and compound (98) occurs at similar rates. As compound (98) possesses one more nitro group than compound (93) the former conclusion is preferred[26,101,106-7]. This is because a considerable activation of the molecule to nucleophilic attack is usually observed.

Similarly the values for k_{2f}($25000M^{-1}s^{-1}$ at 27.7°C) for the reaction of hydroxide ion(addition) with compound (98) in aqueous DMSO(1:9) is 28 times greater than for reaction with compound (93) in the same solvent(k_{2f}=$884M^{-1}s^{-1}$ at 26.3°C).

4.3.2 Reaction of 2,4,6,8-tetranitro-1,5-dimethylnaphthalene with sulphite ion

Sulphite ion reacts by C-3 addition with compound (98) in aqueous DMSO(2:3). Rate constants spanning the range $350\text{-}770M^{-1}s^{-1}$ at 27°C were measured(See also next section).

4.4.1 Reaction of 1,4,5,7-tetranitro-2,3-dimethylnaphthalene(161) with sulphite ion

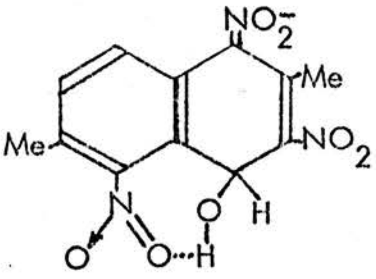
Sulphite ion reacts by C-8 addition with 1,4,5,7-tetranitro-2,3-dimethylnaphthalene in aqueous DMSO(1:4). The rate constant(k_{2f} spans the range $72000\text{-}237000M^{-1}s^{-1}$) is greater than for the reaction of compound (98) (see above) by a factor of approximately 275. Allowing a factor of 10 for the difference in rates for the two solvent mixtures, the reaction of compound (161) is still ~30 times greater than that for compound (98) with sulphite ion. The two reactions differ widely with respect to rate as might be expected from steric and electronic factors. Sterically the C-8 position of compound (161) is much more accessible than the C-3 position of compound (98). Considering the factors determining the electron distribution in compound (161), the ring attacked by the nucleophile(sulphite ion) possesses no deactivating methyl group directly bonded to it.

For comparison, the rate constants for the reaction of sulphite ion with substituted-trinitrobenzenes in water($k_{2f} \sim 4 \times 10^3 M^{-1} s^{-1}$ at 25°C) are intermediate between those for the two above mentioned reactions(See Table 1.4.7)

4.5.1 Reaction of 1,3,5-trinitro-2,6-dimethylnaphthalene with hydroxide ion

Reaction of 1,3,5-trinitro-2,6-dimethylnaphthalene with hydroxide ion in aqueous DMSO(1:4) gives the C-4 addition product with rate constant $k_{2f} = 37.8 M^{-1} s^{-1}$ and equilibrium constant, $K = 7340 M^{-1}$ at 27.4°C. The enthalpy of activation for the forward reaction, $\Delta H_f^* = 61.8 kJmol^{-1}$, is similar to that for reaction of hydroxide ion with 1,3,5-TNB in water[168]($\Delta H_f^* = 65.3 kJmol^{-1}$). By comparison, the entropy of activation for the forward reaction which has a value of $-164 Jmol^{-1}K^{-1}$ is $20 Jmol^{-1}K^{-1}$ lower than for the reaction of TNB and hydroxide ion in water. ΔS_f^* for the reaction of 1,3,8-trinitronaphthalene with hydroxide ion in aqueous dioxan(19:1) is $-39.3 Jmol^{-1}K^{-1}$.

The overall entropy change, ΔS for the reaction of compound (162) and hydroxide ion in aqueous DMSO(1:4) varies between -77 to $-53 Jmol^{-1}K^{-1}$ whilst for the reaction of 1,3,5-TNB and hydroxide ion in water the value for ΔS is $128 Jmol^{-1}K^{-1}$. This large difference may be interpreted as being due to the formation of intramolecular hydrogen bonds between the C-4 hydroxyl proton and oxygen of the peri-nitro group rather than the C-3 nitro group in the case of the product formed from compound (162) (see structure(163)). The construction of a molecular model confirms this hypothesis.



(163)

The entropy of activation for the reverse reaction for the reaction of compound (162) with hydroxide ion varies between approximately 37 to 61 $Jmol^{-1}K^{-1}$ and for 1,3,5-TNB and other related compounds, ΔS_r^* in aqueous and alcoholic solvents ranges from -8 to $-123Jmol^{-1}K^{-1}$(ref 168). The corresponding ΔH_r^* values are $77-96kJmol^{-1}$ for compound (162) in aqueous DMSO(1:4) and from 30.6 to $83.7kJmol^{-1}$ for the Meisenheimer complexes formed from 1,3,5-TNB and related compounds with hydroxide ion in aqueous and alcoholic solvents. It would seem that to form the transition state from the hydrogen bonded product (163) more energy and a much greater increase in entropy are required than for other Meisenheimer complexes as might be expected.

At other solvent compositions(10 and 30% water) two overlapping processes are observed for the reaction of compound (162) with hydroxide ion which preclude precise kinetic analysis.

APPENDIX 1 Synthesis of Polynitrodimethylnaphthalenes

A.1.1 Derivatives of 1,5-Dimethylnaphthalene

2,4,8-Trinitro-(93) and 2,4,6,8-tetranitro-(98) -dimethylnaphthalenes were prepared sequentially via 4,8-dinitro-1,5-dimethylnaphthalene from 1,5-dimethylnaphthalene(1,5-DMN).

4,8-Dinitro-1.5-dimethylnaphthalene

1,5-DMN(4g)(recrystallised from ethanol) was dissolved in 1,2-dichloroethane(80cm^3) and cooled in an ice-bath. Fuming nitric acid(d = 1.5. 8cm^3) was added with stirring over 5 minutes. After 30 minutes at 0°C the stoppered flask was allowed to stand at room temperature for 75 minutes. The ruby coloured solution was washed thrice with water and the solvent evaporated to give impure yellow crystals. Recrystallisation from hot benzene yielded pale yellow crystals of 4,8-dinitro-1,5-dimethylnaphthalene which were dried in vacuo. M.Pt. 171°C; PMR spectrum($CDCl_3$) τ 2.38 and 2.60(4H,ABq,J_{AB} ~8Hz) and 7.40(6H,s).

2,4,8-Trinitro-1,5-dimethylnaphthalene(93)

4,8-Dinitro-1,5-dimethylnaphthalene(2.07g) was dissolved in sulphuric acid(d = 1.84,125cm^3) at 48°C and treated with nitric acid(d = 1.42,0.52cm^3) for 10 minutes. The product was precipitated by pouring onto ice and thoroughly washed with water. Recrystallisation from hot glacial acetic acid and drying in vacuo gave compound (93)(1.34g). M.Pt. 220°C; PMR spectrum (d_6-DMSO) τ 1.24(1H,s),1.71 and 2.12(2H,ABq,J_{AB} 8Hz),7.47(3H,s) and 7.53(3H,s).

2,4,6,8-Tetranitro-1,5-dimethylnaphthalene(98)

Compound (93)(0.3g) was dissolved in sulphuric acid(d = 1.84,5cm^3) and nitric acid(d = 1.42,0.4cm^3) added dropwise. After stirring at 20°C for 1 hour, the reaction mixture was poured onto ice(20g) and the solid product collected. Recrystallisation from glacial acetic acid gave crystals of compound (98). M.Pt. 239°C; PMR spectrum(d_6-DMSO) τ 1.04(2H,s) and 7.49(6H,s).

A.1.2 Derivatives of 1,8-dimethylnaphthalene

2,4,5-Trinitro-1,8-dimethylnaphthalene(106) was prepared by the stepwise direct nitration of 1,8-DMN; and 2,4,5,7-tetranitro-1,8-dimethylnaphthalene(107) was prepared likewise from 4-nitro-1,8-dimethylnaphthalene. 1,8-DMN was prepared by the modified method of Beyler and Sarett.[111]

4-Nitro-1,8-dimethylnaphthalene

1,8-DMN(3.27g) in glacial acetic acid(40cm^3) was treated with nitric acid(d = 1.42,4cm^3) for 15 minutes. The solution was then added to water(200cm^3) with the formation of a yellow precipitate which rapidly turned dark green if left in solution. After filtration and drying, extraction with hot n-hexane followed by cooling yielded yellow crystals of 4-nitro-1,8-dimethylnaphthalene.

4,5-Dinitro-1,8-dimethylnaphthalene

(a) 4-Nitro-1,8-dimethylnaphthalene(2.24g) in 1,2-dichloroethane (20cm^3) was treated with nitric acid(d = 1.5,4.5cm^3) at 50°C for 250 minutes. The solution was twice washed with water and the 1,2-dichloroethane evaporated to yield an impure product.

(b) 1,8-DMN(0.65g) in 1,2-dichloroethane(6.5cm^3) was treated with nitric acid(d = 1.5,1.3cm^3) and heated to 50°C for 15 minutes. After a total of 270 minutes the solution was washed twice with water and the 1,2-dichloroethane evaporated to give 4,5-dinitro-(major) and 2,5-dinitro-(minor)-dimethylnaphthalenes. Recrystallisation of the combined batches from hot benzene yielded light yellow crystals of 4,5-dinitro-1,8-dimethylnaphthalene. M.Pt. 186°C; PMR spectrum($CDCl_3$) τ 1.91 and 2.54(4H,ABq,J_{AB} ~ 8Hz) and 6.98(6H,s).

2,4,5-Trinitro-1,8-dimethylnaphthalene(106)

4,5-Dinitro-1,8-dimethylnaphthalene(1.09g) in sulphuric acid(d = 1.84, 30cm^3) at 0°C was treated over 5 minutes with nitric acid(d = 1.5,0.2cm^3) in sulphuric acid(d = 1.84,4cm^3). The mixture was stirred at ambient temperature for 30 minutes and then poured on ice. The sticky precipitate gradually solidified to a hard mass which was broken up and filtered. This was followed by thorough washing with water and drying in vacuo. The product obtained ~80% of compound (106) and ~20% of compound (107). 'Dry' column chromatography(500 x 15mm) on Kieselgel 60 in benzene gave progressive separation; the low r_f section(~ $\frac{1}{3}$ total) contained almost pure compound (106) (<1% compound (107)). Dissection of the plastic column and extraction of the above section in acetone yielded 20mg solid. Recrystallisation of this solid from glacial acetic acid gave compound (106). (Rather unusually the tetranitro compound (107) has a greater solubility than the trinitro compound (106) in glacial acetic acid). M.Pt. 160°C; PMR spectrum(d_6-DMSO) τ 1.14(1H,s), 1.53 and 2.12(2H,ABq,J_{AB}~ 8.0Hz),6.95(3H,s) and 7.07(3H,s).

2,4,5,7-Tetranitro-1,8-dimethylnaphthalene(107)

4-Nitro-1,8-dimethylnaphthalene(0.5g) was added in portions to a stirred mixture of nitric acid(d = 1.42, $1cm^3$) and sulphuric acid(d = 1.84, $10cm^3$) during 5 minutes. Any lumps which formed were broken up and the mixture was then stirred for 5 minutes, poured onto 50g crushed ice and the buff precipitate filtered off, washed thoroughly with water and dried in vacuo. Recrystallisation from glacial acetic acid gave a product (107) with M.Pt. 215°C; PMR spectrum(d_6-DMSO) τ 0.94(2H,s),7.06(6H,s).

A.1.3 Derivatives of 2,3-dimethylnaphthalene

1,5,7-Trinitro-2,3-dimethylnaphthalene was prepared via 5,7-dinitro-2,3-dimethylnaphthalene from 5-acetamido-2,3-dimethylnaphthalene; 1,4,5,7-tetranitro-2,3-dimethylnaphthalene was made directly from 4-nitro-2,3-dimethylnaphthalene; 5-acetamido-2,3-dimethylnaphthalene was prepared by reduction and acetylation of 5-nitro-2,3-dimethylnaphthalene.

5,7-Dinitro-2,3-dimethylnaphthalene

5-Acetamido-2,3-dimethylnaphthalene(8g) was dissolved in acetic anhydride($100cm^3$) and nitric acid(d = 1.50, $4cm^3$) added dropwise, with stirring, over a period of 15 minutes, the temperature being maintained below 10°C in an ice-bath. The mixture was poured into water($500cm^3$) and the product filtered off and dried. Recrystallisation from 95% ethanol gave 5-acetamido-6,8-dinitro-2,3-dimethylnaphthalene. 4.6g of this compound were refluxed for 16 hours in 95% ethanol containing 70% sulphuric acid($15cm^3$). Cooling and neutralising the reaction mixture with N-sodium hydroxide($300cm^3$) resulted in the precipitation of 5-amino-6,8-dinitro-2,3-dimethylnaphthalene which was filtered off and dried. Diazotisation was effected by adding 0.6g of this compound to a mixture of sulphuric acid(d = 1.84, 2cm^3) and glacial acetic acid(15cm^3), the resulting mixture being cooled to 5°C in an ice-bath, and then added to a solution of sodium nitrite(1g) in sulphuric acid(d = 1.84, 5cm^3). After standing for 30 minutes the red diazonium solution was poured into a solution of ferrous sulphate(10g) and ethylene glycol (20cm^3) in water(30cm^3). The brown precipitate was filtered off, dried, and column chromatographed on Kieselgel 60 in benzene to give 5,7-dinitro-2,3-dimethylnaphthalene. M.Pt. 156°C; PMR spectrum($CDCl_3$) τ 1.10(2H,s), 1.60(1H,s), 2.08(1H,s), 7.43 (3H,s) and 7.47(3H,s).

1,5,7-Trinitro-2,3-dimethylnaphthalene(156)

Nitric acid(d = 1.42, 0.12cm^3) was added to a solution of 5,7-dinitro-2,3-dimethylnaphthalene in sulphuric acid(d = 1.84, 20cm^3). The mixture was stirred at 20°C for 2 hours, and then poured onto crushed ice(50g). The precipitate was filtered off, washed with water, and dried in vacuo to give a pale yellow solid. Column chromatography on Merck silica gel (0.05-0.2mm) using 400 x 20mm columns and eluting with 1:1 benzene-petroleum spirit(B.Pt. 60-80°C) gave 2 fractions. The first fraction yielded yellow needles of 1,5,7-trinitro-2,3-dimethylnaphthalene. M.Pt. 169°C; PMR spectrum($CDCl_3$) τ 1.05 and 1.21(2H,ABq,J_{AB} 2Hz), 1.46(1H,s), 7.35(3H,s) and 7.54(3H,s). (The second fraction gave 1,6,8-trinitro-2,3-dimethylnaphthalene).

1,4,5,7-Tetranitro-2,3-dimethylnaphthalene(161)

1-Nitro-2,3-dimethylnaphthalene(10g) was dissolved in sulphuric acid (d = 1.84, 250cm^3) and nitric acid(d = 1.42, 20cm^3) added dropwise with stirring. After 1 hour the mixture was poured onto ice and the resulting solid washed thoroughly with water, dried and recrystallised twice from glacial acetic acid to yield compound (161). M.Pt. 279°C; PMR spectrum(d_6-DMSO) τ 0.93 and 1.36(2H,ABq,J_{AB} 2Hz), 7.45(3H,s) and 7.49(3H,s).

A.1.4 Derivatives of 2,6-dimethylnaphthalene

The only highly nitrated 2,6-dimethylnaphthalene to be previously synthesised was the 1,4,5,8-tetranitro- species[206] via 1,5-dinitro-2,6-

dimethylnaphthalene. Preparation of the new 1,3,5-;1,4,5-trinitro- and 1,3,5,7-;1,3,5,8-tetranitro- compounds are reported below.[207] 2,6-DMN was recrystallised from industrial methylated spirit and dried in vacuo prior to use.

1,5-Dinitro-2,6-dimethylnaphthalene

A slurry of 2,6-DMN(23.4g) in acetic anhydride(105cm^3) was cooled to 5°C on a cold plate and nitric acid(d = 1.5,18.9cm^3) added dropwise with stirring over 4 hours.[208] The temperature was kept between 5 and 10°C by cooling. After approximately one half of the acid had been added, a yellow precipitate of the crude dinitro- compound began to separate and finally a very thick slurry formed. The whole was then heated to 50°C over a period of 40 minutes and a more marked evolution of brown fumes started. As the temperature was raised to 65°C this evolution intensified and so did the exothermicity of reaction. The temperature was not allowed to exceed 70°C by cooling in a water-bath, and the mass kept for 20 minutes between 70°C and 55°C. After rapid cooling to 15°C(ice-bath) the thick slurry was filtered on a sinter-glass funnel, and most of the mother liquor rinsed out with glacial acetic acid(15cm^3). After thoroughly removing the acids by washing with water, the cake was dried in vacuo at 60°C. Purification was based on the lower solubility of the dinitro- and better solubility of the mono- and tri- nitro- compounds in acetone. The crude material(44.6g) was dissolved in acetone(1340cm^3) under reflux and the solution allowed to cool spontaneously to room temperature whence the crystals which formed were filtered off and dried in vacuo. Yield 5.2g(12% of crude). The yellow needles obtained had M.Pt. 206°C (lit. 198°C-200°C) PMR spectrum(d_6-DMSO) τ 2.24(4H,s) and 7.55(6H,s).

1,3,5-Trinitro-2,6-dimethylnaphthalene(162)

To a stirred solution of 1,5-dinitro-2,6-DMN(5g) in acetic anhydride (300cm^3) was added nitric acid(d = 1.42,40cm^3) at such a rate that the temperature did not exceed 40°C. After the addition, the solution was allowed to stand for 16 hours, and then nitric acid(d = 1.50,30cm^3) was added over a period of 4 hours. After which time sulphuric acid(d = 1.84,1.5cm^3) was added. The temperature of the reactant solution was slowly increased to 70°C whilst stirring continuously, and then after 5 minutes vigorous evolution of fumes, the reactants were quenched in excess water. (Caution has to be taken on heating owing to the formation of tetranitromethane in the reactant mixture[209]). After 18 hours the precipitated solid was filtered off and recrystallised from acetone followed by acetic acid to give 1,3,5-trinitro-2,6-dimethylnaphthalene(162) (1.5g(25%)). M.Pt. 176°C; (Found C,49.7; H,3.3; N,14.7 $C_{12}H_9N_3O_6$ requires C,49.5; H,3.1; N,14.4%) PMR spectra ($CDCl_3$) τ 1.56(1H,s),2.26 (2H,s) and 7.41(6H,s); (DMSO-d_6) τ 1.40(1H,s),2.03 and 2.06(2H,ABq,J_{AB} 9.2Hz),7.45(3H,s) and 7.48(3H,s) m/e 291 $[M^+]$. The mass spectrum (fig.A.1.4.1(a)) did not show a base peak at $[M-NO_2{}^{\cdot}]^+$ which indicated that the nitro- substitution pattern was 1,3,5-[210]).

1,4,5-Trinitro-2,6-dimethylnaphthalene(169)

To a stirred solution of 1,5-dinitro-2,6-dimethylnaphthalene(2g) in sulphuric acid(d = 1.84,600cm^3) was added nitric acid(d = 1.42,0.6cm^3). After 2 hours the mixture was poured onto ice and the precipitated solid filtered off. washed thoroughly with water, dried in vacuo and washed with toluene(15cm^3). The toluene washings contained a small quantity of 1,3,5-trinitro-2.6-dimethylnaphthalene(162) (1% of total yield) which was separated from 1,4,5-trinitro-2,6-dimethylnaphthalene by column chromatography on Merck silica gel(0.06-0.2mm) using 20x500mm columns and eluting with 1:1 toluene/petroleum spirit(B.Pt. 40-60°C). The bands were visible by irradiation of the column with UV light. Elution occurred in the order, 1,5-dinitro- followed by 1,3,5-trinitro- and finally 1,4,5-trinitro-2,6-dimethylnaphthalene.
Recrystallisation of the toluene washed material from glacial acetic acid gave 1,4,5-trinitro-2,6-dimethylnaphthalene(1.54g, 65% yield). M.Pt. 193°C; (Found C,49.4; H,3.3; N,14.6 $C_{12}H_9N_3O_6$ requires C,49.5; H,3.1; N,14.4%) PMR spectra($CDCl_3$) τ 1.96(1H,s),2.23 and 2.35(2H,ABq,J_{AB} 9.0Hz),7.37(3H,s) and 7.46(3H,s). m/e 291 $[M^+]$, 245(base peak). The base peak corresponding to $[M-NO_2]^+$ showed that peri-nitro groups were present in the compound structure[210] (fig.A.1.4.1(b)).

1,3,5,7-Tetranitro-2,6-dimethylnaphthalene(177)

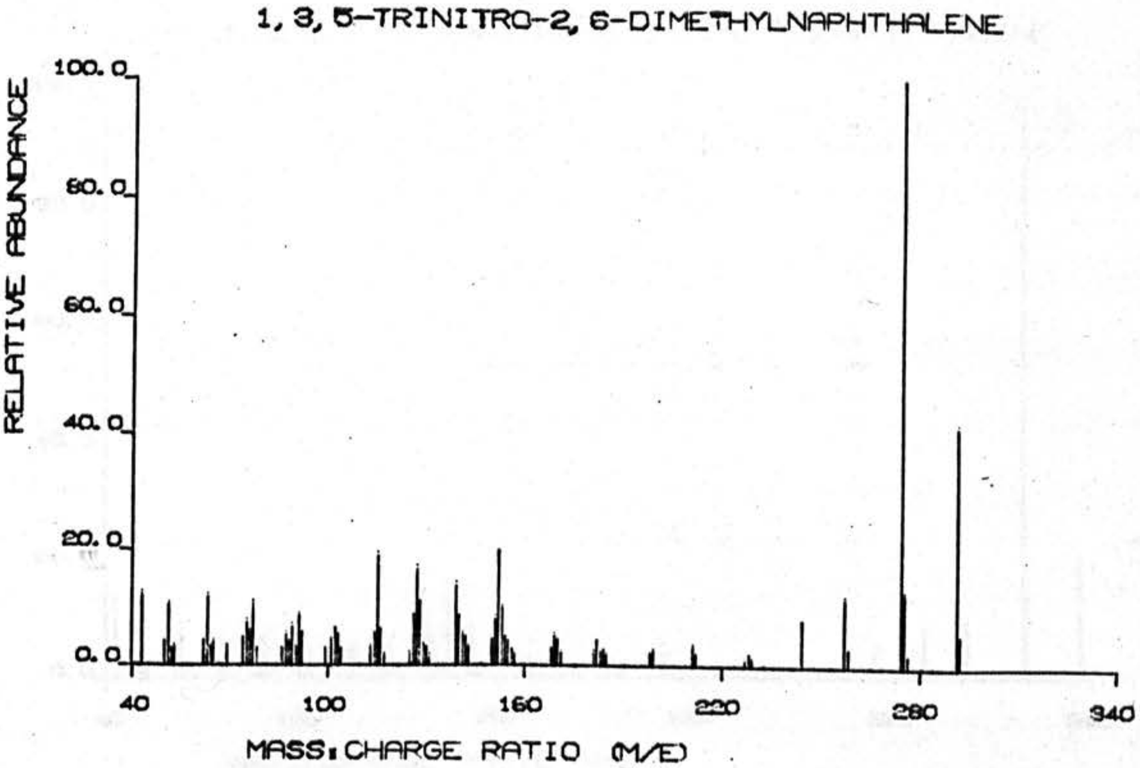
A solution of 1,3,5-trinitro-2,6-dimethylnaphthalene(3g) in acetic anhydride(300cm^3) was treated in exactly the same manner as for preparation of (162). Recrystallisation as specified above gave 1,3,5,7-tetranitro-2,6-dimethylnaphthalene(0.3g; 9% yield). M.Pt. 332°C; (Found C,42.8; H,2.5; $C_{12}H_8N_4O_8$ requires C,42.9; H,2.4) PMR spectrum(DMSO-d$_6$) τ 1.35(2H,s) and 7.48(6H,s). m/e 336 [M$^+$] (fig.A.1.4.2(a)).

1,3,5,8-Tetranitro-2,6-dimethylnaphthalene(181)

Nitric acid(d = 1.50,4cm^3) was added dropwise with stirring to a solution of 13g(162) in sulphuric acid(d = 1.84,400cm^3) in a vessel fitted with a drying trap. After standing for 30 hours the reaction mixture was poured onto ice, and the precipitated product thoroughly washed with water, and then thrice recrystallised from glacial acetic acid to give 1,3,5,8-tetranitro-2,6-dimethylnaphthalene(6.0g(40%)). M.Pt. 302°C; PMR spectrum(DMSO-d$_6$) τ 1.22(1H,s),1.24(1H,s),7.41(3H,s) and 7.47(3H,s). m/e 336 [M$^+$] 290(base peak). As before, the base peak corresponding to $[M-NO_2{}^{\cdot}]^+$ ion indicated the presence of peri-nitro groups(fig.A.1.4.2(b)).

1,4,5,8-Tetranitro-2,6-dimethylnaphthalene(190)

A stirred solution of 1,5-dinitro-2,6-dimethylnaphthalene(5g) in sulphuric acid(d = 1.84,1000cm^3) was treated with nitric acid(d = 1.5,3.6cm^3) for 6 days. The reaction mixture was precipitated on ice, filtered and thoroughly washed with water before drying in vacuo. Four recrystallisations from glacial acetic acid gave 1,4,5,8-tetranitro-2,6-dimethylnaphthalene(2g) (35% yield)). M.Pt. 280°C; PMR spectrum(DMSO-d$_6$) τ 1.21(2H,s) and 7.34 (6H,s). m/e 336 [M$^+$] . 244(base peak). Base peak corresponded to $[M-2NO_2]^+$ indicating 2 sets of peri-nitro groups(fig.A.1.4.3).



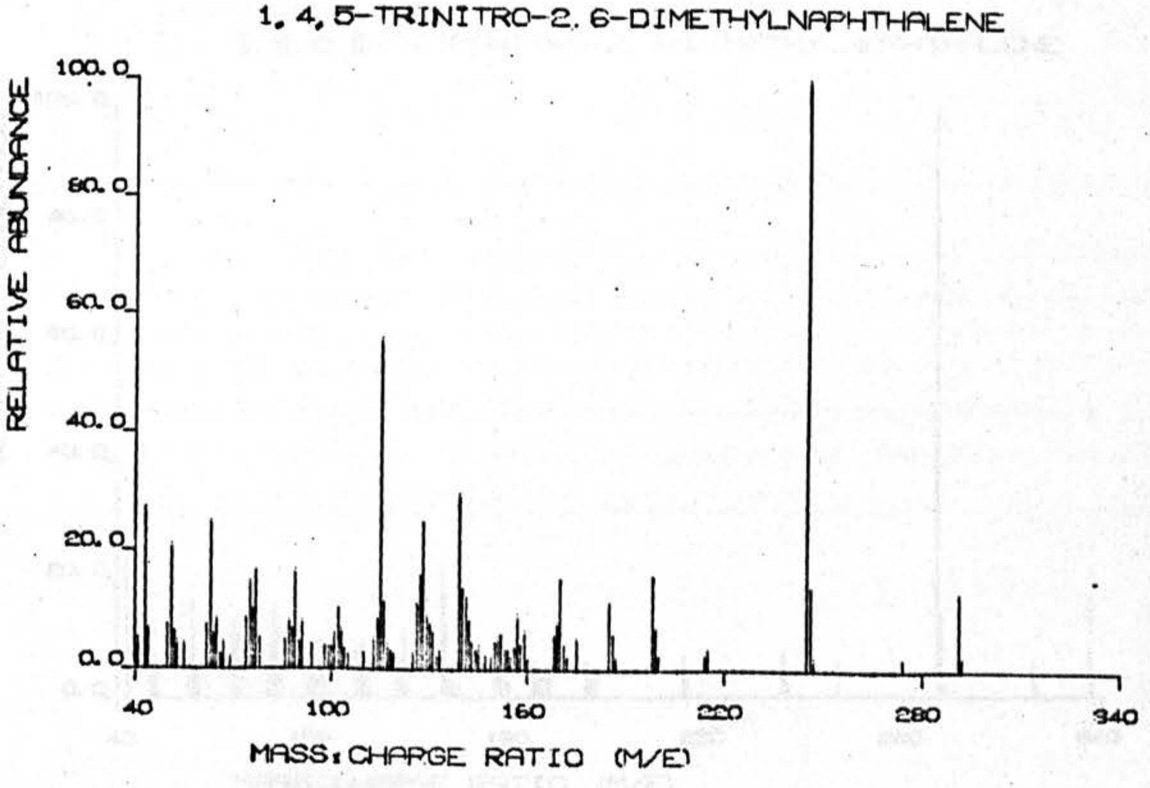
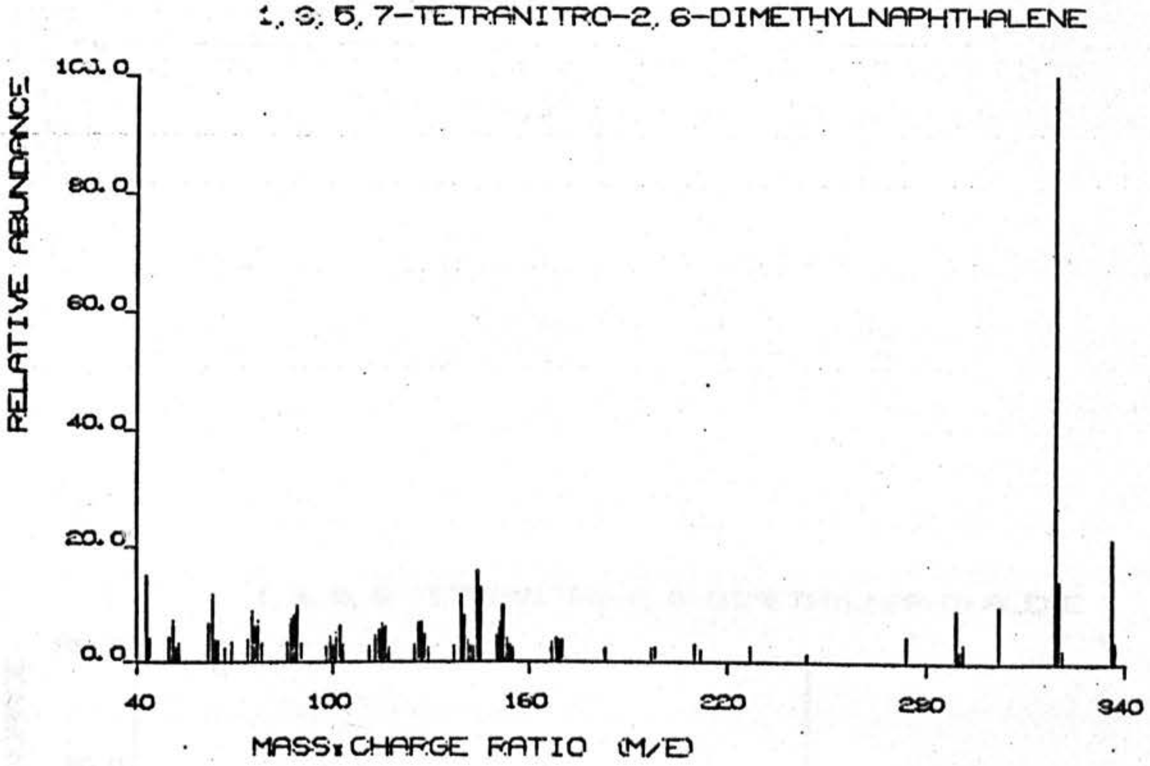


Fig A.1.4.1 Positive ion mass spectra of:- (a) 1,3,5-trinitro-2,6-dimethylnaphthalene and (b) 1,4,5-trinitro-2,6-dimethylnaphthalene.


1,3,5,7-TETRANITRO-2,6-DIMETHYLNAPHTHALENE

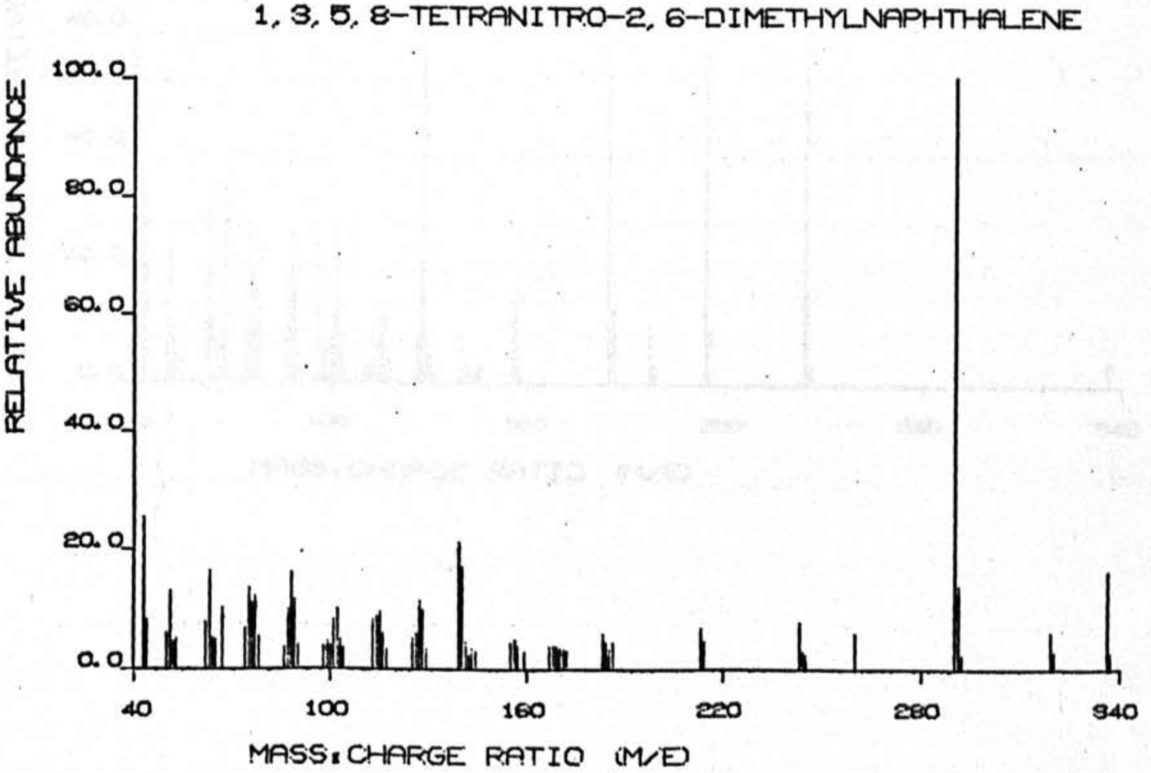

1,3,5,8-TETRANITRO-2,6-DIMETHYLNAPHTHALENE

Fig A.1.4.2 Positive ion mass spectra of:- (a) 1,3,5,7-tetranitro-2,6-dimethylnaphthalene and (b) 1,3,5,8-tetranitro-2,6-dimethylnaphthalene.

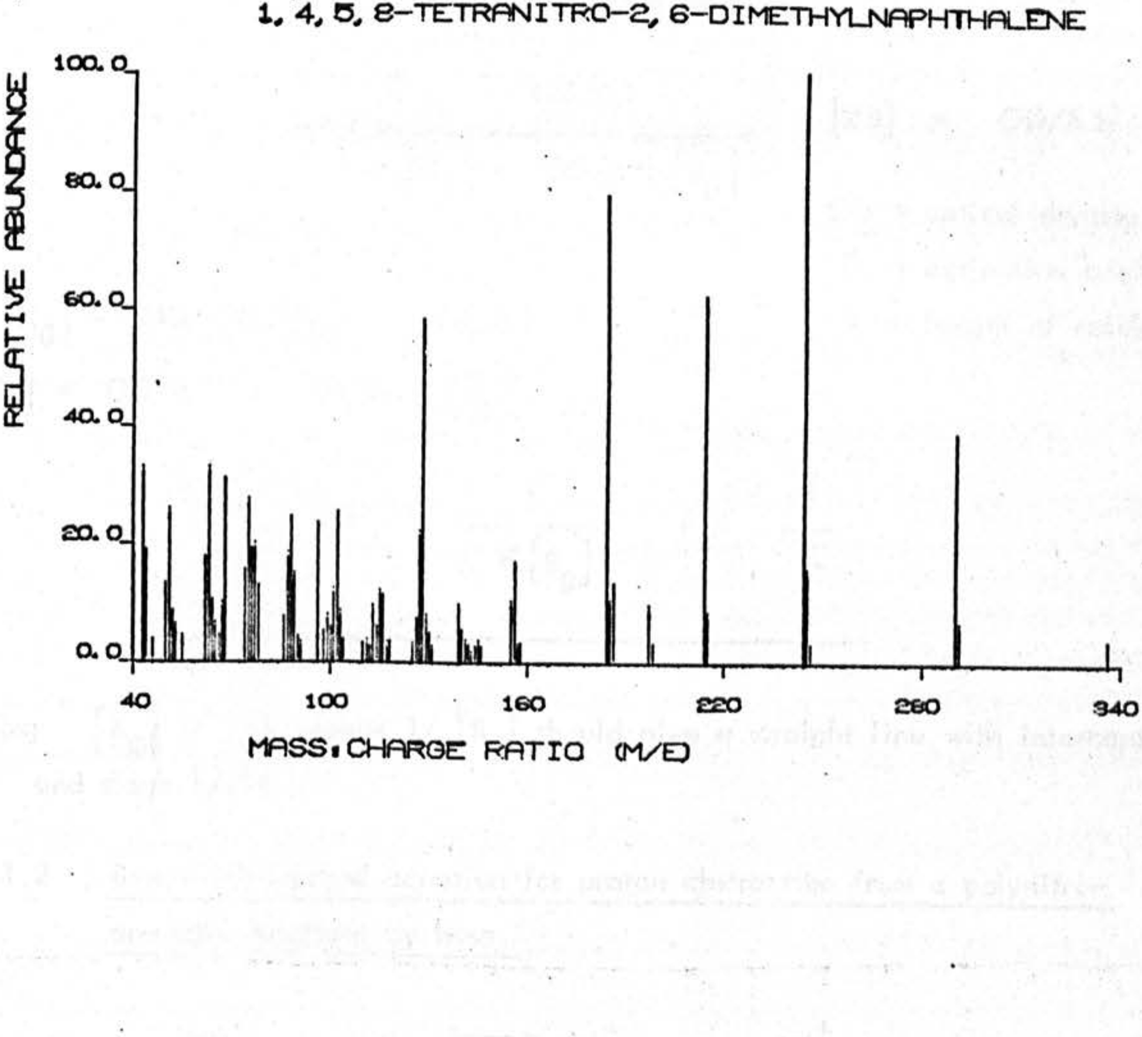


Fig A.1.4.3 Positive ion mass spectrum of 1,4,5,8-tetranitro-2,6-dimethylnaphthalene.

APPENDIX 2.1

A.2.1.1 Benesi-Hildebrand equation for sigma-addition complex formation.

$$X + B \rightleftharpoons XB$$

$$K = \frac{[XB]}{([X_0] - [XB])([B_0] - [XB])}$$

$$= \frac{[XB]}{([X_0] - [XB])[B_0]} \quad \text{as} \quad [B_0] \gg [XB]$$

$$= \frac{OD/\varepsilon l}{([X_0] - OD/\varepsilon l)[B_0]} \qquad [XB] = OD/\varepsilon l$$

OD = optical density

ε = extinction coeff^t.

l = length of cell(cm)

$$K([X_0] - OD/\varepsilon l)[B_0] = OD/\varepsilon l$$

$$[X_0] = OD/\varepsilon l = OD/\varepsilon l K[B_0]$$

$$\frac{[X_0]\,l}{OD} = \frac{1}{K\,\varepsilon[B_0]} + \frac{1}{\varepsilon}$$

Plotting $[X_0]\,l/\,OD$ against $1/[B_0]$ should give a straight line with intercept $1/\varepsilon$ and slope $1/K\varepsilon$.

A.2.1.2 Benesi-Hildebrand equation for proton abstraction from a polynitroaromatic substrate by base.

$$XH + B \rightleftharpoons X^- + BH^+$$

$$K = \frac{[X^-][BH^+]}{[XH][B]}$$

$$= \frac{x^2\,[XH_0]^2}{[X_0](1-x)[B_0]}$$ assuming $[B_0] \gg x\,[X_0]$

x = fraction of X converted to $X^- = \text{OD}/\ X_0\, l$.

$$= \frac{\text{OD}^2/\varepsilon^2 l^2}{([X_0] - \text{OD}/\varepsilon l)\,[B_0]}$$

$$K([X_0] - \text{OD}/\varepsilon l)\,[B_0] = \text{OD}^2/\varepsilon^2 l^2 \qquad \text{eq. 1.}$$

$$[X_0] - \text{OD}/\varepsilon l = \text{OD}^2/K\,[B_0]\,\varepsilon^2 l^2$$

$$\frac{[X_0]}{\text{OD}} = \frac{\text{OD}}{K\varepsilon^2 l^2 [B_0]} + \frac{1}{\varepsilon l}$$

Plotting $\frac{[X_0]}{\text{OD}}$ against $\frac{\text{OD}}{[B_0]}$ should give a straight line with intercept $1/\varepsilon l$ and slope $1/K\varepsilon^2 l^2$.

$$K = \text{intercept}^2/\text{slope}.$$

A.2.1.3 Modified Benesi-Hildebrand equation for proton abstraction.

Multiplying eq.1 by $1/\text{OD}^2 K$

$$\frac{[X_0][B_0]\,\varepsilon l}{\text{OD}^2} - \frac{[B_0]}{\text{OD}} = \frac{1}{K\varepsilon l}.$$

Plotting $[B_0]/\text{OD}$ against $[X_0][B_0]/\text{OD}^2$ should give a straight line with slope εl and intercept $-1/K\varepsilon l$.

A.2.1.4 <u>Benesi-Hildebrand equation for proton abstraction(BH$^+$ in excess)</u>

$$XH \quad + \quad B \quad \rightleftharpoons \quad X^- \quad + \quad BH^+$$

at equilibrium:- $[XH] = XH_0 - x_e$ $[B] = b$ $[X^-] = x_e$ $[BH^+] = d$

$$K = \frac{x_e\, d}{(XH_0 - x_e)\, b} \qquad OD_e = x_e \varepsilon l$$

$$= \frac{OD_e\, d}{(XH_0 \varepsilon l - OD_e) b}$$

$$K\, XH_0 \varepsilon l - K\, OD_e = OD_e\, d/b$$

$$\frac{XH_0}{OD_e} = \frac{d}{K \varepsilon l b} + \frac{1}{\varepsilon l}$$

Plotting XH_0/OD_e against $1/b$ should give a straight line with intercept $1/\varepsilon l$ and slope $d/K\varepsilon l$.

APPENDIX 2.2

A.2.2.1 <u>'Spot-value' method for determination of K</u> (Meisenheimer complex <u>formation</u>).

$$\begin{matrix} A & + & B & \rightleftharpoons & C \\ (1-x)[A_0] & & (N-x)[A_0] & & x[A_0] \end{matrix}$$

$$K = \frac{x[A_0]}{(1-x)[A_0](N-x)[A_0]} \qquad x = OD/\varepsilon[A_0]l$$

$$= \frac{OD/\varepsilon}{(1 - OD/\varepsilon[A_0])[A_0](N - OD/\ [A_0])[A_0]}$$

$$K = \frac{1}{\varepsilon N[A_0]^2/OD + OD/\varepsilon - [A_0](1+N)}$$

The term OD/ε is very small and may be neglected.

A.2.2.2 'Spot-value' method for determination of K (Proton abstraction)

$$\begin{array}{ccccccc} A & + & B & \rightleftharpoons & C & + & D \\ [A_0](1-x) & & [A_0](N-x) & & [A_0]x & & [A_0]x \end{array}$$

$$K = \frac{[A_0]^2\, x^2}{[A_0]^2 (1-x)(N-x)} = \frac{x^2}{N + x^2 - x(1+N)}$$

$$K = \frac{1}{\dfrac{N\varepsilon^2[A_0]^2}{OD^2} + 1 - \dfrac{[A_0]\,(1+N)}{OD}}$$

APPENDIX 2.3 Kinetic equations.

A.2.3.1. Reversible 1st order reactions.

$$A \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} B$$

$$\ln\left(\frac{A_0 - A_e}{A - A_e}\right) = (k_{1f} + k_{1r})t$$

If we have a pseudo 1st order reaction in the forward direction i.e.

$A + B \rightleftharpoons C$ $\quad [B_0] \gg [A_0]$

then $$\ln\left(\frac{[A_0] - A_e}{A - A_e}\right) = (k_{1f}[B_0] + k_{1r})t$$

---

where $[A_0]$ = initial concentration of A; A_e = equilibrium concentration of A; A = concentration of A at time t; $[B_0]$ = base concentration; $k_{2f}/[B_0]$.

A.2.3.2 Reversible 2nd order reactions(excess of B)

$$A + B \underset{k_{2r}}{\overset{k_{2f}}{\rightleftharpoons}} C + D$$

e.g. XH $\quad RNH_2 \quad X^- \quad R\overset{+}{N}H_3$

$[B_0] \gg [A_0]$ and $[C_0] = [D_0] = 0.$

$$[C] = [D] = [A_0] - [A]$$

$$-\frac{dA}{dt} = k_{2f}AB - k_{2r}CD = k_{1f}A - k_{2r}(A_0 - A)^2$$

writing $[A] = A$; $[B] = B$ etc. where $k_{1f} = k_{2f}[B_0]$

at equilibrium $\quad k_{2f}A_e B_e = k_{2r}C_e D_e$

$$k_{1f}A_e = k_{2r}(A_0 - A_e)^2 .$$

$$k_{2r} = \frac{k_{1f}A_e}{(A_0 - A_e)^2}$$

$$-\frac{dA}{dt} = k_{1f}A - k_{1f}A_e\frac{(A_0 - A)^2}{(A_0 - A_e)^2}$$

$$= \frac{k_{1f}}{(A_0 - A_e)^2}\ A(A_0 - A_e)^2 - A_e(A_0 - A)^2$$

$$= \frac{k_{1f}}{(A_0 - A_e)^2}\ -A_eA^2 + (A_0^2 + A_e^2)A - A_eA_0^2$$

Integration by parts gives:-

$$= \frac{1}{s^{\frac{1}{2}}}\ln\frac{-2A_eA + (A_0^2 + A_e^2) - s^{\frac{1}{2}}}{-2A_eA + (A_0^2 + A_e^2) + s^{\frac{1}{2}}}$$

$$= \frac{k_{1f}t}{(A_0 - A_e)^2} + C$$

where $s^{\frac{1}{2}} = A_0^2 - A_e^2$

$$-\frac{1}{(A_0^2 - A_e^2)} \ln \frac{-2A_0A + A_0^2 + A_e^2 - (A_0^2 - A_e^2)}{-2A_eA + A_0^2 + A_e^2 + (A_0^2 - A_e^2)} = \frac{k_{1f}t}{(A_0 - A_e)^2} + C$$

$$-\ln \frac{-2A_0A + 2A_e^2}{-2A_eA + 2A_0^2} = k_{1f}t\,\frac{(A_0 - A_e)(A_0 + A_e)}{(A_0 - A_e)^2} + C$$

$$-\ln \frac{A_e^2 - A_eA}{A_0^2 - A_eA} = k_{1f}t\,\frac{A_0 + A_e}{A_0 - A_e} + C \qquad \text{eq. 2.}$$

when $t=0, A=A_0$

$$C = -\ln \frac{A_e^2 - A_eA_0}{A_0^2 - A_eA_0}$$

subst. in eq. 2.

$$-\ln \frac{(A_e^2 - A_eA)(A_0^2 - A_eA_0)}{(A_0^2 - A_eA)(A_e^2 - A_eA_0)} = k_{1f}t\,\frac{A_0 + A_e}{A_0 - A_e}$$

or $$-\ln \frac{A_0(A - A_e)}{(A_0^2 - A_eA)} = k_{1f}t\,\frac{A_0 + A_e}{A_0 - A_e}$$

Let $x = A_0 - A = C$ $\qquad A_e = a - x_e \qquad A = a - x$

and $a = A_0$ $\qquad A - A_e = x_e - x$

$$\ln\left[\frac{a x_e + x(a - x_e)}{a(x_e - x)}\right] = \left[\frac{2a - x_e}{x_e}\right] k_{1f} t$$

If absorbance of C = OD $x = OD/\varepsilon l$; $x_e = OD_e/\varepsilon l$

$$\ln\left[\frac{a\,OD_e + OD(a - OD_e/\varepsilon l)}{a(OD_0 - OD)}\right] = \left[\frac{2a\varepsilon l}{OD_e} - 1\right] k_{1f} t$$

A.2.3.3. Reversible 2nd order reactions(excess of B and D)

$$A + B \underset{k_{2r}}{\overset{k_{2f}}{\rightleftharpoons}} C + D$$

e.g. XH RNH_2 X^- $R\overset{+}{N}H_3$

$A_0 = a$ $B_0 = b$ $C = x$ $D_0 = d$

$$-\frac{dA}{dt} = \frac{dx}{dt} = k_{2f}AB - k_{2r}CD = k_{2f}Ab - k_{2r}xd$$

At equilibrium $k_{2f}(a - x_e)b = k_{2r}x_e d$

$$k_{2r} = k_{2f}(a - x_e)b/x_e d$$

$$\frac{dx}{dt} = k_{2f}\left[(a - x)b - bx(a - x_e)/x_e\right]$$

$$= bk_{2f}(a - ax/x_e) = abk_{2f}(1 - x/x_e)$$

$$\frac{dx}{(1 - x/x_e)} = abk_{2f}dt$$

$$-x_e \ln(1 - x/x_e) = abk_{2f}t \qquad x = OD/\varepsilon l; \quad x_e = OD_e/\varepsilon l$$

$$\frac{-OD_e}{\varepsilon\, l\, a\, b} \ln(1 - OD/OD_e) = k_{2f}t \qquad \text{where } bk_{2f} = k_{1f}$$

A.2.3.4. 2nd order forward and 1st order reverse reaction.

$$A + B \underset{k_{2r}}{\overset{k_{2f}}{\rightleftharpoons}} C + D$$

e.g. XH OH^- X^- H_2O in aqueous solution

assume B not in great excess $[C] = [A_0] - [A]$

let $[A_0] = a$, $[B_0] = b$, $[C] = x$

$$\frac{dx}{dt} = k_{2f}(a - x)(b - x) - k_{2r}\, x\, [D]$$

$$= k_{2f}(a - x)(b - x) - k_{1r}x \quad \text{where } k_{1r} = k_{2r}[D]$$

at equilibrium $k_{2f}(a - x_e)(b - x_e) = k_{1r}x_e$

$$k_{1r} = \frac{k_{2f}(a - x_e)(b - x_e)}{x_e}$$

hence $dx/dt = k_{2f} \; x^2 - x(ab/x_e + x_e) + ab$

Integration:-

$$\frac{1}{s^{\frac{1}{2}}} \ln\left[\frac{2x - (ab/x_e + x_e) - s^{\frac{1}{2}}}{2x - (ab/x_e + x_e) + s^{\frac{1}{2}}}\right] = k_{2f}t + \text{const}$$

$$s^{\frac{1}{2}} = ab/x_e - x_e$$

$$\therefore \frac{1}{(ab/x_e - x_e)} \ln\left[\frac{x - ab/x_e}{x - x_e}\right] + \text{const} = k_{2f}t$$

---

where $x = OD/\varepsilon l$ and $x_e \doteq OD_e/\varepsilon l$

A.2.3.5. 2nd order forward and 2nd reverse reaction.

$$A + B \underset{k_{2r}}{\overset{k_{2f}}{\rightleftharpoons}} C + D$$

$$[A_0] \qquad [B_0] \qquad [A_0] = a \qquad [B_0] = b$$

$$dx/dt = k_{2f}(a - x)(b - x) - k_{2r}x^2$$

at equilibrium $\quad k_{2f}(a - x_e)(b - x_e) = k_{2r}x_e^2$

$$k_{2r} = k_{2f}(a - x_e)(b - x_e)/x_e^2$$

$$dx/dt = k_{2f}(a - x)(b - x) - \frac{k_{2f}(a - x_e)(b - x_e)x^2}{x_e^2}$$

$$= \frac{k_{2f}}{x_e^2} \left[x^2(a x_e + b x_e - ab) - x(x_e^2)(a + b) + x_e^2 ab \right]$$

Integration by parts of $dx/dt = cx^2 + c_1 x + c_2$

$$\frac{1}{s^{\frac{1}{2}}} \ln \left[\frac{2cA + c_1 - s^{\frac{1}{2}}}{2cA + c_1 + s^{\frac{1}{2}}} \right] = t + \text{const}$$

$$s^{\frac{1}{2}} = (c_1^2 - 4cc_2)^{\frac{1}{2}}$$

hence $s^{\frac{1}{2}} = x_e \left[x_e(a + b) - 2ab \right]$

$$\frac{1}{s^{\frac{1}{2}}} \ln \left[\frac{2(ax_e + bx_e - ab)x - x_e^2(a + b) - x_e(x_e(a + b) - 2ab)}{2(ax_e + bx_e - ab)x - x_e^2(a + b) + x_e(x_e(a + b) - 2ab)} \right] = \frac{k_{2f}t}{x_e^2} + \text{const}$$

$$\text{const} = \frac{1}{s^{\frac{1}{2}}} \ln \left[\frac{x_e(a + b) - ab}{ab} \right]$$

hence $\ln \left[\frac{(x_e - x)ab}{x_e ab - x(ax_e + bx_e - ab)} \right] = \left[\frac{x_e(a + b) - 2ab}{x_e} \right] k_{2f}t$

A.2.3.6. Reversal of 2nd order forward and 2nd order reverse reaction (excess of B and D)

$$A + B \underset{k_{2f}}{\overset{k_{2r}}{\rightleftharpoons}} C + D$$

X^- Et_3NH^+ XH Et_3N

$$-\frac{dA}{dt} = k_{2r}AB - k_{2f}CD$$

$[B_0] = b \qquad [D_0] = d$

$$-dA/dt = k_{2r}Ab - k_{2f}Cd$$

$$= k_{2r}Ab - k_{2f}(C_0 + A_0 - A)d$$

at equilibrium $\qquad k_{2r}A_eB_e = k_{2f}C_eD_e$

$$k_{2r}A_eb = k_{2f}C_ed = k_{2f}(C_0 + A_0 - A_e)d$$

$$k_{2f} = k_{2r}A_eb/d(C_0 + A_0 - A_e)$$

$$-dA/dt = k_{2r}[Ab - A_eb(C_0 + A_0 - A)/(C_0 + A_0 - A_e)]$$

$$= k_{2r}b[A(1 + (A_e/(C_0 + A_0 - A_e))) - (C_0 + A_0)A_e/(C_0 + A_0 - A_e)]$$

Integration gives

$$\frac{-1}{b(1 + A_e/(C_0 + A_0 - A_e))} \ln (A(1 + A_e/(C_0 + A_0 - A_e)) - (C_0 + A_0)A_e/(C_0 + A_0 - A_e))$$

$$= k_{2r}t$$

let $m = \varepsilon(C_0 + A_0) - OD_e$

$$-1/b(1 + OD_e/m) \ln [OD(1 + OD_e/m)/\varepsilon - OD_e(C_0 + A_0)/m] = k_{2r}t$$

A.2.3.7. Reversal of 1st order forward(pseudo) and 2nd order reverse reaction.

Displacement to a new equilibrium position by addition of co-solvent

$$A \quad + \quad B \underset{k_{2f}}{\overset{k_{2r}}{\rightleftharpoons}} C \quad + \quad D$$

$$\text{e.g.} \qquad X^- \qquad RNH_3^+ \qquad RNH_2 \qquad XH$$

$$[A_0] = [B_0] \qquad [C_0] >> [D_0] \quad \text{or} \quad [A_0] \quad \text{or} \quad [B_0]$$

$$-\,dA/dt = k_{2r}AB - k_{2f}CD = k_{2r}A^2 - k_{2f}CD$$

$$= k_{2r}A^2 - k_{2f}(C_0 + A_0 - A)(D_0 + A_0 - A)$$

$$k_{2r}A_eB_e = k_{2f}C_eD_e$$

$$k_{2r}A_e^2 = k_{2f}(C_0 + A_0 - A_e)(D_0 + A_0 - A_e)$$

$$\text{hence} \quad -\frac{dA}{dt} = k_{2r}A^2 - k_{2r}A_e^2\left[\frac{(C_0 + A_0 - A)(D_0 + A_0 - A)}{(C_0 + A_0 - A_e)(D_0 + A_0 - A_e)}\right]$$

$$= k_{2r}(A^2 + lA - lm)$$

where $l = A_e^2/(D_0 + A_0 - A_e)$ and $m = D_0 + A_0$

Integration by parts gives

$$-\frac{1}{s^{\frac{1}{2}}}\left[\ln\frac{2A + l' - s^{\frac{1}{2}}}{2A + l' + s^{\frac{1}{2}}}\right] = k_{2r}t + \text{const}$$

where $l' = A_e^2/(D - A_e)$ and $s^{\frac{1}{2}} = l'^2 + 4l'D^{\frac{1}{2}}$

or $$-\frac{1}{s^{\frac{1}{2}}} \ln\left[\frac{2OD/\varepsilon l + l' - s^{\frac{1}{2}}}{2OD/\varepsilon l + l' + s^{\frac{1}{2}}}\right] = k_{2r}t + \text{const}$$

where D = original concentration of nitroaromatic

A = final equilibrium concentration of $X^- = OD_{e_2}/\varepsilon l$

A.2.3.8. Reversal of 2nd order forward and 2nd order reverse reaction.

$$\begin{array}{ccccccc} A & + & B & \underset{k_{2f}}{\overset{k_{2r}}{\rightleftharpoons}} & C & + & D \\ X^- & & BH^+ & & B & & XH \end{array}$$

$$[A_0] = [B_0]$$

$$-dA/dt = k_{2r}AB - k_{2f}CD = k_{2r}A^2 - k_{2f}CD$$

$$= k_{2r}A^2 - k_{2f}(C_0 + A_0 - A)(D_0 + A_0 - A)$$

at equilibrium $$k_{2r}A_e^2 = k_{2f}(C_0 + A_0 - A_e)(D_0 + A_0 - A_e)$$

$$k_{2f} = k_{2r}A_e^2/(C_0 + A_0 - A_e)(D_0 + A_0 - A_e)$$

$$-dA/dt = k_{2r}A^2 - \frac{k_{2r}A_e^2(C_0 + A_0 - A)(D_0 + A_0 - A)}{(C_0 + A_0 - A_e)(D_0 + A_0 - A_e)}$$

$$C_0 + A_0 = C_{\text{initial}} = C_i$$

$$D_0 + A_0 = D_{\text{initial}} = D_i$$

$$-dA/dt = k_{2r}A^2 - k_{2r}A_e^2(C_i - A)(D_i - A)/(C_i - A_e)(D_i - A_e)$$

$$= k_{2r}A^2 - \frac{k_{2r}A_e^2(C_iD_i - A(C_i + D_i) + A^2)}{(C_i - A_e)(D_i - A_e)}$$

$$I = A_e^2/(C_i - A_e)(D_i - A_e)$$

$$-dA/dt = k_{2r}\left[A^2 - IC_iD_i + I(C_i + D_i)A - IA^2\right]$$

$$= k_{2r}\left[A^2(1-I) + AI(C_i + D_i) - IC_iD_i\right]$$

Integration:- $$\frac{1}{s^{\frac{1}{2}}} \ln\left[\frac{2Ac + c_1 - s^{\frac{1}{2}}}{2Ac + c_1 + s^{\frac{1}{2}}}\right] = k_{2r}t + \text{const}$$

$$s^{\frac{1}{2}} = (c_1^2 - 4cc_2)^{\frac{1}{2}} = \left[I^2(C_i + D_i)^2 + 4(1 - I)(IC_iD_i)\right]^{\frac{1}{2}}$$

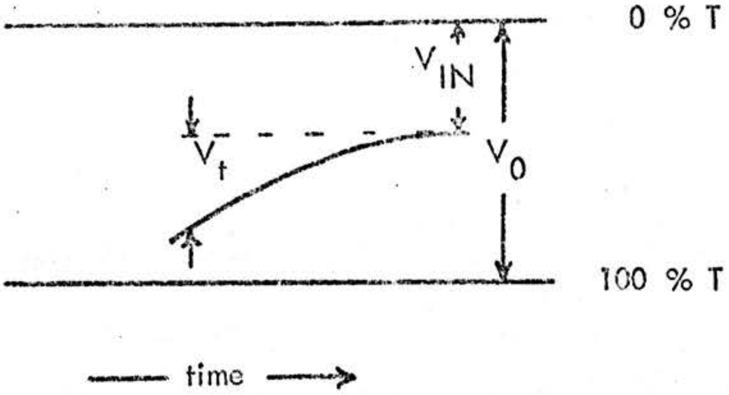
$$= \left[I^2(C_i - D_i)^2 + 4IC_iD_i\right]^{\frac{1}{2}}$$

$$-\frac{1}{s^{\frac{1}{2}}} \ln\left[\frac{2A(1-I) + I(C_i + D_i) - (I^2(C_i - D_i)^2 + 4IC_iD_i)^{\frac{1}{2}}}{2A(1-I) + I(C_i + D_i) + (I^2(C_i - D_i)^2 + 4IC_iD_i)^{\frac{1}{2}}}\right] = kt + \text{const}$$

A.2.3.9. Stopped-flow voltage-time trace analysis.

Reversible first order reaction.

Increasing absorbance.



$$- \ln(\log_{10}(V_0/V_{IN}) - \log_{10}(V_0/(V_t + V_{IN})))$$

$$= \quad - \ln(\ln((V_t + V_{IN})/V_{IN}))/\ln(10) \; = \; (k_{1f} + k_{1r})t$$

Decreasing absorbance.

both V_{IN}
and V_0 are -ve.

$$- \ln(\log_{10}(V_0/(V_t + V_{IN})) - \log_{10}(V_0/V_{IN}))$$

$$= \quad - \ln(\ln(V_{IN}/(V_t + V_{IN})))/\ln(10) = (k_{1f} + k_{1r})t$$

Thermodynamic Parameters.

$$\ln(k) = \ln(A) - E_a/RT$$

Plot of $\ln(k)$ against $1/T$ gives:-

$$E_{ac} = -R.\text{slope}.$$

$$\Delta H^* = E_a - RT.$$

$$\Delta S^* = R(\ln(Ah/k_B T_e))$$

$$\ln(k) = -\Delta H/RT + \text{const}.$$

Plot of $\ln(K)$ against $1/T$ gives:-

$$\Delta H = -R.\text{slope} = \Delta H_f^* - \Delta H_r^*$$

APPENDIX 2.4

A.2.4.1. List of programs for analysis and plotting of kinetic data.

	Quantities calculated
KD11	k_{1f} of first order forward and first order reverse reaction.
KD12	k_{1f} of first order forward and second order reverse reaction (e.g. proton abstraction)
KD21	k_{2f} of second order forward and first order reverse reaction.
KD22	k_{2f} of second order forward and second order reverse reaction.
K22R	k_{2r} of second order forward and second order reverse reaction.
SF11 SF12 SF21	Similar to KD11, KD12 and KD21 except that input data is from stopped-flow voltage-time trace.
BH11	ε and K. Benesi-Hildebrand treatment. 1st order forward and 1st order reverse reaction.
BH12	1st order forward and 2nd order reverse reaction.
BE12	Modified Benesi-Hildebrand equation for 1st order forward and 2nd reverse reaction.
TD25	$\Delta H^*, \Delta S^*$ for forward or reverse reactions.
DH	ΔH_{Total}.

Input data for programs.

A.2.4.2 Program KD11

NUMBERRUNS(number of sets of kinetic data)

NPT(number of points per data set)

OD0(initial optical density)

OD[1]	T[1]	(pairs of optical density and time(seconds) values)
⋮	⋮	
OD[NPT]	T[NPT]	

EPSILON(extinction coefficient; if not known then = 0)

LENGTHCELL(path length of cell)

VOLCELL(volume of cell in ml.)

CNC0(initial concentration of nitroaromatic)

ODEQ(equilibrium optical density)

BASEEQ(number of base equivalents)

VOLBASE(base volume in microlitres)

VOLOTHER(volume of co-solvent(ml) if a reaction product e.g. H_2O;if none = 0)

J W[J] (in pairs; point J given weighting W[J] ; if 0 no action; terminate list with 0; W[J] = 0 then omitted from least squares calculation)

DATA[5] (plotter axes text height	1	0.07"
	2	0.10"
	3	0.15"

TITLE e.g. 2,4,8-TN-1,5-DMN IN DMSO BASE ET_3N**

DATERUN e.g. 5/11/75**

WAVELENGTH e.g. 560NM**

TEMPERATURE e.g. 25.25** (centigrade)

OTHER(co-solvent e.g.␣␣H_2O =**; if VOLOTHER=0 then **; if VOLOTHER # 0 then number of characters in other e.g. 7)

A.2.4.3. Programs KD12, KD21 and KD22.

```
NUMBERRUNS
NPT
OD0
OD[1]             T[1]          (in pairs; time in seconds)
 |                 |
 |                 |
 |                 |
OD[NPT]           T[NPT]
EPSILON
LENGTHCELL
VOLCELL
CNC0(concentration of nitro compound uncorrected for dilution by base)
ODEQ
BASEEQ
VOLBASE
VOLOTHER
J                 W[J]          (see KD11)
DATA [5]
TITLE**
DATERUN**
WAVELENGTH**
TEMPERATURE**
OTHER**
LOTHER**
```

A.2.4.4. Programs K12R and K22R.

NUMBERRUNS

NPT

OD0

EPSILON

LENGTHCELL

OD[J]   TM[J]   (pairs; time in minutes)
⋮   ⋮
OD[NPT]   TM[NPT]

VOLCELL

CNC0(initial undiluted concentration of nitro compound; if set to 0 then ODEQ1 used)

ODEQ1(before dilution)

BASEEQ

VOLBASE

VOLOTHER

VOLCHANGE (volume of reaction mixture removed and replaced by solvent)

J   W[J]   (see KD11)

DATA[5]

TITLE

DATERUN**

WAVELENGTH**

TEMPERATURE**

OTHER**

A.2.4.5 Program SF11.

NUMBERRUNS

NPT

VIN(infinity voltage)

V[1]   TMS[1]   (in pairs; time in mS)
| |
| |
| |
| |
V[NPT]   TMS[NPT]

CNC0(nitro compound concentration before dilution)

BASEEQ

J   W[J]   (see KD11)

DATA[5]

TITLE e.g. SF P1 2,4,8-TN-1,5-DMN IN DMSO/H_2O(9:1) BASE NAOH**

DATERUN**

WAVELENGTH**

TEMPERATURE**

A.2.4.6. Program SF12 and SF21.

```
NUMBERRUNS
NPT
VIN
V0
V[1]            T[1]        (in pairs; time in seconds)
 |               |
 |               |
 |               |
 |               |
V[NPT]          T[NPT]
EPSILON
LENGTHCELL
CNC0
BASEEQ
J               W[J]        (see KD11)
DATA[5]
TITLE**
DATERUN**
WAVELENGTH**
TEMPERATURE**
```

A.2.4.7. Programs BH11, BH12 and BE12.

```
NUMBERRUNS
NPT
OD[1]       BASEEQ[1]       CNC0[1]       (in triplets)
 |            |               |
 |            |               |
 |            |               |
 |            |               |
OD[NPT]     BASEEQ[NPT]     CNC0[NPT]
J           W[J]            (see KD11)
DATA[5]
TITLE**
DATERUN**
WAVELENGTH**
TEMPERATURE**
```

A.2.4.8. Program RC11.

NUMBERUNS

NPT

K1[1]	BASEEQ[1]	(in pairs K1 = k_ψ)
¦	¦	
K1[NPT]	BASEEQ[NPT]	

CNC0

CD(concentration D :- A + B $\rightleftharpoons$ C + D; where D in excess; =1 for Meisenheimer complex formation)

J W[J]

DATA[5]

TITLE**

DATERUN**

WAVELENGTH**

TEMPERATURE**

OTHER e.g. H2O =** (for Meisenheimer complex formation D =**)

LOTHER e.g. 7(5)**

A.2.4.9. Program RC12.

NUMBERRUNS

NPT

K[1]	BASEEQ [1]	CORCNC0[1]
¦	¦	¦
K[NPT]	BASEEQ[NPT]	CORCNC0[NPT]

EPSILON

DATA [14]

DATA[5]

TITLE**

DATERUN**

WAVELENGTH**

TEMPERATURE**

A.2.4.10 Program TD25.

NUMBERRUNS

DATA [14] (alignment of graphs)

DATA [5]

NPT

TITLE**

DATERUN**

WAVELENGTH**

```
TEMP[1]        K2[1]        (in pairs; K2 = k_2)
   |              |
   |              |
   |              |
   |              |
TEMP[NPT]      K2[NPT]
```

A.2.4.11. Program DH.

NUMBERRUNS

NPT

```
KC[1]          TEMP[1]      (pairs; KC = equilibrium constant and
  |              |           temperature (°C))
  |              |
  |              |
  |              |
KC[NPT]        TEMP[NPT]
J              W[J]         (see KD11)
```

DATA [5]

TITLE**

DATERUN**

WAVELENGTH**

A.2.4.12.

PROGRAM K22R

```
JOB STCP-JE,CP,K22R
VOLUME 5000
CARA1 1,TR0(BASK),TR0(DATA)
****
'LIBRARY'(ED,SUBGROUPEDGP)
'LIBRARY'(ED,SUBGROUPSRA3)
'LIBRARY'(ED,SUBGROUPFSCE)
'LIBRARY'(ED,SUBGROUPSRF7)
'PROGRAM'(K22RBASERATES)
'INPUT' 1=TR0
'INPUT' 2=CR0
'OUTPUT' 1=LP0
'OUTPUT' 3=LP1
'COMPACT DATA'
'TRACE' 2
'BEGIN'
   'PROCEDURE' PLOT ARRT(A);
   'INTEGER' 'ARRAY' A;
   'ALGOL';
   'PROCEDURE'ARRTEXT(A);
   'ARRAY'A;
   'EXTERNAL';
   'BOOLEAN''PROCEDURE' TEST(N);
   'VALUE'N;
   'INTEGER'N;
   'EXTERNAL';
   'PROCEDURE'LSQPNW(NPT,X,Y,W,R,ERROR,STDV,ORDER,Q);
   'VALUE'NPT,ORDER;
   'INTEGER'NPT,ORDER;
   'REAL'ERROR,STDV;
   'ARRAY'X,Y,W,R,Q;
   'ALGOL';
   'INTEGER''ARRAY'DATA[1:50];
   'PROCEDURE'PLOTDISC(MODE,NAME,DATA,MONCHAN,CONSCHAN,
                                                XSIZE,YSIZE);
   'VALUE'MODE,MONCHAN,CONSCHAN,XSIZE,YSIZE;
   'INTEGER'MODE,MONCHAN,CONSCHAN,XSIZE,YSIZE;
   'INTEGER''ARRAY'DATA;
   'STRING'NAME;
   'ALGOL';
   'PROCEDURE'SETTEXT(X,Y,HT,THETA);
   'VALUE'X,Y,HT,THETA;
   'REAL'X,Y,HT,THETA;
   'ALGOL';
   'PROCEDURE'PLOTWRITE(S);
```

```
    'STRING'S;
    'ALGOL';
    'PROCEDURE'PLOTPRINT(X,I,J);
    'VALUE'X,I,J;
    'REAL'X;
    'INTEGER'I,J;
    'ALGOL';
    'PROCEDURE'STRARR(A,N,S);
    'ARRAY'A;
    'INTEGER'N;
    'STRING'S;
    'EXTERNAL';
    'INTEGER''PROCEDURE'INSTRARR(S,A);
    'STRING'S;
    'ARRAY'A;
    'EXTERNAL';
    'PROCEDURE'PLOTGRAPH(X,Y,C,N,XTITLE,YTITLE,TITLE,XMIN,XMAX,
                                                          YMIN,YMAX);
    'VALUE'C,N,XMIN,XMAX,YMIN,YMAX,XTITLE,YTITLE,TITLE;
    'REAL'XMIN,XMAX,YMIN,YMAX;
    'INTEGER'N;
    'ARRAY'X,Y;
    'INTEGER''ARRAY'C,XTITLE,YTITLE,TITLE;
    'ALGOL';
'PROCEDURE'VARRTEXT(A,N);
'VALUE'A,N;
'INTEGER'N;
'ARRAY'A;
'EXTERNAL';
'REAL'CNC0,BASEEQ,CORCNC0,VOLCELL,VOLBASE,RMSE,STDV,
VOLCHANGE,CORODEQ1,VOLOTHER,ODCELL,ODEQ1,ODEQ2,CBASE,
                                                   LPRIME,ROOTS;
    'INTEGER'NUMBERRUNS,NPT,I,J,K,EPSILON,LENGTHCELL,LOTHER;
    'INTEGER''ARRAY'XT,YT,TT[1:20],TEMP,DATERUN,WAVEL[1:3],OTHER[1:10];
    'IF'TEST(1) 'THEN' SELECT INPUT(2) 'ELSE' SELECT INPUT(1);
    SELECT OUTPUT(1);
    NUMBERRUNS: = READ;
    'FOR'I: = 1'STEP'1'UNTIL'NUMBERRUNS'DO'
    'BEGIN'NPT: = READ;
        ODCELL: = READ;EPSILON: = READ;LENGTHCELL: = READ;
        'BEGIN''INTEGER''ARRAY'C[1:NPT];
'ARRAY'OD,T,R,W,CBTA[1:NPT],TM,POD[1:NPT+2],Q[1:2];
'FOR'J: = 1'STEP'1'UNTIL'NPT'DO''BEGIN'
OD[J]: = READ;
OD[J]: = OD[J]-ODCELL;
CBTA[J]: = OD[J]/(EPSILON*LENGTHCELL);
TM[J]: = READ;
```

```
T[J]: = TM[J]*60;
C[J]: = 3;
'END';
VOLCELL: = READ;CNC0: = READ;ODEQ1: = READ;BASEEQ: = READ;VOLBASE: = READ;
VOLOTHER: = READ;VOLCHANGE: = READ;ODEQ2: = READ;
ODEQ1: = ODEQ1-ODCELL;
ODEQ2: = ODEQ2-ODCELL;
CORODEQ1: = ODEQ1*(VOLCELL+(VOLBASE+VOLOTHER)/1000-VOLCHANGE)/
(VOLCELL+(VOLBASE+VOLOTHER)/1000);
'IF' CNC0=0'THEN' CORCNC0 :=CORODEQ1/(EPSILON * LENGTHCELL) 'ELSE'
CORCNC0 :=CNC0 * VOLCELL/(VOLCELL + (VOLBASE +VOLOTHER)/1000) *
(VOLCELL + (VOLBASE +VOLOTHER)/1000 - VOLCHANGE)/(VOLCELL + (VOLBASE
+VOLOTHER)/1000);
CBASE :=CORCNC0 * BASEEQ;
LPRIME :=(ODEQ2 2)/(((CBASE * LENGTHCELL * EPSILON) - ODEQ2) * ((CORCNC0 *
LENGTHCELL * EPSILON) - ODEQ2));
ROOTS :=SQRT((LPRIME 2 * ((CBASE - CORCNC0) 2)) + (4*LPRIME * CBASE*
CORCNC0));
'FOR' J := 1 'STEP' 1 'UNTIL' NPT 'DO'
'BEGIN' POD [J] :=-LN(((2 * CBTA [J] * (1 - LPRIME)) + (LPRIME * (CBASE+CORCNC0))
- ROOTS)/((2 * CBTA [J] * (1- LPRIME)) + (LPRIME *  (CBASE +CORCNC0)) +ROOTS))/
ROOTS;
W [J] :=1;
'END';
'FOR' J :=READ 'WHILE' J =0 'DO'
'BEGIN' W[J] :=READ;C[J] :=7;
'END';
LSQPNW(NPT,T,POD,W,R,RMSE,STDV,1,Q);
K:±0;
'FOR' J :=1 'STEP' 1 'UNTIL' NPT 'DO'
'BEGIN'
'IF' R [J]<0 'THEN' R [J] :=-R [J];
'IF' R [J]>2 * RMSE'AND' W[J]  #0 'THEN'
'BEGIN'
W [J] :=0;C[J] :=6;K :=K+1;
'END';'END';
'IF' K=0 'THEN' 'GO   TO' NEXT;
'IF' K<NPT -2 'THEN' LSQPNW(NPT,T,POD,W,R,RMSE,STDV,1,Q);
NEXT :'BEGIN'
'REAL' K2;
K2 :=Q [2];
'IF' I = 1 'THEN''BEGIN' J := NUMBERRUNS * 700;
PLOTDISC(0, '('STCP-JE%%PNMNBASEK22R')', DATA,3,J,5,4);
'END';
TM [NPT + 1] :=0;
TM [NPT +2] :=TM [NPT] ;
POD [NPT + 1] :=Q[1];
```

```
POD[NPT + 2] :=Q[2] * T[NPT] + Q[1];
DATA[5]:=READ;
STRARR(XT,J,'('TIME%IN%MINUTES')');
STRARR(YT,J,'('2ND%ORDER%REVERSE%FUNCTION')');
INSTRARR('('**')',TT);
PLOTGRAPH(TM,POD,C,NPT,XT,YT,TT,0,0,0,0);
INSTRARR('('**')',DATERUN);
NEWLINE(4);
WRITETEXT('(''('5S')'DATERUN%')');
ARRTEXT(DATERUN);
SPACE(16);
ARRTEXT(TT);
INSTRARR('('**')',WAVEL);
INSTRARR('('**')',TEMP);
INSTRARR('('**')',OTHER);
NEWLINE(3);
SPACE(5);
WRITETEXT('('WAVELENGTH%=')');
ARRTEXT(WAVEL);
SPACE(5);
WRITETEXT('('CONCENTRATION%NITRO%COMPOUND(M)%=')');
OUTPUT(CORCNC0);
NEWLINE(1);
SPACE(3);
VARRTEXT(TEMP,7);
WRITETEXT('('%%DEG%CENTIGRADE')');
WRITETEXT('(''('8S')'BASE%EQUIVALENTS%=')');
PRINT(BASEEQ,4,0);
NEWLINE(2);
SPACE(5);
WRITETEXT('('EPSILON%=')');
PRINT(EPSILON,5,0);
WRITETEXT('('LITRES/MOLE/CM')');
NEWLINE(3);
WRITETEXT('(''('20S')'CELL%VOLUME%=')');
PRINT(VOLCELL,1,1);
WRITETEXT('('ML')');
SPACE(10);
WRITETEXT('('INITIAL%BASE%VOLUME%=')');
PRINT(VOLBASE,3,3);
WRITETEXT('('MICROLITRES')');
'IF' VOLOTHER#0'THEN' 'BEGIN'
NEWLINE(3);
SPACE(20);
WRITETEXT('('INITIAL%VOLUME')');
LOTHER :=READ;
VARRTEXT(OTHER,LOTHER);
PRINT(VOLOTHER,3,1);
WRITETEXT('('MICROLITRES')');
'END';
NEWLINE(3);
SPACE(20);
```

```
WRITETEXT('('VOLUME%CHANGE%=')');
PRINT(VOLCHANGE,1,2);
WRITETEXT('('ML')');
NEWLINE(3);
SPACE(20);
WRITETEXT('('FINAL%EQUILIBRIUM%OPTICAL%DENSITY%=')');
PRINT(ODEQ2,1,3);
NEWLINE(4);
WRITETEXT('(''('20S')'TIME%IN%MINUTES'('5S')'OPTICAL%DENSITY'('5S')'
2ND%ORDER%REVERSE%FN')');
NEWLINE(2);
SPACE(24);
'FOR'J:= 1'STEP'1'UNTIL'NPT'DO'
'BEGIN'PRINT(TM[J],3,0);
SPACE(13);
PRINT(OD[J],1,3);
SPACE(14);
PRINT(POD[J],3,3);
NEWLINE(1);
SPACE(24);
'END';
NEWLINE(4);
SPACE(20);
WRITETEXT('('SECOND%ORDER%REVERSE%RATE%CONSTANT(LITRES/MOLE/
SECOND)%=')');
OUTPUT(K2);
NEWLINE(6);
SPACE(20);
WRITETEXT('('STANDARD%DEVIATION%=')');
OUTPUT(STDV);
PAPERTHROW;
SETTEXT(0.3,3.6,0.07,0);
PLOTWRITE('('DATE%RUN')');
PLOTARRT(DATERUN);
PLOTWRITE('('%%%%')');
PLOTARRT(TEMP);
PLOTWRITE('('%DEG%CENTIGRADE%%%%')');
SETTEXT(0.18,3.4,0.07,0);
PLOTARRT(WAVEL);
PLOTWRITE('('%%%%CONCN%NITRO%CMPD%=')');
PLOTPRINT(CORCNC0,1,8);
PLOTWRITE('('M')');
SETTEXT(0.3,3.2,0.07,0);
PLOTWRITE('('BASE%EQ%=')');
PLOTPRINT(BASEEQ,4,0);
SETTEXT(2.6,0.8,0.07,0);
PLOTWRITE('('K%2ND%ORDER%=')');
```

```
K :=-1;
'FOR' K :=K+1 'WHILE' K2*(10  K) 'LE' 1 'DO';
PLOTPRINT(K2,1,K+3);
'IF' I=NUMBERRUNS 'THEN'
PLOTDISC(-1,'('')',DATA,0,0,0,0);
'END';
'END';
'END';
'END';
```

APPENDIX 2.5 Courses attended during the period of this study in fulfilment of C.N.A.A. regulations

1974-5

Introduction to chromatography.

A research colloquium on rapid reaction techniques was given.

1975-6

Use of the maximop computer terminal system(lecture and practical).

A research colloquium on the reaction of base with polynitro-dimethylnaphthalenes was given.

1976-7

A one day symposium on the advances in ultrasonic medical equipment was attended.

Various research colloquia given by internal and external lecturers at Kingston Polytechnic were attended during the period of this study.

APPENDIX 3.1 Reaction of 2,4,5,7-tetranitro-1-methylnaphthalene(199) with base

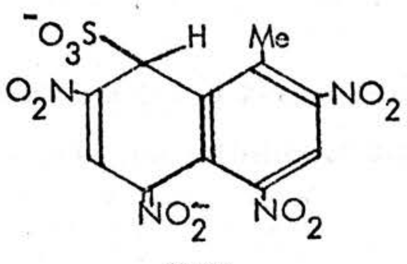
As mentioned in section 1.3.4 the reaction of 2,4,5-trinitro-1-methylnaphthalene with base has only been studied qualitatively[130]. However, as compound (199) is intermediate in structure between polynitro-naphthalenes and polynitro-dimethylnaphthalenes it was thought to be of value to study the reaction of base with this compound.

Alkoxide and diethylamine

The products of the reaction of methoxide ion with compound (199) in d_6-DMSO solution were studied by 90MHz PMR. Broadened spectra were obtained probably due to the presence of free radicals. It would appear that substitution products are mainly formed. Reaction of compound (199) with diethylamine in d_6-DMSO also gave a broadened PMR spectrum probably for the reasons outlined above.

Sulphite ion

The products of reaction of from one to three equivalents of sulphite ion with compound (199) in aqueous d_6-DMSO were studied by 90MHz PMR. The spectrum is shown in fig A.3.1.1(b) and would appear to indicate formation of the C-8 mono-adduct (200) as the C-8 aromatic proton resonance of compound (199) is replaced by one in the mid-field region(i.e. resonance is due to a proton attached to an sp^3 carbon). Addition at C-8 rather than C-6 has been noted for other similarly substituted compounds(e.g. 1,4,5,7-tetranitro-2,3-dimethylnaphthalene)[109]. Complex (200) possesses a visible absorbtion maximum at 522nm.



(200)

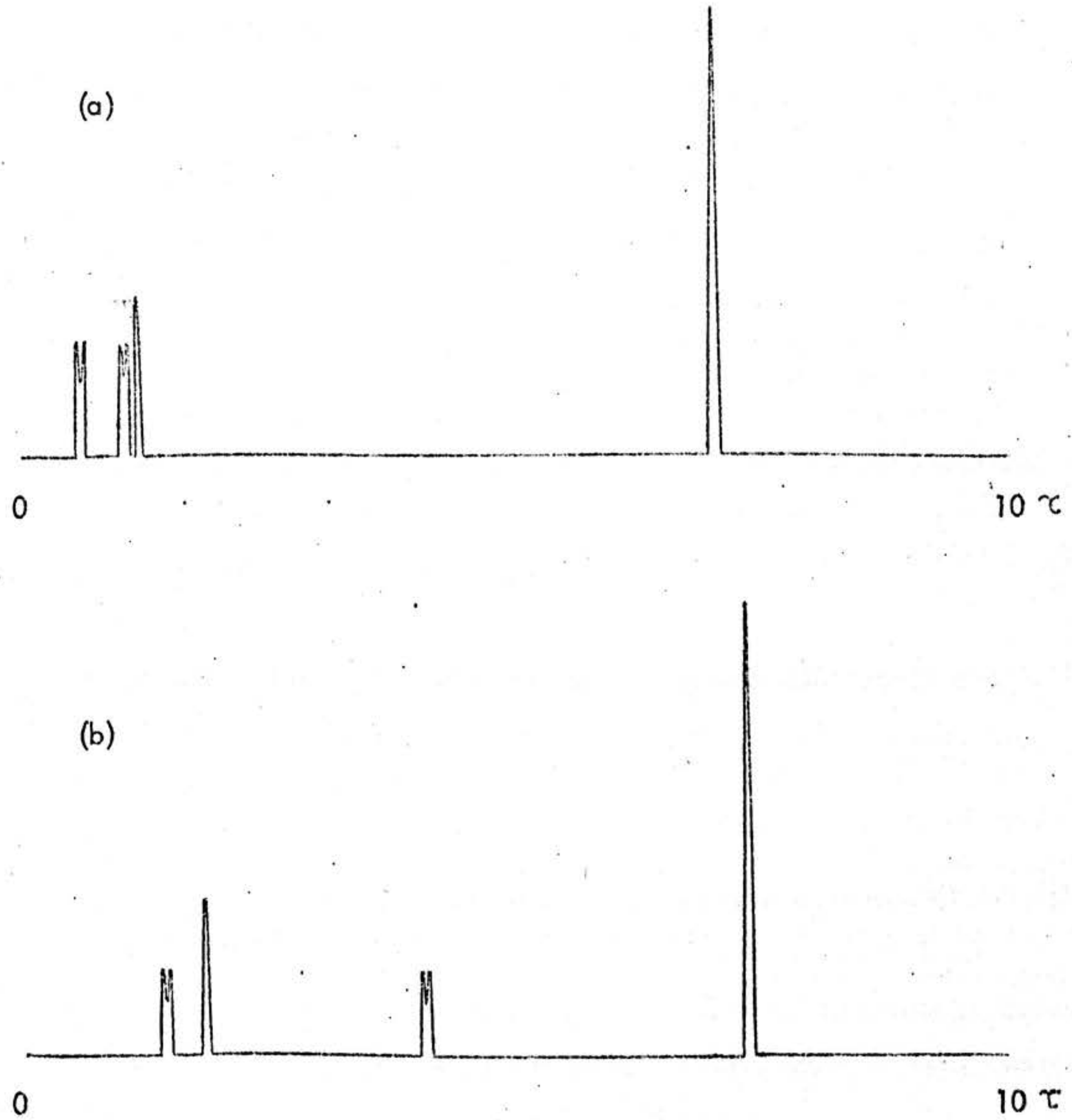


Fig.A.3.1.1 (a) PMR spectrum of 2,4,5,7-tetranitro-1-methylnaphthalene(199) in d_6-DMSO. (b) Spectrum after the addition of 3 equivalents of sodium sulphite.

Experimental Section

Preparation of 2,4,5,7-tetranitro-1-methylnaphthalene(199) was achieved by the addition, with stirring, of 1-methylnaphthalene(2g) to a solution containing sulphuric acid(d = 1.84,50cm^3) and nitric acid(d = 1.5,5cm^3) cooled in an ice-bath. The mixture was then removed from the ice-bath, stirred at room temperature for 1 hour before precipitation on ice(200g). Filtration and washing with water was followed by recrystallisation from glacial acid and drying in vacuo at 70°C.

2,4,5,7-tetranitro-1-methylnaphthalene(0.0321g) was dissolved in d_6-DMSO(0.4cm^3) and the 90MHz PMR spectrum recorded(fig.A.3.1.1(a)):- τ 0.89(1H,s),0.44 and 0.79(2H,ABq,J_{AB} 2Hz) and 6.97(3H,s).

Methoxide ion

Compound (199)(0.057g) was dissolved in d_6-DMSO(0.4cm^3) and 2M sodium methoxide-d_3 in CD_3OD(0.05cm^3) added. The 90MHz PMR spectrum was recorded but gave only broadened lines.

Diethylamine

Compound (199)(0.0335g) was dissolved in d_6-DMSO(0.4cm^3) and diethylamine(0.025cm^3) added. The 90MHz PMR spectrum was recorded but this showed broadened lines only.

Sulphite ion

Compound (199)(0.0644g) was dissolved in aqueous d_6-DMSO(1.2cm^3) in a stoppered 10cm^3 QF conical flask and 1M sodium sulphite in D_2O (0.6cm^3) added with magnetic stirring. The 90MHz PMR FT spectrum of 0.4cm^3 of the filtered reaction mixture was recorded(fig.A.3.1.1(b)):- τ 1.41 and 4.01(2H,ABq,J_{AB} 1.6Hz),1.82(1H,s) and 7.32(3H,s).

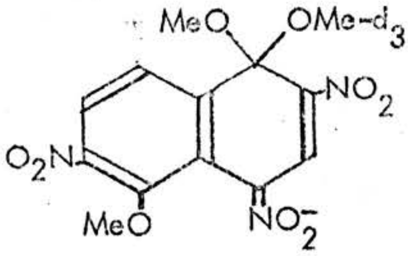
A few microlitres of the PMR sample were diluted with DMSO(3cm^3) and the UV-visible spectrum recorded; λ_{max} was at 522nm.

APPENDIX 3.2 Reaction of several polynitrodimethoxynaphthalenes with base

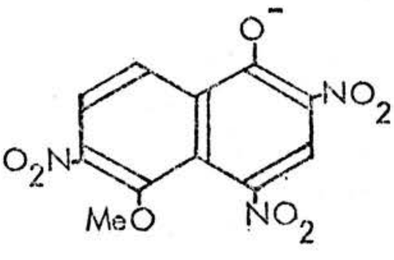
A.3.2.1 2,4,6-Trinitro-1,5-dimethoxynaphthalene(201)

(A) Methoxide and hydoxide ions

The products of the reaction of 1 equivalent of methoxide ion with 2,4,6-trinitro-1,5-dimethoxynaphthalene in d_6-DMSO were studied by PMR. The spectrum is shown in fig.A.3.2.1(b) and would appear to indicate formation of the C-1 mono-adduct(202).

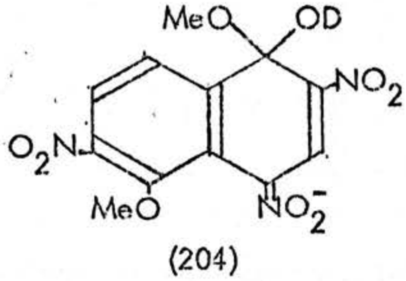


(202)



(203)

The PMR spectrum of the products formed by reaction of sodium deuterioxide with compound (201) in d_6-DMSO is shown in fig.A.3.2.1(c). Formation of the 2,4,6-trinitro-1-methoxy-5-naphthalate anion (203) by displacement of methoxide is indicated. Displacement of methoxide ion by hydroxide ion from 2,4,6-trinitroanisole to form the picrate ion has been noted previously[34] and it is likely that the unstable species (204) is formed prior to compound (203).



(204)

Complex (202) is apparently formed also, by reaction of unreacted compound (201) with the methoxide liberated in the reaction with hydroxide ion.

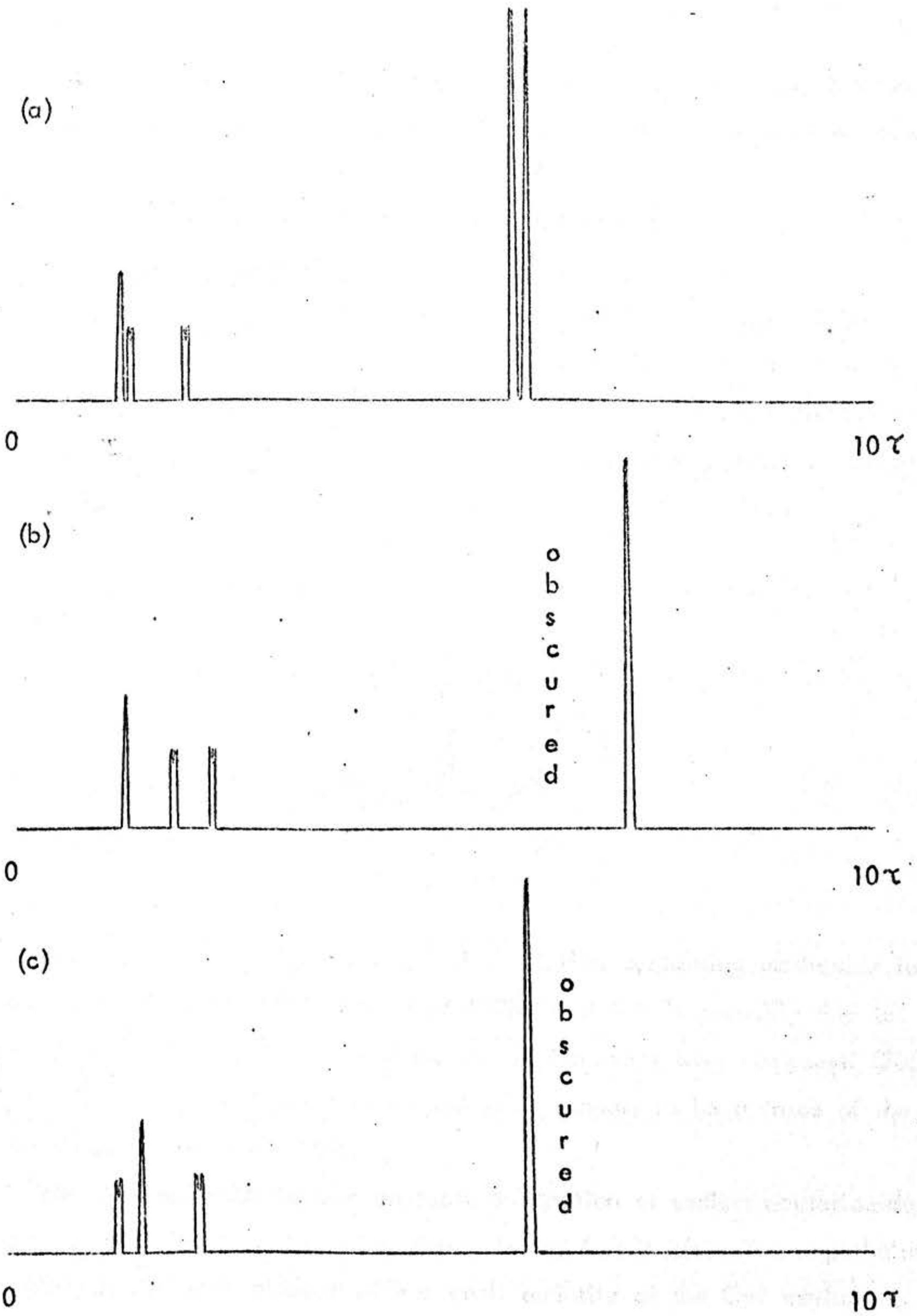


Fig.A.3.2.1 (a) PMR spectrum of 2,4,6-trinitro-1,5-dimethoxynaphthalene(201) in d_6-DMSO. (b) Spectrum after the addition of 1 equivalent of sodium methoxide-d_3 to a solution of compound (201) in d_6-DMSO. (c) Spectrum after the addition of 1 equivalent of sodium deuterioxide to a solution of compound (201) in d_6-DMSO.

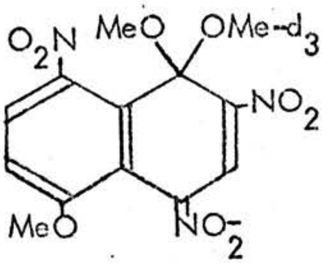
(B) Other bases

PMR indicates that compound (203) is the only product formed on reaction of compound (201) with diethylamine in d_6-DMSO. Hydrazine hydrate appears to give the C-1 substitution product.

A.3.2.2 2,4,8-Trinitro-1,5-dimethoxynaphthalene(205)

(A) Methoxide and hydroxide ion

One equivalent of methoxide ion reacts with 2,4,8-trinitro-1,5-dimethylnaphthalene in d_6-DMSO to yield products which have the PMR spectrum shown in fig.A.3.2.2(b). Formation of the C-1 adduct (206) is indicated and this decomposes over a period of several days to give the naphthalate anion (207) analogous to compound (203).



(206)

The visible absorbtion maximum of a solution containing methoxide ion and compound (205) in DMSO occurs at 497nm and this is probably due to compound (206). Two equivalents of methoxide ion react with compound (205) in d_6-DMSO to give compound (206) and what appears to be a trace of the 1,3-diadduct, as shown by PMR.

The PMR spectrum for the products of reaction of sodium deuterioxide and compound (205) in d_6-DMSO is shown in fig.A.3.2.2(c). The naphthalate anion (207) is the main product with a small quantity of the C-1 methoxy addition complex (206) produced by a mechanism similar to the reaction of compound (201).

(B) Other bases

Reaction of compound (205) and diethylamine in d_6-DMSO yields a

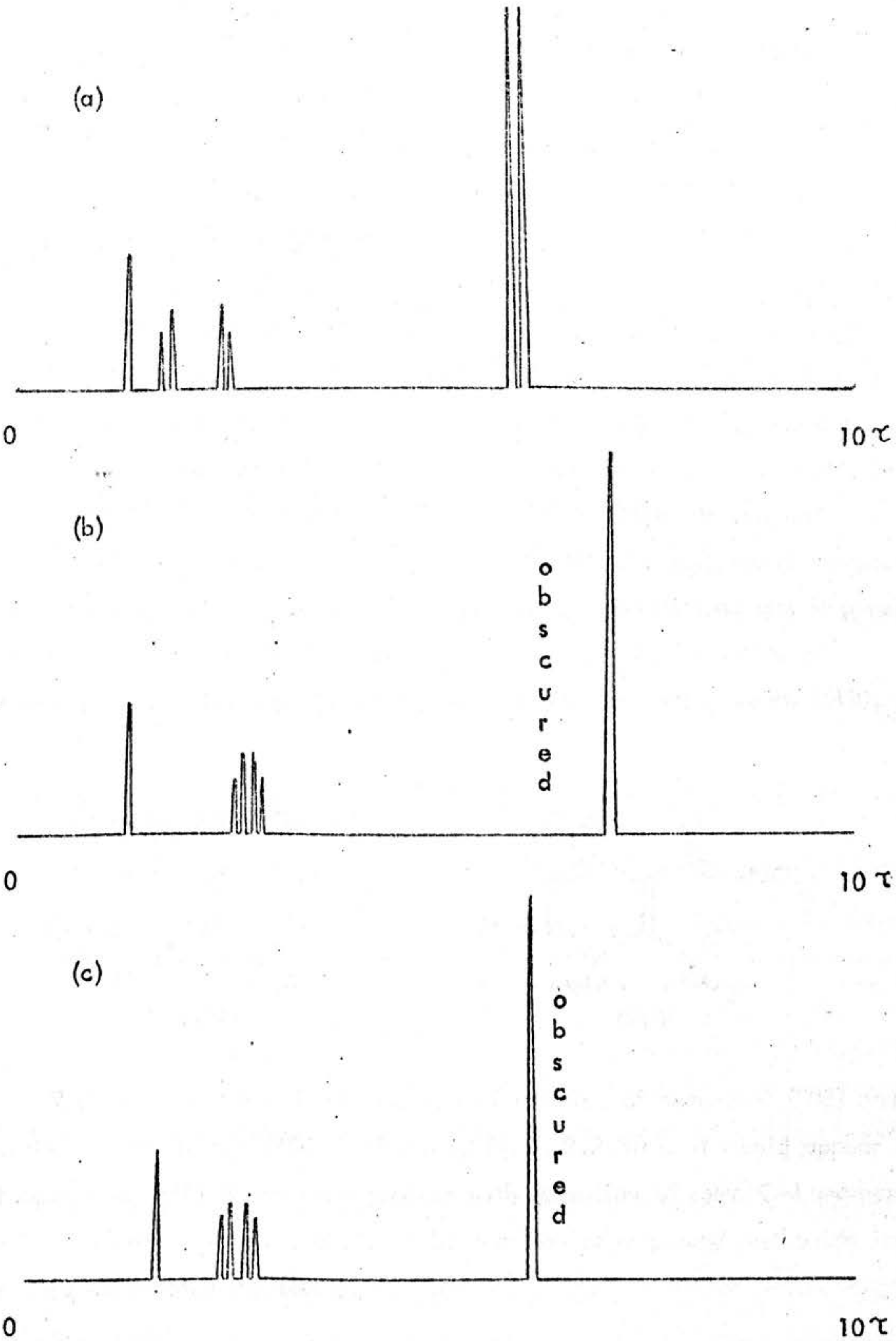


Fig. A.3.2.2 (a) PMR spectrum of 2,4,8-trinitro-1,5-dimethoxynaphthalene(205) in d_6-DMSO. (b) Spectrum after the addition of 1 equivalent of sodium methoxide-d_3 to a solution of compound (205) in d_6-DMSO. (c) Spectrum after the addition of 1 equivalent of sodium deuterioxide to a solution of compound (205) in d_6-DMSO.

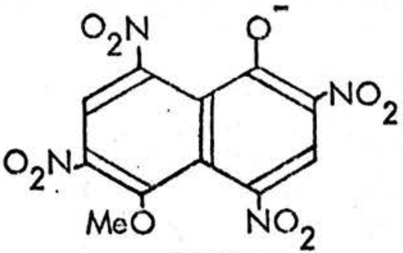
product which gives a PMR spectrum characteristic of compound (207). Hydrazine hydrate would appear to give the C-1 substitution product on reaction with compound (205) in d_6-DMSO, as shown by PMR.

A.3.2.3 2,4,6,8-Tetranitro-1,5-dimethoxynaphthalene(208)

(A) Methoxide and hydroxide ions

One equivalent of methoxide ion reacts with 2,4,6,8-tetranitro-1,5-dimethoxynaphthalene in d_6-DMSO to give a product which has the PMR spectrum as shown in fig.A.3.2.3(b). Formation of the C-1 adduct (209) is indicated, but not the C-3 isomer which would probably undergo rapid conversion into compound (209) before PMR measurements could be made. The visible absorbtion maximum of a solution containing methoxide ion and compound (208) in DMSO occurs at 486nm. This may be assigned to compound (209). Complex (209) is unstable in the presence of excess base and it gives a PMR spectrum similar to that obtained for the product of reaction of deuterioxide ion with compound (208), due to the naphthalate anion (210).

(209)



(210)

The PMR spectrum of the products of reaction of compound (208) and deuterioxide ion in d_6-DMSO is shown in fig.A.3.2.3(c). It would appear that compound (210) is the main product with formation of some C-1 methoxy addition complex (209) (i.e. produced by reaction of displaced methoxide ion with unreacted compound (208)).

(B) Other bases

Reaction of compound (208) with diethylamine or hydrazine hydrate in d_6-DMSO would seem to give substitution products as the only stable species, as shown by PMR.

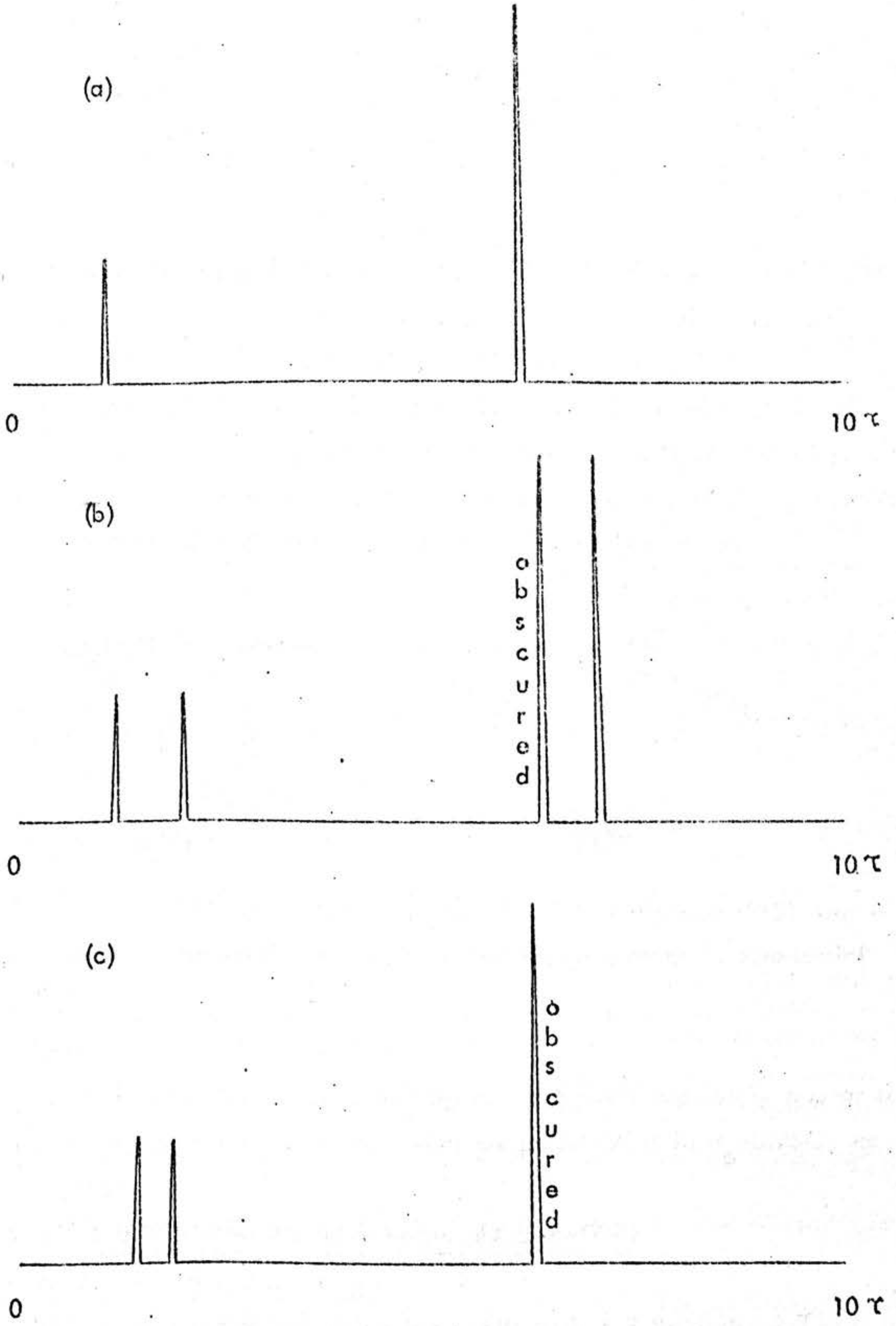


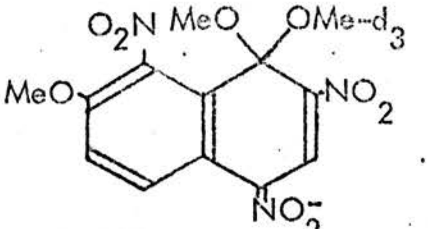
Fig.A.3.2.3 (a) PMR spectrum of 2,4,6,8-tetranitro-1,5-dimethoxynaphthalene (208) in d_6-DMSO. (b) Spectrum after the addition of 1 equivalent of sodium methoxide-d_3 to a solution of compound (208) in d_6-DMSO. (c) Spectrum after the addition of 1 equivalent of sodium deuterioxide to a solution of compound (208) in d_6-DMSO.

A.3.2.4 2,4,8-Trinitro-1,7-dimethoxynaphthalene(211)

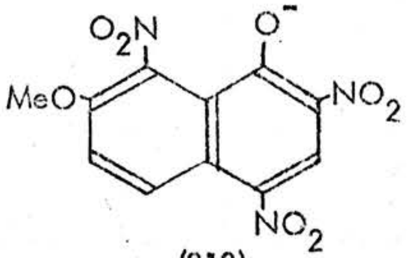
(A) Methoxide and hydroxide ion

One equivalent of methoxide ion reacts with compound (211) in d_6-DMSO to give a product which possesses the PMR spectrum shown in fig.A.3.2.4(b). This is probably due to the C-1 addition complex (212). The visible absorbtion maximum of a solution containing compound (211) and methoxide ion in DMSO occurs at 510nm with a shoulder at 460nm.

The PMR spectrum shown by the products of reaction of deuterioxide ion and compound (211) in d_6-DMSO solution is given in fig.A.3.2.4(c). Formation of the naphthalate anion (213) and also compound (212)(by reaction of compound (211) with displaced methoxide ion) probably occurs.



(212)



(213)

Compound (211) in d_6-DMSO is hydrolysed to compound (213) over a period of days by the small quantity of water always present in commercial d_6-DMSO.

(B) Other bases

Diethylamine, benzylamine and hydrazine hydrate separately appear to give substitution products on reaction with compound (211) in d_6-DMSO, as shown by PMR.

A.3.2.5 1,3,8-Trinitro-2,7-dimethoxynaphthalene(214)

(A) Methoxide and hydroxide ions

One equivalent of methoxide ion reacts with 1,3,8-trinitro-2,7-dimethoxynaphthalene in d_6-DMSO to yield a product which gives the PMR spectrum shown in fig.A.3.2.5(b). The C-4 adduct (215) would appear to be formed. The visible absorbtion maximum of a solution containing compound (214)

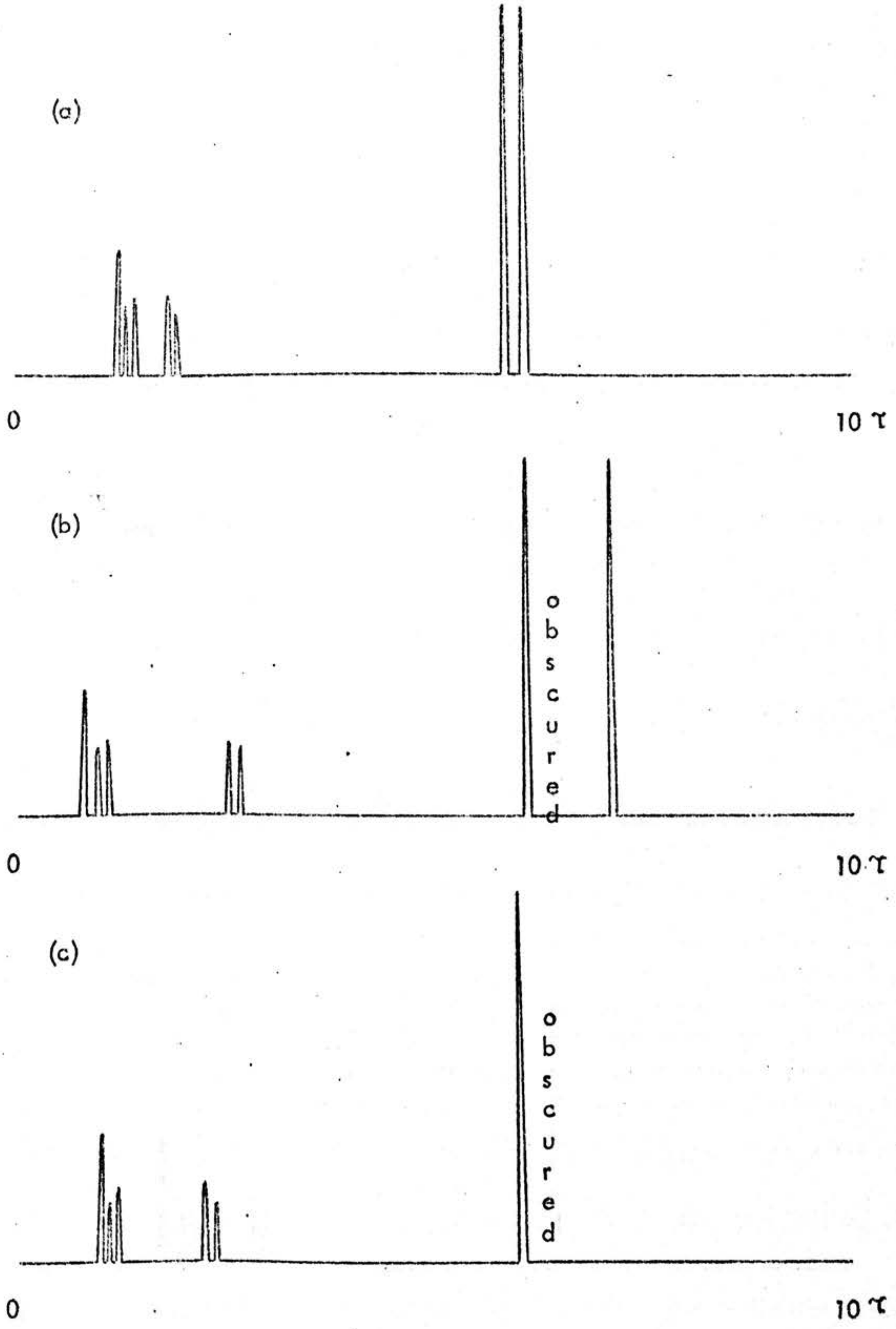


Fig.A.3.2.4 (a) PMR spectrum of 2,4,8-trinitro-1,7-dimethoxynaphthalene(211) in d_6-DMSO. (b) Spectrum after the addition of 1 equivalent of sodium methoxide-d_3 to a solution of compound (211) in d_6-DMSO. (c) Spectrum after the addition of 1 equivalent of sodium deuterioxide to a solution of compound (211) in d_6-DMSO.

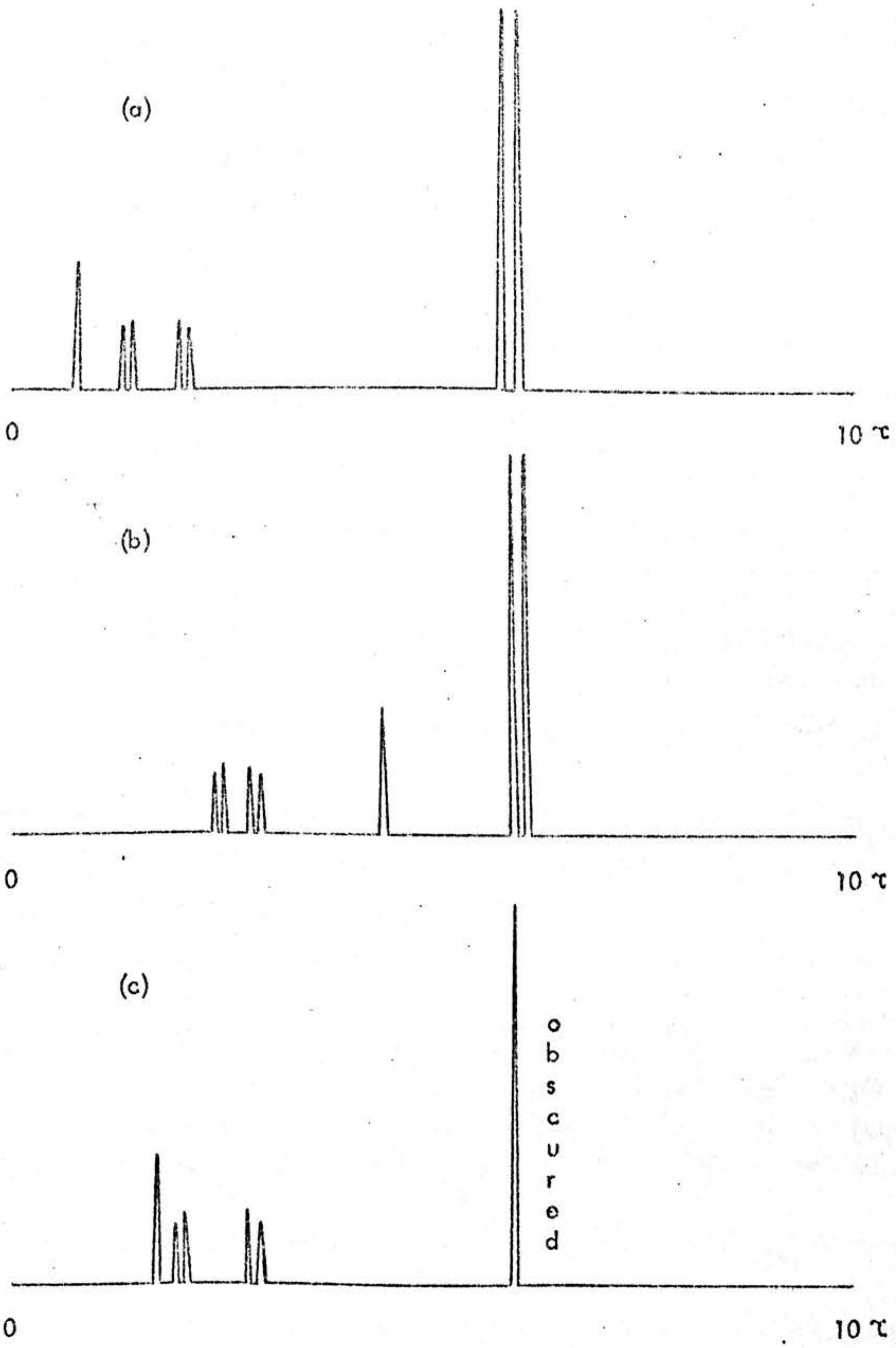
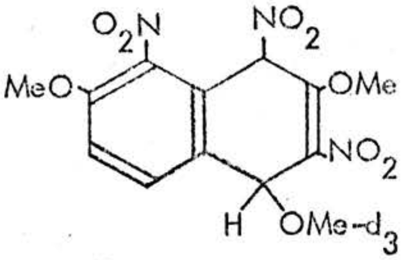
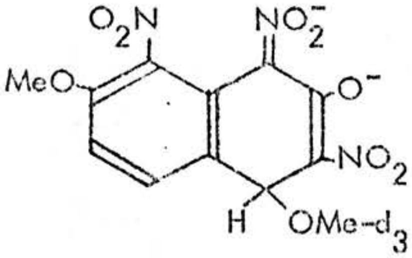


Fig.A.3.2.5 (a) PMR spectrum of 1,3,8-trinitro-2,7-dimethoxynaphthalene(214) in d_6-DMSO. (b) Spectrum after the addition of 1 equivalent of sodium methoxide-d_3 to a solution of compound (214) in d_6-DMSO. (c) Spectrum after the addition of 1 equivalent of sodium deuterioxide to a solution of compound (214) in d_6-DMSO.

and methoxide ion in DMSO occurs at 455nm. PMR indicates that addition of excess base to a d_6-DMSO solution containing compound (215) appears to form the C-4 adduct of the naphthalate anion (216).

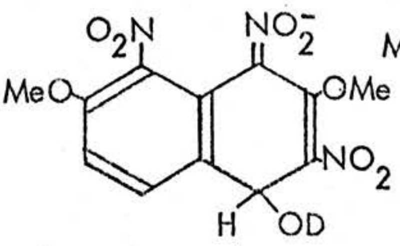


(215)

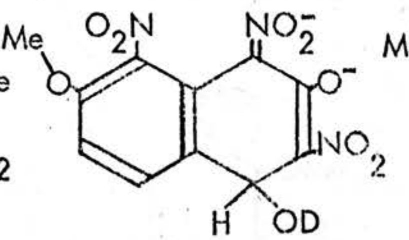


(216)

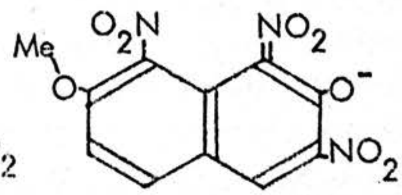
PMR indicates that the reaction of deuterioxide ion with compound (214) in d_6-DMSO is more complicated than the deuterioxide-polynitrodimethoxynaphthalene reactions considered previously. It would appear that the unstable C-4 addition product (217) is formed, followed by the C-4 adduct of the naphthalate anion (218); and the naphthalate anion (219). A small amount of compound (216) also seems to be produced by reaction of compound (214) with liberated methoxide ion. Fig.A.3.2.5(c) shows the major product of the reaction, namely compound (219).



(217)



(218)



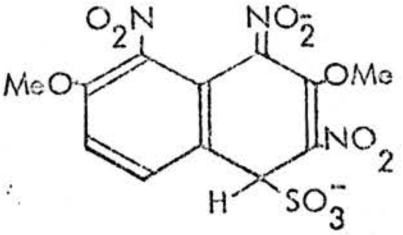
(219)

(B) Amines

PMR indicates that amines react with compound (214) in d_6-DMSO solution to give the following products:- diethylamine produces compound (219); hydrazine hydrate probably gives a substitution product; and benzylamine possibly gives an unstable C-4 addition complex.

(C) Sulphite ion

Three equivalents of sulphite ion react with compound (214) in aqueous d_6-DMSO to give a product with PMR spectrum as shown in fig.A.3.2.6(b). Formation of the C-4 adduct (220) is indicated.



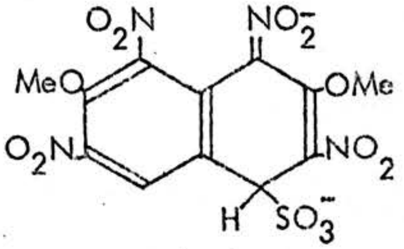
(220)

The visible absorbtion maximum of a solution containing sulphite ion and compound (214) in DMSO occurs at 475nm.

A.3.2.6 1,3,6,8-Tetranitro-2,7-dimethoxynaphthalene(221)

(A) Sulphite ion

The product of the reaction of two equivalents of sulphite ion with compound (221) in aqueous d_6-DMSO gives a PMR spectrum which is shown in fig.A.2.3.7(b). Formation of the C-4 mono-addition complex (222) is indicated. The visible absorbtion maximum of a DMSO solution containing compound (221) and sulphite ion occurs at 458nm.



(222)

A.3.2.7 1,4,5-Trinitro-2,6-dimethoxynaphthalene(223)

(A) Methoxide ion

The PMR spectrum of the reaction product given by one equivalent of methoxide ion and 1,4,5-trinitro-2,6-dimethoxynaphthalene in d_6-DMSO is

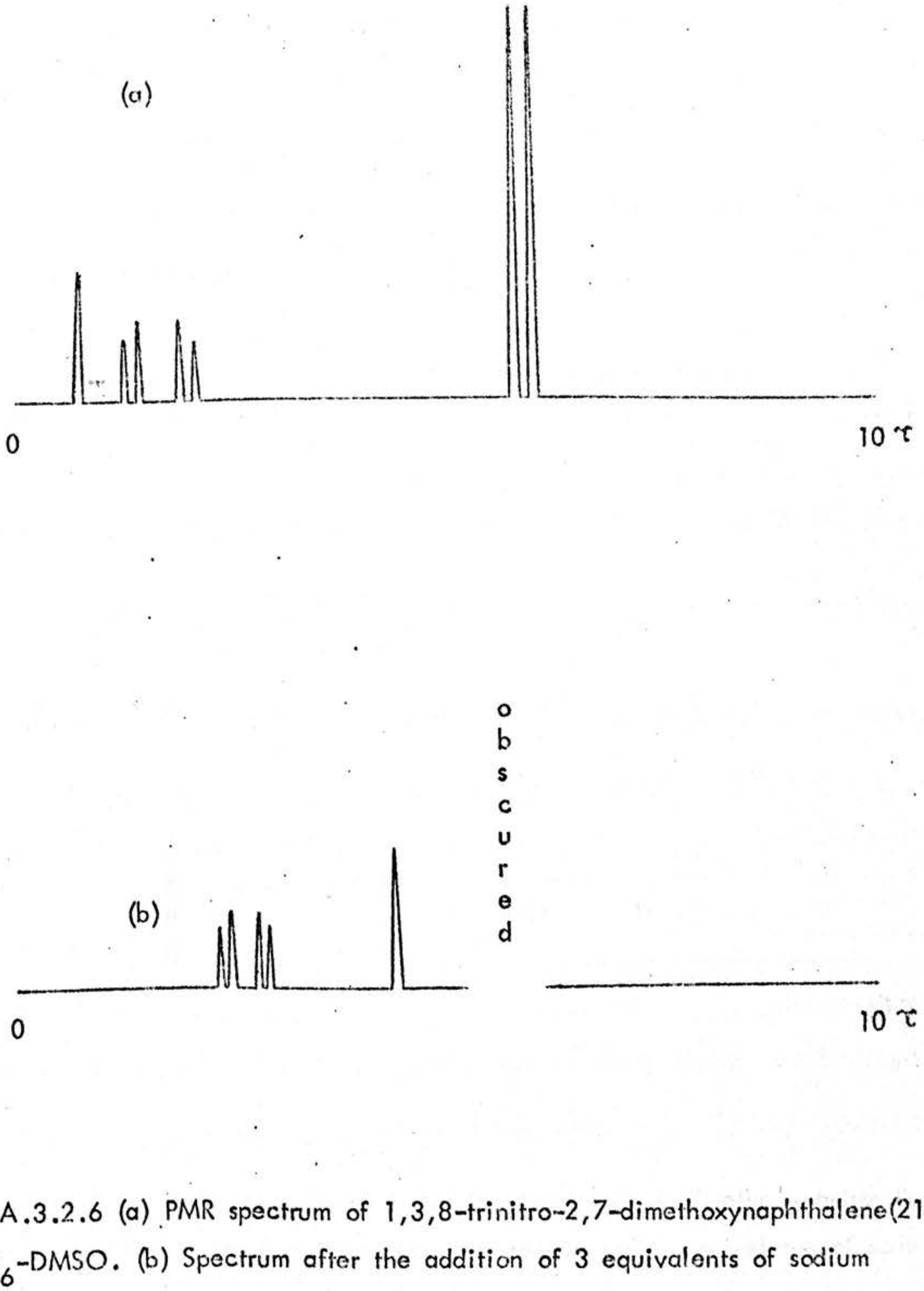


Fig. A.3.2.6 (a) PMR spectrum of 1,3,8-trinitro-2,7-dimethoxynaphthalene (214) in d_6-DMSO. (b) Spectrum after the addition of 3 equivalents of sodium sulphite.

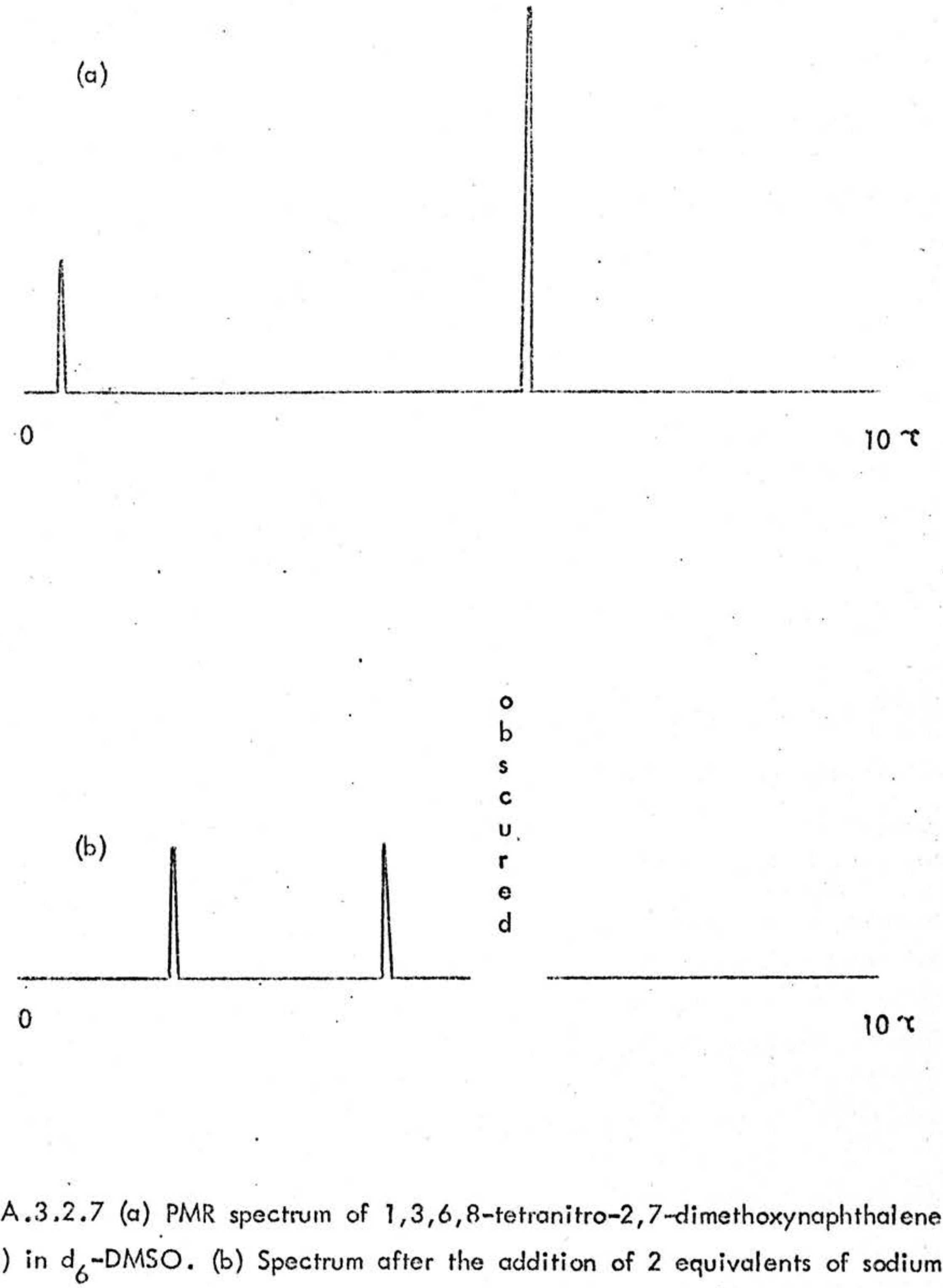
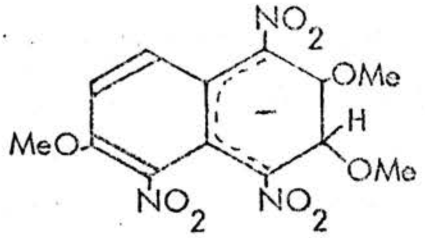


Fig.A.3.2.7 (a) PMR spectrum of 1,3,6,8-tetranitro-2,7-dimethoxynaphthalene (221) in d_6-DMSO. (b) Spectrum after the addition of 2 equivalents of sodium sulphite.

not clearly identified but it appears that formation of the C-3 addition complex (224).



(224)

A.3.2.8 2,4,6-Trinitro-1,5-dimethoxynaphthalene(201)

2,4,6-Trinitro-1,5-dimethoxynaphthalene was prepared by the method of Thomson and Race[211].

1,5-Diacetoxynaphthalene(10g) was added gradually to a well-stirred solution of nitric acid(d = 1.42,50cm^3) at 50°C. When addition was complete the suspension was cooled rapidly to 0°C and the product filtered off and washed with water. Recrystallisation from glacial acetic acid gave yellow needles of 2,4,6-trinitro-5-acetoxy-1-naphthol.

A suspension of 2,4,6-trinitro-5-acetoxy-1-naphthol(2g) in sodium hydroxide solution(20cm^3;2%) was boiled. The solution was then diluted with water and acidified. The precipitate was filtered off and recrystallised from dilute acetic acid to give yellow needles of 2,4,6-trinitro-1,5-dihydroxynaphthalene.

A suspension of 2,4,6-trinitro-1,5-dihydroxynaphthalene(1g) in ether (50cm^3) was methylated with diazomethane to give 2,4,6-trinitro-1,5-dimethoxynaphthalene.M.Pt.238°C.

2,4,6-Trinitro-1,5-dimethoxynaphthalene(0.0323g) was dissolved in d_6-DMSO(0.4cm^3) and the 90MHz PMR FT spectrum recorded(fig.A.3.2.1(a)):- τ 1.25(1H,s),1.29 and 1.98(2H,ABq,J_{AB} 2.0Hz),5.82(3H,s) and 5.95(3H,s).

(A) Methoxide and hydroxide ions

Compound (201)(0.0368g) was dissolved in d_6-DMSO(0.4cm^3) and 2M sodium methoxide-d_3 in CD_3OD(0.06cm^3) added. The 90MHz FT PMR spectrum was recorded(fig.A.3.2.1(b)):- τ 1.29(1H,s),1.87 and 2.31(2H,ABq,J_{AB} 2.2Hz), 6.09(3H,s) and 7.17(3H,s).

Compound (201)(0.030g) was dissolved in d_6-DMSO(0.4cm^3) and 5M sodium deuterioxide(0.02cm^3) added. The 90MHz FT PMR spectrum was recorded (fig.A.3.2.1(c)):- τ 1.50(1H,s),1.23 and 2.20(2H,ABq,J_{AB} 2.2Hz) and 6.06 (3H,s); and lines due to compound (202).

A.3.2.9 2,4,8-Trinitro-1,5-dimethoxynaphthalene(205)

1,5-dimethoxynaphthalene(10.17g) in glacial acetic acid(100cm^3) was treated with nitric acid(d=1.5,10cm^3) over a period of 20 minutes. The precipitate that had formed was filtered off and washed well with water to give 4,8-dinitro-1,5-dimethoxynaphthalene(12.6g).

4,8-Dinitro-1,5-dimethoxynaphthalene(6g) in glacial acetic acid(30cm^3) was treated with nitric acid(d = 1.5,30cm^3). After 2 minutes exothermic reaction the mixture was added to water(500cm^3) to precipitate a yellow-orange solid. This was filtered off, washed thoroughly with water and finally recrystallised from dilute acetic acid to give 2,4,8-trinitro-1,5-dimethoxynaphthalene. M.Pt. 180°C.

2,4,8-Trinitro-1,5-dimethoxynaphthalene(0.0323g) was dissolved in d_6-DMSO(0.4cm^3) and the 90MHz PMR spectrum recorded(fig.A.3.2.2(a)):- τ 1.33(1H,s),1.79 and 2.48(2H,ABq,J_{AB} 8.0Hz),6.03(3H,s) and 6.14(3H,s).

(A) Methoxide and hydroxide ions

Compound (205)(0.0331g) was dissolved in d_6-DMSO(0.4cm^3) and 2M sodium methoxide-d_3 in CD_3OD(0.05cm^3) added. The 90MHz PMR spectrum was recorded (fig.A.3.2.2(b)):- τ 1.31(1H,s),2.65 and 2.89(2H,ABq,J_{AB} 9.0Hz), 6.19(3H,s) and 7.12(3H,s).

The PMR spectrum was re-recorded after the addition of a further 0.05cm^3 of 2M sodium methoxide-d_3 and a line at τ 3.67 noted.

Compound (205)(0.032g) was dissolved in d_6-DMSO(0.4cm^3) and 5M sodium deuterioxide in D_2O(0.02cm^3) added. The 90MHz PMR spectrum was recorded (fig.A.3.2.2(c)):- τ 1.57(1H,s),2.43 and 2.73(2H,ABq,J_{AB} 8Hz) and 6.12(3H,s); and lines due to compound (206).

A.3.2.10 2,4,6,8-Tetranitro-1,5-dimethoxynaphthalene(208)

2,4,8-Trinitro-1,5-dimethoxynaphthalene(2g) was added to nitric acid (d = 1.5,20cm^3) at 0°C with stirring. After 30 minutes reaction the red solution was precipitated on ice and the orange solid obtained was thoroughly washed with water and dried in vacuo. Extraction of this solid with toluene gave 2,4,6,8-tetranitro-1,5-dimethoxynaphthalene after evaporation of the solvent. M.Pt. 255°C.

2,4,6,8-Tetranitro-1,5-dimethoxynaphthalene(0.0368g) was dissolved in d_6-DMSO(0.4cm^3) and the 90MHz PMR spectrum recorded (fig.A.3.2.3(a)):-

τ 1.07(2H,s) and 6.12(6H,s).

(A) Methoxide and hydroxide ions

Compound (208)(0.0305g) was dissolved in d_6-DMSO($0.4cm^3$) and 2M sodium methoxide in CD_3OD($0.04cm^3$) added. The 90MHz PMR spectrum was recorded (fig.A.3.2.3(b)):- τ 1.15(1H,s),2.00(1H,s),6.38(3H,s) and 7.09(3H,s).

Compound (208)(0.0307g) was dissolved in d_6-DMSO($0.4cm^3$) and 5M sodium deuterioxide($0.02cm^3$) added. The 90MHz PMR spectrum was recorded (fig.A.3.2.3(c)):- τ 1.45(1H,s),1.83(1H,s) and 6.3(3H,s); and lines due to compound (209).

A.3.2.11 2,4,8-Trinitro-1,7-dimethoxynaphthalene(211)

1,7-Dimethoxynaphthalene(8g) was dissolved in glacial acetic acid ($200cm^3$) and nitric acid(d = 1.5,$8cm^3$) added over a period of 40 minutes. After 5 hours reaction time the mixture was filtered to give a yellow solid which was thoroughly washed with water. Recrystallisation from hot benzene gave 4,8-dinitro-1,7-dimethoxynaphthalene(8.69g).

4,8-Dinitro-1,7-dimethoxynaphthalene(2g) dissolved in glacial acetic acid($10cm^3$) was treated with nitric acid($10cm^3$). The precipitate which formed was filtered off after 15 minutes and washed with water. Recrystallisation from hot acetone gave 2,4,8-trinitro-1,7-dimethoxynaphthalene.[212] M.Pt. 179°C.

2,4,8-Trinitro-1,7-dimethoxynaphthalene(0.0327g) was dissolved in d_6-DMSO($0.4cm^3$) and the 90MHz PMR spectrum recorded (fig.A.3.2.4(a)):- τ 1.25(1H,s),1.38 and 1.88(2H,ABq,J_{AB} 10.0Hz),5.91(3H,s) and 6.14(3H,s).

(A) Methoxide and hydroxide ions

Compound (211)(0.0327g) was dissolved in d_6-DMSO($0.4cm^3$) and 2M sodium methoxide-d_3 in CD_3OD($0.06cm^3$) added. The 90MHz PMR spectrum was recorded (fig.A.3.2.4(b)):- τ 0.81(1H,s),1.01 and 2.62(2H,ABq,J_{AB} 9.0Hz),6.14(3H,s) and 7.20(3H,s).

Compound (211)(0.0326g) was dissolved in d_6-DMSO($0.4cm^3$) and 5M sodium deuterioxide in D_2O($0.02cm^3$) added. The 90MHz PMR spectrum was recorded (fig.A.3.2.4(c)):- τ 0.94(1H,s),1.08 and 2.29(2H,ABq,J_{AB} 10.0Hz) and 6.05(3H,s); and lines due to compound (212).

A.3.2.12 1,3,8-Trinitro-2,7-dimethoxynaphthalene(214)

2,7-Dihydroxynaphthalene(100g) in dilute sodium hydroxide solution ($800cm^3$) was treated with dimethylsulphate($120cm^3$) and solid sodium hydroxide alternately with continuous stirring. Sufficient base was added to render the reaction mixture alkaline. After 4 hours an excess of sodium hydroxide was was added and the mixture heated on a steam bath for 15 minutes. After cooling, filtration of the mixture gave 2,7-dimethoxynaphthalene which was thoroughly washed with water and dried in vacuo.

2,7-Dimethoxynaphthalene(11.66g) was dissolved in glacial acetic acid ($60cm^3$) and treated with nitric acid($d = 1.5, 8cm^3$) for 1 hour. The orange precipitate that formed was filtered off and washed thoroughly with water to give 1,8-dinitro-2,7-dimethoxynaphthalene.

A slurry of 1,8-dinitro-2,7-dimethoxynaphthalene(5.8g) in glacial acetic acid($15cm^3$) was stirred with nitric acid($d = 1.5, 29cm^3$) in a closed vessel for 2 hours. The reaction mixture was added to water($400cm^3$) and filtered and washed thoroughly with water. Recrystallisation from hot acetone gave orange crystals of 1,3,8-trinitro-2,7-dimethoxynaphthalene. M.Pt. 215°C.

1,3,8-Trinitro-2,7-dimethoxynaphthalene(0.0326g) was dissolved in d_6-DMSO($0.4cm^3$) and the 90MHz PMR spectrum recorded (fig.A.3.2.5(a)):- τ 0.77(1H,s),1.39 and 2.06(2H,ABq,J_{AB} 9Hz),5.87(3H,s) and 6.02(3H,s).

(A) Methoxide and hydroxide ions

Compound (214)(0.0326g) was dissolved in d_6-DMSO($0.4cm^3$) and 2M sodium methoxide-d_3 in CD_3OD($0.04cm^3$) added. The 90MHz PMR spectrum was recorded (fig.A.3.2.5(b)):- τ 2.49 and 2.94(2H,ABq,J_{AB} 9.0Hz),4.44(1H,s), 6.03(3H,s) and 6.14(3H,s).

A further $0.02cm^3$ of 2M sodium methoxide-d_3 was added to the PMR sample and the spectrum re-recorded:- τ 2.61 and 3.08(2H,ABq,J_{AB} 9.0Hz), 4.38(1H,s) and 6.16(3H,s).

Compound (214)(0.0326g) was dissolved in d_6-DMSO($0.4cm^3$) and 5M sodium deuterioxide in D_2O($0.02cm^3$) added. The 90MHz PMR spectrum was recorded immediately and a short lived resonance at τ 4.11 observed. Three other products also gave spectral lines:- τ 2.55 and 2.96(2H,ABq,J_{AB} 9.0Hz), 4.23(1H,s) and 6.06(3H,s); τ 1.73(1H,s),2.03 and 2.91(2H,ABq,J_{AB} 10Hz) and 6.02(3H,s); and lines due to compound (214)(fig.A.3.2.5(c)).

(B) Sulphite ion

Compound (214)(0.0644g) was dissolved in DMSO(1.2cm^3) in a stoppered 10cm^3 QF conical flask and 3 equivalents of 1M sodium sulphite in D_2O(0.6cm^3) added with magnetic stirring. The 90MHz PMR spectrum of 0.4cm^3 of the filtered reaction mixture was recorded (fig.A.3.2.6(b)):- τ 2.47 and 2.88 (2H,ABq,J_{AB} 8.0Hz),4.44(1H,s),methyl resonances obscured.

A.3.2.13 1,3,6,8-Tetranitro-2,7-dimethoxynaphthalene(221)

1,3,8-Trinitro-2,7-dimethoxy(2.2g) was added with stirring to nitric acid(d = 1.5,22cm^3) at 0°C in a closed vessel. After 4 hours reaction the mixture was precipitated on ice, filtered and washed with water. Heating in vacuo at 80°C to remove volatile impurities was followed by recrystallisation from acetone to give 1,3,6,8-tetranitro-2,7-dimethoxynaphthalene. M.Pt. 268°C.

1,3,6,8-Tetranitro-2,7-dimethoxynaphthalene(221)(0.0348g) was dissolved in d_6-DMSO(0.6cm^3) and the 90MHz PMR spectrum recorded (fig.A.3.2.7(a)):- τ 0.45(2H,s) and 5.96(6H,s).

(A) Sulphite ion

Compound (221)(0.0348g) was dissolved in d_6-DMSO(0.6cm^3) in a stoppered 10cm^3 QF conical flask and 1M sodium sulphite in D_2O(0.2cm^3) added with magnetic stirring. The 90MHz PMR spectrum was recorded (fig.A.3.2.7(b)):- τ 1.85(1H,s),4.35(1H,s); methyl resonances obscured.

A.3.2.14 1,4,5-Trinitro-2,6-dimethoxynaphthalene(223)

2,6-Dimethoxynaphthalene(4g) suspended in 1,2-dichloroethane(200cm^3) at 0°C was treated with nitric acid(d = 1.5,3cm^3) over a period of 15 minutes with continuous stirring. The solution was allowed to warm to room temperature and stirred for a further 140 minutes. The green precipitate that had formed was filtered off and washed with water to give 1,5-dinitro-2,6-dimethoxynaphthalene.

1,5-Dinitro-2,6-dimethoxynaphthalene(1.4g) suspended in glacial acetic acid(7cm^3) was treated with nitric acid(d = 1.5,7cm^3) with stirring. The precipitate which formed was filtered off after 10 minutes reaction time and thoroughly washed with water. Recrystallisation from glacial acetic acid gave 1,4,5-trinitro-2,6-dimethoxynaphthalene.

1,4,5-Trinitro-2,6-dimethoxynaphthalene(0.0327g) was dissolved in d_6-DMSO(0.4cm^3) and the 90MHz PMR spectrum recorded:- τ 1.46(1H,s), 1.99(2H,s),5.87(3H,s) and 5.90(3H,s).

(A) Methoxide ion

Compound (223)(0.0326g) was dissolved in d_6-DMSO(0.4cm^3) and 2M sodium methoxide-d_3 in CD_3OD(0.04cm^3) added. The 90MHz PMR spectrum was recorded:- τ 1.10 and 3.17(2H,ABq,J_{AB} 9.0Hz),5.00(1H,s),6.24(3H,s) and 6.67(3H,s).

A summary of the products of reaction of base with polynitrodimethoxynaphthalenes is shown in Table A.3.2.1.

Table A.3.2.1 Products of the reaction of polynitrodimethoxynaphthalenes with base in DMSO.

Base / Nitroaromatic	OH^-	OMe^-	Et_2NH	$PhCH_2NH_2$	$NH_2NH_2 \cdot H_2O$	SO_3^{2-}
2,4,6- & 2,4,8-TN-1,5-DIMEON	(C-1 add^n) & MeO$^-$ displm^t	C-1 add^n	Methoxide ion displacement from C-1	Methoxide ion displacement from C-1	Unknown product	-
2,4,6,8-TETN-1,5-DIMEON	Methoxide ion displacement from C-1	C-1 add^n	Unknown product	-	Unknown product	-
2,4,8-TN-1,7-DIMEON	Methoxide ion displacement from C-1	C-1 add^n	Unknown product	Unknown product	Unknown product	-
1,4,5-TN-2,6-DIMEON	-	C-3 add^n	-	-	-	-
1,3,8-TN-2,7-DIMEON	C-4 add^n & C-4 add^n to naphthalate ion	C-4 add^n & C-4 add^n to naphthalate ion	Unknown product	Transient C-4 add^n	Unknown product	C-4 add^n
1,3,6,8-TETN-2,7-DIMEON	-	C-4 add^n ?	-	-	-	C-4 add^n

APPENDIX 3.3 Kinetics of the reaction of polynitrodimethoxynaphthalenes with hydroxide ion in aqueous DMSO

Table A.3.3.1 lists the approximate 2nd order forward rate constants, k_{2f} (calculated from $k_\psi / [OH^-]$ where $k_\psi \sim k_{1f}$) for the reaction of sodium hydroxide with various polynitrodimethoxynaphthalenes in aqueous DMSO(3:7).

Table A.3.3.1 Rate constants and absorbtion maxima for the reaction of several polynitrodimethoxynaphthalenes with sodium hydroxide in aqueous DMSO(3:7).

	$k_{2f}(M^{-1}s^{-1})$	Temp.	λ_{max}(nm)
(1) 2,4,8-TN-1,5-DIMEON	5.10	27.6°	433
(2) 2,4,8-TN-1,7-DIMEON	28.7	27.9°	450
(3) 1,4,5-TN-2,6-DIMEON	6.49	28.0°	466
(4) 1,3,8-TN-2,7-DIMEON	1.97	26.8°	463
(5) 2,4,6,8-TETN-1,5-DIMEON	195	27.7°	441
(6) 1,3,6,8-TETN-2,7-DIMEON	8400	27.9°	442

$$\text{POLYNITRODIMEON} + OH^- \rightleftharpoons [\text{POLYNITRODIMEONOH}]^-$$

$\dfrac{k_{TETN}}{k_{TN}}$		
	-1,5-DIMEON	38.2
	-2,7-DIMEON	4260

Pseudo 1st order forward and reverse kinetic analysis was applied although this may not be strictly applicable to reactions (1), (2) and (5) where displacement of a methoxy group may occur. However, addition may well precede displacement so that this initial step would be the one measured. The forty-fold difference in rates between the tetranitro-1,5- and -2,7-isomers points to addition at C-1 in the former and C-4(proton bearing) in the latter. Interestingly, reaction (1) is faster than (4) (addition at C-4) so that this may involve addition at C-3. Similar arguments apply for reactions (2) and (3). If steric effects were dominant then although (6) would be expected to be faster than (5), (4) should be faster than (1) which is not the case.

Experimental section

Kinetic measurements were made on an Applied Photophysics stopped-flow spectrophotometer using the following aqueous DMSO(3:7) solutions.

	[nitroaromatic]	[NaOH]
2,4,8-TN-1,5-DIMEON	5×10^{-5}M	0.025M
2,4,8-TN-1,7-DIMEON	5×10^{-5}M	0.025M
1,4,5-TN-2,6-DIMEON	5×10^{-5}M	0.025M
1,3,8-TN-2,7-DIMEON	3.5×10^{-5}M	0.025M
2,4,6,8-TETN-1,5-DIMEON	3.5×10^{-5}M	0.015M
1,3,6,8-TETN-2,7-DIMEON	4.2×10^{-5}M	0.005M

where TN = trinitro-; TETN = tetranitro- and DIMEON = dimethoxynaphthalene.

REFERENCES

1. R.Foster and C.A.Fyfe,Rev. Pure and Applied Chem.,16,61,(1966).
2. E.Buncel,A.R.Norris and K.E.Russell,Quart. Rev.,22,123,(1968).
3. M.R.Crampton,Adv. Phys. Org. Chem.,7,211,(1969).
4. M.J.Strauss,Chem. Rev.,70,667,(1970).
5. R.S.Mulliken,J.A.C.S.,72,600,(1950);74,811,(1952).
6. R.Foster,Organic Charge Transfer Complexes, Academic Press, London and N.Y.,(1969).
7. L.J.Andrews and R.M.Keefer,Molecular Complexes in Organic Chemistry, Holden-Day,San Francisco,(1964).
8. J.N.Murrell,Quart.Rev.,15,191,(1961).
9. G.A.Russell,E.G.Janzen and E.T.Strom,J.A.C.S.,86,1807,(1964).
10. G.Chapelet-Letourneux,H.Lamaire and A.Rassat,Bull. Soc. Chim. France, 444,(1965).
11. A.R.Forrester,J.M.Hay and R.H.Thomson, Organic Chemistry of Stable Radicals,Academic Press, New York,(1968).
12. J.E.Everard,M.Sc. Thesis,University of Surrey,(1973).
13. G.A.Russell,A.J.Moye,E.G.Janzen,S.Mak and E.R.Talaty, J.Org.Chem., 32,137,(1967).
14. G.A.Russell and E.G.Janzen,J.A.C.S.,89,300,(1967).
15. G.A.Russell and E.G.Janzen,J.A.C.S.,84,4153,(1962).
16. E.J.Fendler,J.H.Fendler,N.L.Arthur and C.E.Griffin,J.Org.Chem.,37, 812,(1972).
17. C.A.Fyfe,C.D.Malkiewich,S.W.H.Damji and A.R.Norris,J.A.C.S.,98, 6983,(1976).
18. C.F.Bernasconi, J.Org.Chem.,36,1671,(1971).
19. J.A.A.Ketelaar,A.Bier and H.T.Vlaar,Rec.Trav.Chim.,73,37,(1954).
20. R.E.Miller and W.F.K.Wynne-Jones,J.C.S.,2375 (1959).
21. E.Buncel and E.A.Symons,Can.J.Chem.,44,771,(1966).
22. M.R.Crampton and V.Gold.,J.C.S.(B),498,(1966).
23. J.F.Bunnett and R.E.Zahler,Chem.Rev.,49,273,(1951).
24. J.F.Bunnett,Quart. Rev.,12,1,(1958).

25. J.F.Bunnett and R.H.Garst,J.Org.Chem.,33,2320,(1968).
26. W.L.Hinze,Li-Jen Liu and J.H.Fendler,J.C.S. Perkin 2,1751,(1975).
27. V.Gold and C.H.Rochester,J.C.S.,1692,(1964).
28. P.T.Izzo,J.Org.Chem.,24,2026,(1959).
29. M.R.Crampton and M.El.Ghariani,J.C.S.(B),391,(1970).
30. C.A.Lobry de Brüyn and F.H.Leent,Rec.Trav.Chim.,14,89,(1895).
31. M.R.Crampton and V.Gold,J.C.S.,4293,(1964).
32. R.Foster and C.A.Fyfe,Tetrahedron,21,3363,(1965).
33. R.Foster and R.K.Mackie,J.C.S.,3796,(1963).
34. V.Gold and C.H.Rochester,J.C.S.,1710,(1964).
35. F.Cuta and J.Pisecky,Coll.Czech.Chem.Comm.,23,628,(1958).
36. M.R.Crampton and V.Gold,J.C.S.,4293,(1964).
37. M.R.Crampton and V.Gold,Chem.Comm.,256,(1965).
38. C.R.Allen,A.J.Brook and E.F.Caldin,J.C.S.,2171,(1961).
39. G.Briegleb,W.Liptay and M.Cantner,Z.Phys.Chem.,26,55,(1960).
40. M.R.Crampton and V.Gold,Chem.Comm.,549,(1965).
41. M.R.Crampton and V.Gold,J.C.S.(B),23,(1967).
42. R.Foster and C.A.Fyfe,J.C.S.(B),53,(1966).
43. M.J.Strauss and H.Schran,J.A.C.S.,91,3974,(1969).
44. R.Foster and C.A.Fyfe,Tetrahedron,22,1831,(1966).
45. M.I.Foreman,R.Foster and M.J.Strauss,J.C.S.(C),2112,(1969).
46. M.J.Strauss,H.Schran,T.Jensen and K.O'Connor,J.Org.Chem.,35,383,(1970).
47. R.A.Henry, J.Org.Chem.,27,2637,(1962).
48. F.Cuta and E.Beranek,Coll.Czech.Chem.Comm.,23,1501,(1958).
49. A.R.Norris,Can.J.Chem.,45,175,(1967).
50. M.R.Crampton,J.C.S(B).,1341,(1967).
51. M.R.Crampton and M.J.Willison,Chem.Comm.,215,(1973).
52. M.J.Strauss and S.P.B.Taylor,J.A.C.S.,95,3813,(1973).
53. M.R.Crampton,J.C.S.(B),1208,(1968).
54. M.R.Crampton and M.El.Ghariani,J.C.S.(B),1043,(1971).
55. A.R.Norris,Can.J.Chem.,45,2703,(1967).

56. E.Buncel,A.R.Norris and W.Proudlock,Can.J.Chem.,46,2759,(1968).
57. A.R.Norris,J.Org.Chem.,34,1486,(1969).
58. S.M.Shein,A.D.Khmelinskaya and V.U.Brovko,Chem.Comm.,1043,(1969).
59. C.A.Fyfe,M.I.Foreman and R.Foster,Tet.Let.,20,1521,(1969).
60. C.A.Fyfe,Can.J.Chem.,46,3047,(1968).
61. C.L.Jackson and F.H.Gazzolo,Am.Chem.J.,23,376,(1900).
62. J.Meisenheimer,Annalen.,323,205,(1902).
63. R.Foster and D.L.Hammick,J.C.S.,2153,(1954).
64. L.K.Dyall,J.C.S.,5160,(1960).
65. R.Foster,C.A.Fyfe and J.W.Morris,Rec.Trav.Chim.,84,516,(1965).
66. R.Destro,C.Grammacioli and M.Simonetta,Acta.Cryst.,24,1369,(1968).
67. P.Caveng,P.Fischer,E.Heilbronner,A.L.Miller and H.Zollinger,Helv.Chim.
Acta.,50,848,(1967).
68. H.Hosoya,S.Hosoya,S.Nagakura,Theor.Chim.Acta.,12,117,(1968).
69. K.L.Servis,J.A.C.S.,87,5495,(1965).
70. M.R.Crampton and V.Gold,J.C.S.(B),893,(1966).
71. J.B.Ainscough and E.F.Caldin,J.C.S.,2528,(1956).
72. V.Gold and C.H.Rochester,J.C.S.,1687,(1964).
73. K.L.Servis,J.A.C.S.,89,1508,(1967).
74. C.H.Rochester,J.C.S.,2404,(1965).
75. T.Abe,Bull.Chem.Soc.Japan.,39,627,(1966).
76. K.L.Servis,Personal Communication to M.J.Strauss.
77. L.B.Clapp,H.Lacey,G.G.Beckwith,R.M.Srivastava and N.Muhammed,
J.Org.Chem.,33,4262,(1968).
78. A.R.Norris,Can.J.Chem.,47,2895,(1969).
79. R.Foster,C.A.Fyfe,P.H.Emslie and M.I.Foreman,Tetrahedron,23,227,(1967).
80. J.Murto,Suomen.Kem.B.,38,255,(1965).
81. M.R.Crampton and M.J.Willison,J.C.S. Perkin 2.,901,(1976).
82. C.F.Bernasconi,R.H.de Rossi and C.L.Gehriger,J.Org.Chem.,38,2838,(1973).
83. C.F.Bernasconi and C.L.Gehriger,J.A.C.S.,96,1092,(1974).
84. G.Biggi and F.Pietra,J.C.S. Perkin 1,1980,(1973).
85. R.Foster and C.A.Fyfe,Chem.Comm.,1219,(1967).

86. J.V.Janovsky and L.Erb,Ber.,19,2155,(1886).

87. S.S.Gitis and A.I.Glaz,J.Gen.Chem.USSR.,28,1393,(1958).

88. S.S.Gitis,G.M.Oksengendler and A.Y.Kaminskii,J.Gen.Chem.USSR., 29,2948.

89. S.S.Gitis,A.I.Glaz and A.Y.Kaminskii,J.Gen.Chem.USSR.,33,3229,(1963).

90. W.E.Byrne,E.J.Fendler,J.H.Fendler and C.E.Griffin,J.Org.Chem.,32, 2506,(1967).

91. S.S.Gitis and A.Y.Kaminski,J.Gen.Chem.USSR.,30,3810,(1960).

92. E.J.Fendler,J.H.Fendler,W.E.Byrne and C.E.Griffin,J.Org.Chem.,33, 4141,(1968).

93. M.I.Foreman and R.Foster,Can.J.Chem.,47,729,(1969).

94. F.Millot and F.Terrier,Bull.Soc.Chim.Fr.,1823,(1974).

95. C.A.Fyfe,M.Cocivera,S.W.H.Damji,J.A.C.S.,97,5707,(1975).

96. C.A.Fyfe,M.Cocivera,S.W.H.Damji,T.A.Hostetter,D.Sproat and J.O'Brien,J.Mag.Res.,23,377,(1976).

97. M.R.Crampton and H.A.Khan,J.C.S. Perkin 2,733,(1972).

98. M.R.Crampton and H.A.Khan,J.C.S. Perkin 2,710,(1973).

99. R.J.Pollitt and B.C.Saunders,J.C.S.,4615,(1965).

100. J.H.Fendler,E.J.Fendler and L.M.Casilio,J.Org.Chem.,36,1749,(1971).

101. J.H.Fendler,E.J.Fendler,W.E.Byrne and C.E.Griffin,J.Org.Chem.,33, 977,(1968).

102. F.Millot and F.Terrier,Bull.Soc.Chim.Fr.,2692,(1969);3897,(1971).

103. J.A.Orvik and J.F.Bunnett,J.A.C.S.,92,2417,(1970).

104. C.A.Fyfe,A.Koll,S.W.H.Damji,C.D.Malkiewich and P.A.Forte, Chem.Comm.335,(1977).

105. M.R.Crampton and M.J.Willison,J.C.S. Perkin 2.,1681,(1974).

106. J.H.Fendler and E.J.Fendler,J.Org.Chem.,35,3378,(1970).

107. E.J.Fendler and J.H.Fendler,J.C.S. Perkin 2.,1403,(1972).

108. P.Golding and J.E.Everard,Unpublished observations.

109. S.R.Robinson,Ph.D. Thesis,Kingston Polytechnic,(1974).

110. C.H.J.Wells and J.A.Wilson,Tet.Let.,4521,(1971).

111. B.C.Webb, Ph.D. Thesis, Kingston Polytechnic, (1975).
112. N.P.Norris and J.Osmundson, J.Org.Chem., **30**, 2407, (1965).
113. V.Gold and C.H.Rochester, J.C.S., 1697, (1964).
114. V.Gold and C.H.Rochester, J.C.S., 1727, (1964).
115. M.R.Crampton, J.C.S.(B), 85, (1967).
116. M.R.Crampton and V.Gold, Proc.Chem.Soc., 298, (1964).
117. T.Birchall and W.L.Jolly, J.A.C.S., **88**, 5439, (1966).
118. G.N.Lewis and G.T.Seaborg, J.A.C.S., **62**, 2122, (1940).
119. V.Gold and C.H.Rochester, J.C.S., 1722, (1964).
120. M.R.Crampton and M.El-Ghariani, J.C.S.(B), 330, (1969).
121. M.R.Crampton and M.J.Willison, J.C.S. Perkin 2, 160, (1976).
122. E.F.Caldin and G.Long, Proc.R.Soc.London, Ser.A., 228, 263, (1955).
123. J.B.Ainscough and E.F.Caldin, J.C.S., 2546, (1956).
124. E.Buncel, A.R.Norris, K.E.Russell and R.Tucker, J.A.C.S., **94**, 1646, (1972).
125. E.Buncel, A.R.Norris, K.E.Russell, P.Sheridan and H.Wilson, Can.J.Chem., **52**, 1750, (1974).
126. E.Buncel, A.R.Norris, K.E.Russell and H.Wilson, Can.J.Chem., **52**, 2306, (1974).
127. R.Foster and R.K.Mackie, Tetrahedron, **19**, 691, (1963).
128. H.Muraour, Bull.Soc.Chim.France., **35**, 367, (1924).
129. N.Marendic and A.R.Norris, Can.J.Chem., **51**, 3927, (1973).
130. H.W.Thompson, J.C.S., 2310, (1932).
131. M.Civera and C.Torello, Gazz.Chim.Ital., **86**, 350, (1956); C.Abs., **52**, 335d.
132. S.R.Robinson, B.C.Webb and C.H.J.Wells, J.C.S. Perkin 2, 273, (1976).
133. L.M.Jackman and S.Sternhell, 'Applications of NMR Spectroscopy in Organic Chemistry', Pergamon Press, (1969).
134. C.H.Rochester, 'Acidity Functions', Academic Press, N.York, (1970).
135. F.Terrier, Ann.Chim.(Fr.), **4**, 153, (1969).
136. M.R.Crampton, M.A.El Ghariani and H.A.Khan, J.C.S. Perkin 2., 1178, (1972).
137. K.Bowden and R.Stewart, Tetrahedron, **21**, 261, (1965).
138. M.R.Crampton, J.C.S. Perkin 2, 185, (1975).

139. H.A.Benesi and J.H.Hildebrand,J.A.C.S.,71,2703,(1949).
140. G.D.Johnson and R.E.Bowen,J.A.C.S.,87,1655,(1965).
141. J.S.Coleman,L.P.Varga and S.H.Mastin,Inorg.Chem.,9,1015,(1970).
142. A.Job,Ann.Chim.,9,113,(1928).
143. C.F.Bernasconi,J.A.C.S.,92,4682,(1970).
144. J.H.Fendler,E.J.Fendler and C.E.Griffin,J.Org.Chem.,34,689,(1969).
145. C.F.Bernasconi,J.A.C.S.,93,6975,(1971).
146. F.Terrier,P.Pastour and R.Schaal,Compt.Rend.,260,5783,(1965).
147. C.F.Bernasconi,J.A.C.S.,90,4982,(1968).
148. E.J.Fendler,J.H.Fendler,C.E.Griffin and J.W.Larsen,J.Org.Chem.,35, 287,(1970).
149. E.J.Fendler,W.Ernsberger and J.H.Fendler,J.Org.Chem.,36,2333,(1971).
150. R.M.Murphy,C.A.Wulff and M.J.Strauss,J.A.C.S.,96,2678,(1974).
151. J.H.Fendler,W.L.Hinze and Li-Jen Liu,J.C.S. Perkin 2,1768,(1975).
152. J.H.Fendler,J.A.C.S.,88,1237,(1966).
153. J.W.Larsen,K.Amin and J.H.Fendler,J.A.C.S.,93,2910,(1971).
154. J.W.Larsen,J.H.Fendler and E.J.Fendler,J.A.C.S.,91,5903,(1969).
155. J.Miller,J.A.C.S.,85,1628,(1963).
156. K.C.Ho,J.Miller and K.W.Wong,J.C.S.(B),310,(1966).
157. D.L.Hill,K.C.Ho and J.W.Miller,J.C.S.(B),299,(1966).
158. J.Miller,Aust.J.Chem.,22,921,(1969).
159. T.Abe,Bull.Chem.Soc.Japan.,37,508,(1964).
160. F.Terrier,J.C.Halle and M.P.Simonin,Org.Mag.Res.,3,361,(1971).
161. F.Terrier,F.Millot and R.Schaal,J.C.S. Perkin 2,1192,(1972).
162. J.H.Fendler and J.W.Larsen,J.Org.Chem.,37,2608,(1972).
163. A.J.Parker,Quart.Rev.,16,163,(1962).
164. M.R.Crampton and H.A.Khan,J.C.S. Perkin 2,1173,(1972).
165. M.R.Crampton and H.A.Khan,J.C.S.,Perkin 2,2286,(1972).
166. M.R.Crampton,J.C.S. Perkin 2,825,(1975).
167. M.R.Crampton and H.A.Khan,J.C.S. Perkin 2,1103,(1973).
168. C.F.Bernasconi and R.G.Bergstrom,J.Org.Chem.,36,1325,(1971).
169. C.F.Bernasconi and R.G.Bergstrom,J.A.C.S.,96,2397,(1974).

170. J.B.Ainscough and E.F.Caldin,J.C.S.,2540,(1956).
171. L.H.Gan and A.R.Norris,Can.J.Chem.,49,2490,(1971).
172. E.A.Symons and E.Buncel,Can.J.Chem.,50,1729,(1972).
173. K.Bowden,Chem.Rev.,66,119,(1966).
174. C.F.Bernasconi and R.G.Bergstrom,J.A.C.S.,95,3603,(1973).
175. E.Buncel,A.R.Norris,K.E.Russell and P.J.Sheridan,Can.J.Chem.,52.25,(1974).
176. R.Foster,J.C.S.,3508,(1959).
177. C.F.Bernasconi,J.Org.Chem.,35,1214,(1970).
178. C.F.Bernasconi,J.A.C.S.,92,129,(1970).
179. C.F.Bernasconi,J.Phys.Chem.,75,3636,(1971).
180. C.F.Bernasconi,MTP Internat.Rev.Sci.Org.Chem.Series One,ed.H.Zollinger,Butterworths,London,3,33,(1973).
181. C.F.Bernasconi.J.Org.Chem.,32,2947,(1967).
182. C.F.Bernasconi,R.H.de Rossi and P.Schmid,J.A.C.S.,99,4090,(1977).
183. M.Eigen and L. deMaeyer,'Technique of Organic Chemistry',8,Part 2,Interscience Publishers,N.York.,p.895,(1963).
184. M.Eigen,Angew.Chem.Int.Ed.Engl.,3,1,(1964).
185. E.Buncel,A.R.Norris,W.Proudlock and K.E.Russell,Can.J.Chem.,47,4129,(1969).
186. L.H.Gan and A.R.Norris,Can.J.Chem.,52,1,(1974).
187. L.H.Gan and A.R.Norris,Can.J.Chem.,52,8,(1974).
188. M.R.Crampton,J.C.S.(B),2112,(1971).
189. M.R.Crampton and M.J.Willison,J.C.S. Perkin 2,238,(1974).
190. A.J.Parker,Proc.Chem.Soc.,371,(1961).
191. A.R.Butler,J.C.S. Perkin 1,1557,(1975).
192. C.F.Bernasconi and Hsien-Chang Wang,J.A.C.S.,98,6265,(1976).
193. C.F.Bernasconi and R.H.de Rossi,J.Org.Chem.,38,500,(1973).
194. C.F.Bernasconi and H.S.Cross,J.Org.Chem.,39,1054,(1974).
195. C.F.Bernasconi and F.Terrier,J.A.C.S.,97,7458,(1975).
196. C.F.Bernasconi,C.L.Gehriger and R.H.de Rossi,J.A.C.S.,98,8451,(1976).

197. M.R.Crampton and M.J.Willison, J.C.S. Perkin 2,1686,(1974).

198. M.R.Crampton and M.J.Willison, J.C.S. Perkin 2,155,(1976).

199. M.R.Crampton, J.C.S. Perkin 2,2157,(1973).

200. S.R.Robinson, B.C.Webb and C.H.J.Wells, Chem. and Ind.,519,(1975).

201. V.Gold and C.H.Rochester, J.C.S.,1704,(1964).

202. V.Gold and C.H.Rochester, J.C.S.,1717,(1964).

203. R.Foster and I.B.C.Matheson, Spectrochimica Acta.,23,2037,(1967).

204. R.C.Kerber and A.Porter, J.A.C.S.,91,366,(1969).

205. K.Bowden and R.S.Cook, J.C.S.(B),1770,(1971).

206. J.C.Richer and N.Baskovitch, Can.J.Chem.,46,2975,(1968).

207. E.Buckley, J.E.Everard and C.H.J.Wells, Chem. and Ind.,124,(1978).

208. M.Bil and M.Bernstein, Chem. and Ind.,1221,(1967).

209. T.Urbanski.,'Chemistry and Technology of Explosives',Vol.1,(1964), Pergamon Press.

210. S.R.Robinson, C.H.J.Wells, R.B.Turner and J.F.J.Todd., J.C.S. Perkin 2, 1363,(1976).

211. R.H.Thomson, E.Race and F.M.Rowe., J.C.S.,350,(1947).

212. F.Bell and K.R.Buck, J.C.S.(C),904,(1966).

Synthesis of 1,3,5- and 1,4,5-trinitro- and 1,3,5,7- and 1,3,5,8-tetranitro-2,6-dimethylnaphthalenes

Eric Buckley, John E Everard and Clifford H J Wells
School of Chemical and Physical Sciences, Kingston Polytechnic, Kingston upon Thames, Surrey KT1 2EE

Dimerisation of 2,4,6-trinitrotoluene (TNT) under the action of base yields 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) in good yield,[1] this latter compound being of importance as a thermally stable explosive having applications in space technology.[2,3] Following a report[4] on a large laboratory scale preparation of 1,5-dinitro-2,6-dimethylnaphthalene (I), the authors have investigated the synthesis from this compound of trinitro- and tetranitro-2,6-dimethylnaphthalene which could have the potential for base-induced coupling to give thermally stable explosive materials analogous in structure to HNS.

The reaction of nitric acid and compound (I) in concentrated sulphuric acid gave 1,4,5-trinitro-2,6-dimethylnaphthalene (II) as follows. To a stirred solution of compound (I) (2g) in concentrated sulphuric acid (600cm^3) was added 0·6cm^3 of nitric acid ($d = 1{\cdot}42$). After 2h the mixture was poured onto ice and the precipitated solid filtered off, washed thoroughly with water, dried *in vacuo*, and washed with toluene (15cm^3). Recrystallisation from glacial acetic acid gave compound (II) (1·54g), mp 193°C; n.m.r. spectrum (DMSO-d_6), τ 1·43 (1H, *s*), 1·99 and 2·03 (2H, AB_q, $J_{AB} = 9{\cdot}0$ Hz), 7·39 (3H, *s*) and 7·46 (3H, *s*); mass spectrum, *m/e* 291 (M$^+$), 245 (base peak). The base peak corresponding to $[\mathrm{M}\text{-}\mathrm{NO}_2^{\cdot}]^+$ showed that *peri*-nitro groups were present in the compound structure.[5]

The reaction of nitric acid with compound (I) in acetic anhydride yielded 1,3,5-trinitro-2,6-dimethylnaphthalene(III) as follows. To a stirred solution of compound (I~~I~~) (5g), in acetic anhydride (300cm^3) was added 40cm^3 of nitric acid ($d = 1{\cdot}42$) at a rate such that the temperature did not exceed 40°C. After the addition the solution was allowed to stand for 16h, and then 30cm^3 of nitric acid ($d = 1{\cdot}50$) was added over a period of 4h, after which time 1·5cm^3 of concentrated sulphuric acid was added. The temperature of the reactant solution was slowly increased to 70°C while stirring continuously, and then after 5 min vigorous evolution of fumes the reactants were quenched in excess of water. (Caution has to be taken on heating owing to the formation of tetranitromethane in the reactant mixture.[6]) After 18h the precipitated solid was filtered off and recrystallised from acetone followed by acetic acid to give compound (III) (1·5g), mp 176°C; n.m.r. spectrum (DMSO-d_6), τ 1·40 (1H, *s*), 2·03 and 2·06 (2H, AB_q, $J_{AB} = 9{\cdot}2$Hz), 7·45 (3H, *s*) and 7·48 (3H, *s*); mass spectrum, *m/e* 291 (M$^+$). The mass spectrum of compound (III) differed from that of the isomeric compound (II) in that the base peak did not correspond to $[\mathrm{M}\text{-}\mathrm{NO}_2^{\cdot}]^+$ showing that there were no *peri*-nitro groups present.

Further nitration of compound (III) in fuming nitric acid/sulphuric acid yielded 1,3,5,8,tetranitro-2,6-dimethylnaphthalene (IV) in the following manner: 4cm^3 of nitric acid ($d = 1{\cdot}50$) was added dropwise with stirring to a solution of compound (III) (13g) in concentrated sulphuric acid (400cm^3) in a vessel fitted with a drying trap. After standing for 30h the reaction mixture was poured onto ice and the precipitated product thoroughly washed with water followed by acetone and then recrystallised three times from glacial acetic acid to give compound (IV) (6·0g), mp 302°C; n.m.r. spectrum (DMSO-d_6), τ 1·22 (1H, *s*), 1·24 (1H, *s*), 7·41 (3H, *s*) and 7·47 (3H, *s*); mass spectrum, *m/e* 336 (M$^+$), 290 (base peak). As before, the base peak corresponding to the $[\mathrm{M}\text{-}\mathrm{NO}_2^{\cdot}]^+$ ion indicated the presence of *peri*-nitro groups.

The action of fuming nitric acid on compound (III) in acetic anhydride resulted in the formation of 1,3,5,7-tetranitro-2,6-dimethylnaphthalene (V). Thus, a solution of compound (III) (3g) in acetic anhydride (300cm^3) was treated in exactly the same manner as for the preparation of compound (III). Recrystallisation as specified above yielded compound (V) (0·3g), mp 332°C; n.m.r. spectrum (DMSO-d_6), τ 1·35 (2H, *s*), 7·48 (6H, *s*); mass spectrum, *m/e* 336 (M$^+$).

Dr B. C. Webb of the Rocket Propulsion Establishment, Ministry of Defence, is thanked for discussions.

Received 28 October 1977

References

[1] Shipp, K. G. & Kaplan, L. A., *J. org. Chem.*, 1966, **31**, 857

[2] Bowman, N. J. & Knippenberg, E. F., *J. Spacecraft*, 1966, 3, 1542

[3] Kilmer, E. E., *ibid*, 1968, 5, 1216

[4] Bil, M. & Bernstein, A., *Chem. & Ind.*, 1967, 1221

[5] Robinson, S. R., Wells, C. H. J., Turner, R. B. & Todd, J. F. J., *J. chem. Soc. Perk. II*, 1976, 1363

[6] Urbanski, T., 'Chemistry and technology of explosives', Vol I, 1964, *Pergamon Press*