STUDIES ON THE PHOTO-OXIDATION OF

BIORESMETHRIN AND RELATED COMPOUNDS

by

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A Thesis submitted in partial fulfilment of the requirements of the Council for National Academic Awards for the degree of Doctor of Philosophy.

Kingston Polytechnic. June 1990.

DECLARATION

During the period of registration as a candidate for the degree of Ph.D. the author has not been registered for any other award of the C.N.A.A. or any other university.

The material used in this thesis has not been used in any other submission for an academic award.

June 1990. (P.Clements)

: To my dear Mum and Dad :

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ACKNOWLEDGEMENTS

First and foremost my thanks must go to my Supervisor, Prof. C.H.J. Wells for the guidance and assistance he has given me throughout this project and during the production of this thesis.

I am grateful to my colleagues in the Chemistry Reasearch Laboratories, in particular; Asoka, Simon, Danny and Hush for their friendship, great humour and the encouragement they have shown me during these testing times.

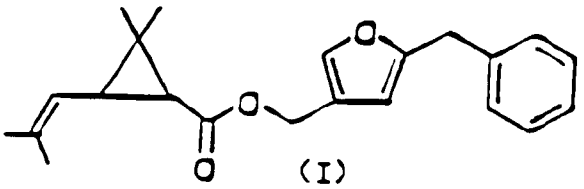
I am deeply indebted to Dr. Derek Kennedy of MSDRL for his efforts and assistance in interpreting the low temperature NMR spectra and expanding my knowledge on the subject.

My thanks must go to the technical staff in the laboratories and workshops of the School of Applied Chemistry for their friendly assistance and advice during the course of this project.

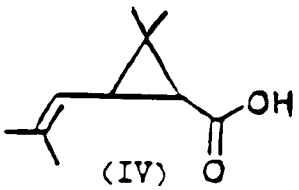
Finally, my appreciation must go to my wife, Deborah, for her assistance and tolerance in the production of this thesis.

Abstract

The sensitised photo-oxidation of the insecticide Bioresmethrin (I) and the structurally related compounds (II) - (V) has been investigated.



(I)



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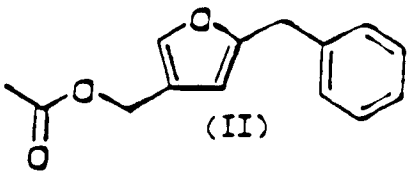
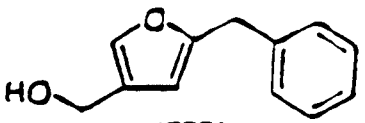


(II)

(V)



(III)

The rate of photo-oxidation of compounds (I) - (V) has been measured, and it has been deduced from the analysis of the kinetic data, the effect of solvent deuteration on reaction rate, and the effect of sodium azide on reaction rate that photo-oxidation occurs primarily via reaction with singlet oxygen. The effect of pH on the reaction rate has also been determined.

The thermodynamic parameters for photo-oxidation have been measured. The rate constant for the reaction of singlet oxygen with compounds possessing a furan ring *viz.* Bioresmethrin and compounds (II) and (III), has a value of the order of 10^8 $mol^{-1}dm^3s^{-1}$, whereas the rate constant for compounds (IV) and (V) containing the isobutenyl group has a value of the order of 10^8 $mol^{-1}dm^3s^{-1}$. The enthalpy of activation for the reaction of singlet oxygen with Bioresmethrin and compounds (II) and (III) is close to 0 $kJmol^{-1}$, whilst the entropy of activation lies in the range - (96-103) $JK^{-1}mol^{-1}$ in methanol and - (75-87) $JK^{-1}mol^{-1}$ in methanol/water. The rate constant with Bioresmethrin of singlet oxygen generated homogeneously, heterogeneously and exogeneously has the same value, within experimental error, and is of the order of 10^8 $mol^{-1}dm^3s^{-1}$. It is deduced from the thermodynamic data parameters for the reaction that the attack of singlet oxygen occurs initially at the furan ring site in Bioremethrin and compounds (II) and (III). Kinetic measurements have shown that approximately one encounter in seventeen between singlet oxygen and Bioresmethrin leads to reaction products, this being a factor of three and fifteen less than for compounds (II) and (III) respectively.

An NMR study of the low temperature dye sensitised photo-oxidation of Bioresmethrin shows that the initial product is 2,5-furan endoperoxide derivative, which is present in two diatsereoisomeric forms.

An autoradiographic study of final products formed in the sensitised photo-oxidation of Bioresmethrin has shown that (a) a complex mixture of products is formed, (b) the rate of reaction is reduced by the singlet oxygen quencher, β-carotene, (c) the product distribution is largely independant of the sensitiser used (Rose Bengal, Methylene Blue,

Chlorophyll), and (d) the product distribution is similar when singlet oxygen is generated homogeneously, heterogeneously and exogeneously.

It has been discovered that soil samples of different pH can act as sensitisers for the exogeneous generation of singlet oxygen. This has implications in that the soil sensitised photo-oxidation of agrochemicals via reaction with singlet oxygen is a possible degradation pathway for such chemicals in the environment.

CHAPTER 1.

Introduction.

1.1. The development and use of insecticides.

1.1.1. Introduction.

> 'And the locusts came ... and settled on the whole country of Egypt ... and they ate all the plants in the land and all the fruit of the trees ... not a green thing remained, neither tree nor plant of the field, through all the land.'
>
> *Exodus* 10:14-15

According to recent discoveries humanoids have existed on earth more than 3 million years, while insects are known to have existed for 250 million years. Yet human beings have learned to live and compete with the insect world. Of the 800,000 species of insects 100,000 plant-eating species add to the devastating loss of crops throughout the world.

It has been estimated that approximately one-third of the world's food crops is destroyed by pests during growth, harvesting and storage(1). Losses are even higher in emerging countries: Latin America loses to pests approximately 40% of everything produced. Cocoa production in Ghana, the largest exporter in the world, has been trebled by the use of insecticides to control just one insect species. Pakistan sugar production was increased 33% through the use of insecticides. The Food and Agriculture Organisation (FAO) has estimated that 50% of cotton production in developing countries would be destroyed without the use of insecticides.

Studies performed in the USA(2) give an indication of the dramatic increase in crop yields that can be acheived through the use of insecticides (Table 1). It can be seen that increased yields of up to

Table 1. Comparison of losses caused by insects in plots treated by conventional use of insecticides and untreated plots.

Commodity	Calculated losses (percentage)		Increased yield (percentage)
	With treatment	Without treatment	
Corn			
Southwestern corn borer	9.9	34.3	24.4
Leafhopper on silage corn	38.3	76.7	38.4
Corn rootworm	5.0	15.7	10.7
Soybeans			
Mexican bean beetle	0.4	26.0	25.6
Stink bugs	8.5	15.0	6.5
Velvet bean caterpillar	2.4	16.6	14.2
Looper caterpillar	10.5	25.5	15.0
Wheat			
Brown wheat mite	21.0	100.0	79.0
Cutworms	7.7	54.7	47.0
White grubs	9.3	39.0	29.7
Cotton			
Boll weevil	19.0	30.9	11.9
Bollworm	12.1	90.8	78.7
Pink bollworm	10.0	25.5	25.5
Thrips	16.7	57.0	40.3
Potatoes			
Colorado potato beetle	1.0	46.6	45.6
European corn borer	1.5	54.3	52.8
Potato leafhopper	0.4	43.2	42.8

50% can be acheived through the control of just one insect species e.g. the European corn borer in potatoes.

1.2. Pyrethrum and pyrethroids.

1.2.1. Pyrethrum - history and its commercial development.

Pyrethrum or "insect powder" refers to the dried and powdered heads of the *Chrysanthemum cinerariaefolium* plant. There are numerous stories as to whom first discovered the insecticidal properties of this substance - the Iranians, the Dalmations or even the Chinese in the 1st century A.D.[3]. What is known is that insect powder was introduced into a number of European countries, from Dalmatia and Iran, in the 2nd and 3rd quarters of the 19th century and in use in Japan by 1885 - although it was in use in Russia well before this period.

Pyrethrum, though readily used in its un-adulterated state, is actually a complex mixture of 6 esters (collectively known as the

pyrethrins) which are the active constituents of pyrethrum[4-6]. The pyrethrins are named according to the parent alcohol, with the parent acid being identified by a roman number i.e. "I" for chrysanthemic acid and "II" for pyrethric acid (Figure 1). Pyrethrum extract usually contains equal proportions of chrysanthemic and pyrethric acid esters. Pyrethrolone esters (pyrethrins I (6) and II (7)) account for 73%, cinerolone esters (cynerins I (8) and II (9)) for 19% and jasmolone esters (jasmolins I (10) and II (11)) 8% of the total[7]. The absolute configuration of pyrethrins has been established[8-15].

1.2.2. Pyrethroids - a definition.

Pyrethroids have been arrived at by synthesis based on natural pyrethrins as models, generally by systematic variation of parts of the molecule for the purpose of determining the effect of biological activity. A few jumps springing from inspiration or from the availability of materials may have been made, but by and large most pyrethroids may be recognised as having been derived from the constituent esters of pyrethrum, perhaps in several stages, even if a direct comparison between the starting point and the end product shows quite startling differences. It is also true that pyrethroids exhibit a range of biological properties, although compounds at opposite ends of this spectrum will differ quite markedly.

One reason for this difficulty of definition may be that structure/activity relationships in pyrethroids are based mainly on considerations of shape and stereochemistry rather than on electronic properties, so that they cannot be defined straightforwardly in terms of specific chemical groups. The only definition that is likely to last is a mutually accepted one based on evolution. A compound may be said to be a pyrethroid if its structure can be reasonably derived from that of

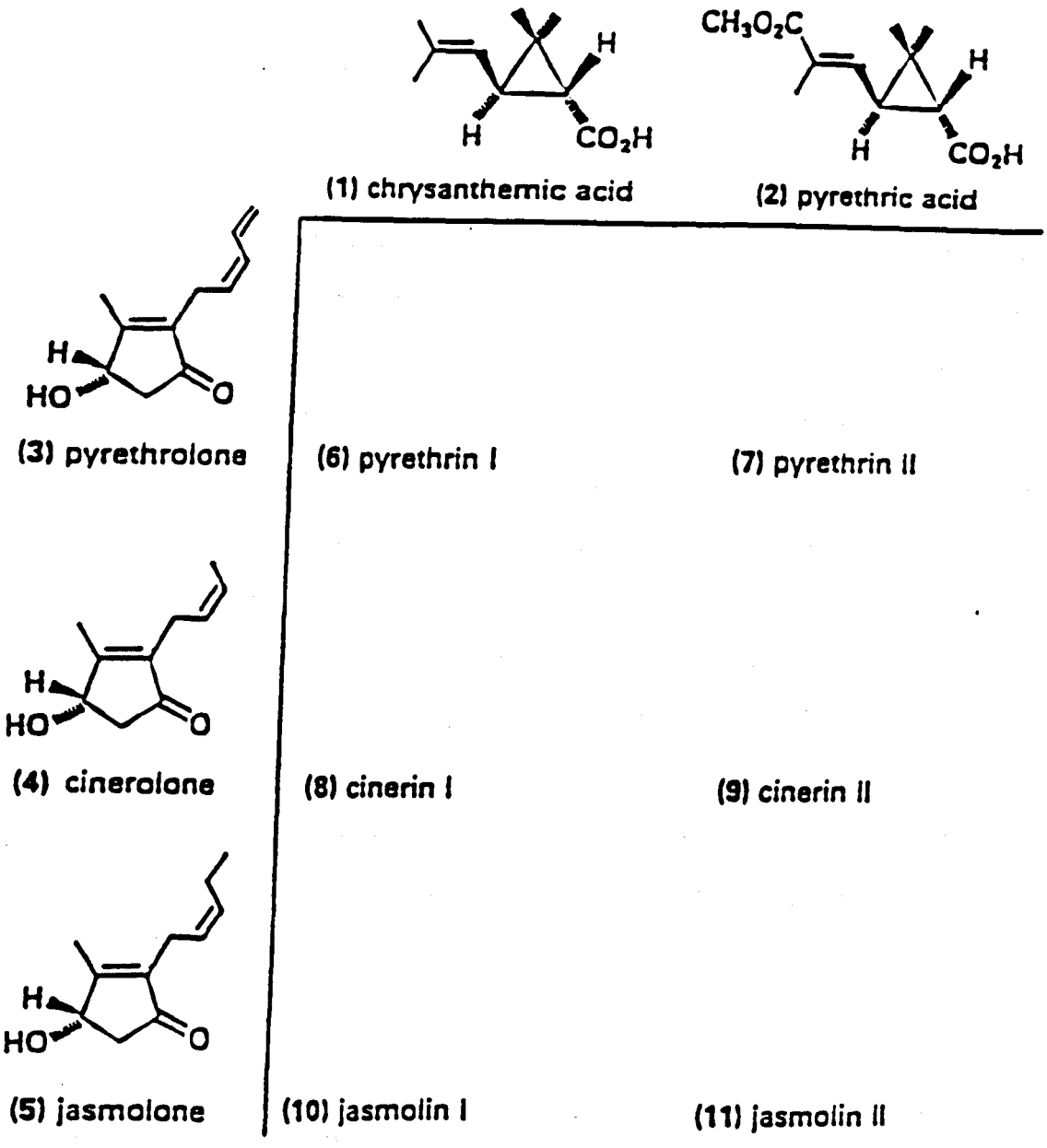
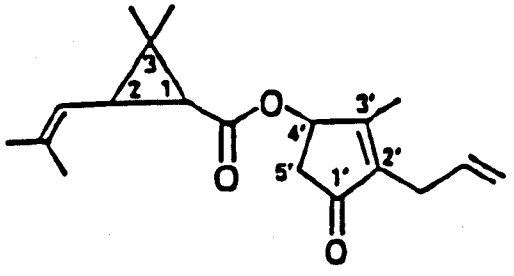


Figure 1. Structures and absolute configurations of the constituent acids and alcohols of the natural pyrethrins and the names of the six esters known collectively as pyrethrins.

the natural pyrethrins, and if it exhibits a range of biological properties that overlap to a considerable degree with those of existing members of the group.

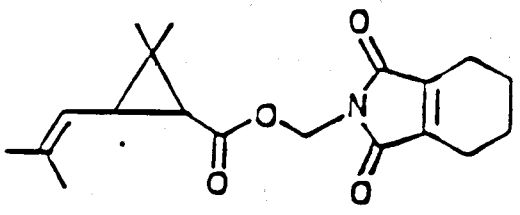
1.2.3. The development of synthetic pyrethroids.

The first pyrethroid allethrin (12), became commercially available in 1949[18,17], it marked the beginning of an era of complex syntheses, involving as many as 22 chemical reactions to produce the final insecticide. Allethrin is merely a synthetic duplicate of cinerin I (a component of pyrethrum), with a slightly more stable side chain, and it is more persistant than pyrethrum. Equally effective against houseflies and mosquitoes, but less so against cockroaches and other insects, it was readily synergised by the common pyrethrum synergists. Allethrin is the ester of racemic allethrolone with racemic *cis/trans* - chrysanthemic acid[17-20]. The ester of allethrolone and the naturally (1R)-*trans* acid is known as bioallethrin (13), and the ester of the (1R)-*trans* acid with (S)-allethrolone as (S)-bioallethrin (14)[21]. The prefix "bio" is generally used to indicate esters of the natural dextrorotatory (1R)-*trans* chrysanthemic acid.

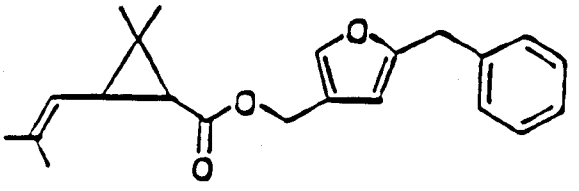


(12) allethrin
(13) bioallethrin [1*R*–*trans*, 4'*RS*]
(14) (*S*)-bioallethrin [1*R*-*trans*, 4'*S*]

The second generation tetramethrin (15), which appeared in 1965[22], gives a stronger knockdown of flying insects than allethrin and is readily synergised. Resmethrin (16) appeared in 1967[23] and is 20 times more effective than pyrethrum in housefly knockdown, and is not synergised to any appreciable extent with pyrethrum synergists. Bioresmethrin (17),

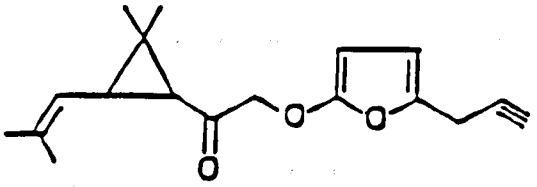


(15) tetramethrin

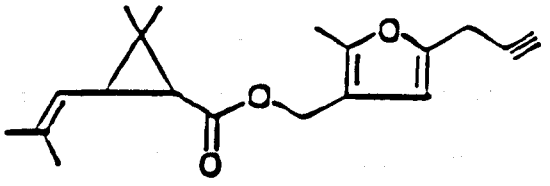


(16) resmethrin

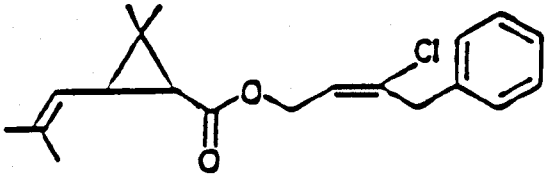
(17) bioresmethrin (1*R*–*trans*)



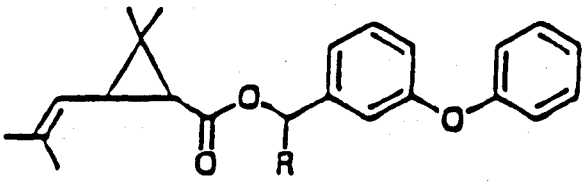
(18) prothrin



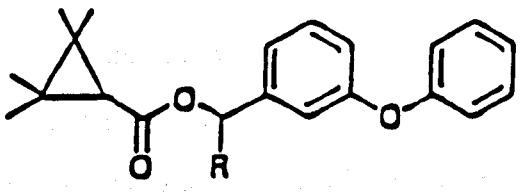
(19) proparthrin



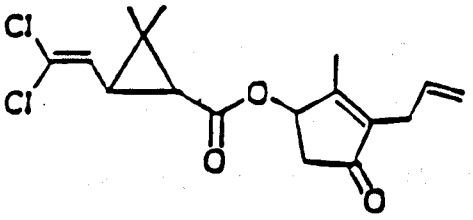
(20) butethrin



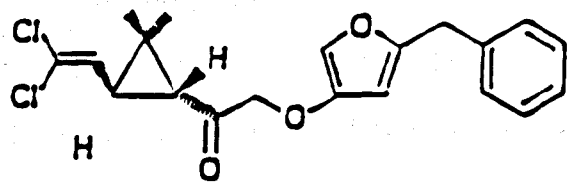
R = H, (21) phenothrin
R = CN, (22) cyphenothrin



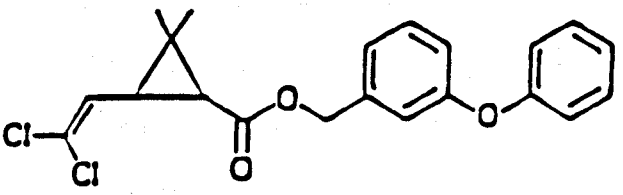
R = H, (23)
R = CN, (24) fenpropathrin



(25) (1*RS*–*trans*, 4'*RS*)



(26) (1*R*–*trans*)



(27) permethrin

also described in 1967[24], is 50 times more effective than pyrethrum against normal (susceptible to insecticides) houseflies, and also not readily synergised by pyrethrum synergists. Both remethrin and bioresmethrin are more stable than pyrethrum, but decompose fairly rapidly on exposure to air and sunlight, which explains why they were never developed for widespread agricultural use. Both of these latter insecticides have become the most used of this generation of pyrethroids for sprays and aerosols to control flying and crawling insects indoors. A number of compounds described during this period appear to have been considered as candidates for commercial development as domestic insecticides - these include prothrin (18)[25], propathrin (19)[26] and butethrin (20)[27].

Sometime after the discovery of benzylfurylchrysanthemates a group of Japanese workers[28,29] made the chrysanthemic acid esters of 3-phenoxybenzyl alcohol - phenothrin (21). As the form enriched in the 1R- isomers (d-phenothrin) this compound is in use as a domestic insecticide. It is the related compound 3-phenoxybenyl-2,2,3,3-tetramethylcylopropane carboxylate (23) that has the distinction of being the first light-stable pyrethroid insecticide made.

Following the discovery of 3-phenoxybenzyl eters, Japanese chemists investigating the effect of substituents at the benzylic carbon atom found that most substituents sharply reduced the activity, but that 2 exceptions were the ethynyl group, which brought about a modest reduction in the activity, and the cyano group, which markedly enhanced the activity[30]. Two compounds - cyphenothrin (22) and fenpropathrin (24) have been developed for agricultural and domestic uses respectively[31,32].

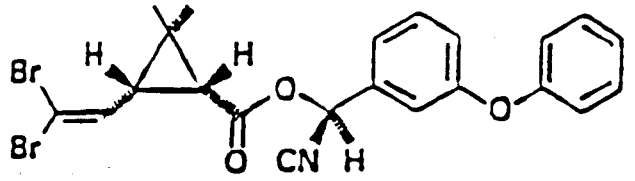
The dichlorovinyl analogues of chrysanthemic acid were first

synthesised around 1957[33] in both *cis* and *trans* forms. The chlorinated analogue of allethrolone (25) had similar activity to its predecessor but the chlorinated analogue of bioresmethrin (26) has twice the activity against houseflies and mustard beetles[33-35]. Further investigation lead to the synthesis of NRDC143 (27), later called permethrin, which was shown to be much more stable than any of the chrysanthemates or benzyl- furyl esters previously synthesised, to have activity of the same order as bioresmethrin, or greater, and to possess low mammalian toxicity. This work was then systematically extended to include the dibromo- and difluorovinylcyclopropanecarboxylic acids with 3-phenoxybenzyl alcohol and α-cyano-3-phenoxybenzyl alcohol.

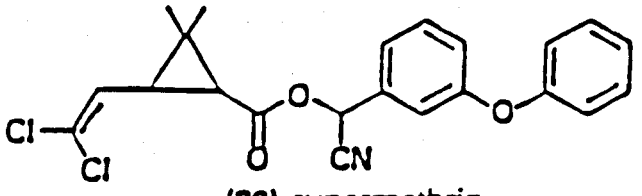
Of the 8 possible isomers deltamethrin (28) is the most singularly effective and was the most active insecticide known at its time[38]. Cypermethrin (29) also emerged at this time as one of the important agricultural insecticides.

One of the suprising developments in pyrethroid synthesis was the discovery of insecticidal activity in a group of phenylacetic acid esters[37] which lead to the synthesis of fenvalerate (30)[38]. Only esters of (S)-2-methyl-3-(4-chlorophenyl)butyric acid have insecticidal activity - this configuration being reconciled with the 1R-configuration of active cyclopropanecarboxylates[38]. Work carried out on a number of cycloalkylidenecyclopropanecarboxylates lead to the synthesis of bioethano-resmethrin (31)[40] and RU15525 (32) - the most active housefly knockdown agent known[41].

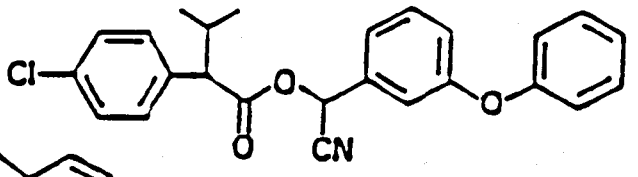
Most recent variations in the acid component of pyrethroids are based on 3-vinylcyclopropanecarboxylic acids, although some sucesful work has been reported on variants of the acyclic phenylacetate series.



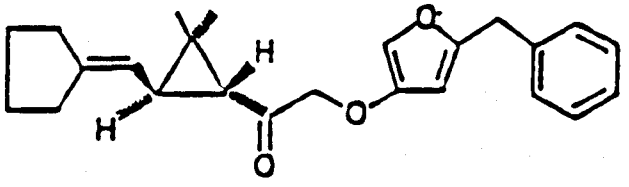
(28) deltamethrin [1*R*–*cis*, α*S*]



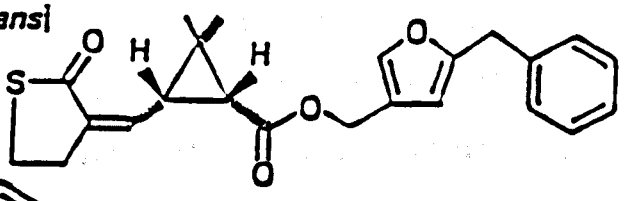
(29) cypermethrin



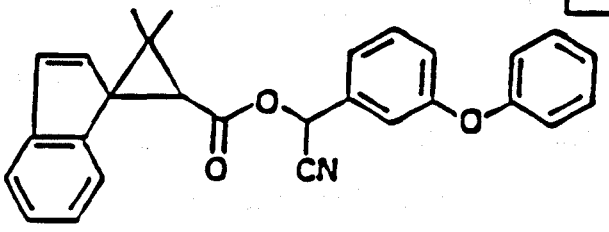
(30) fenvalerate



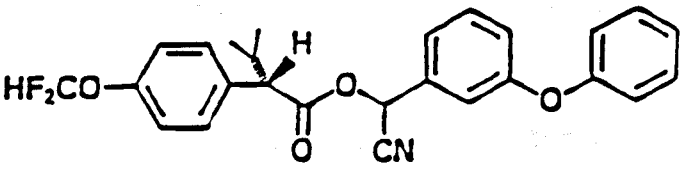
(31) bioethanoresmethrin [1*R*–*trans*]



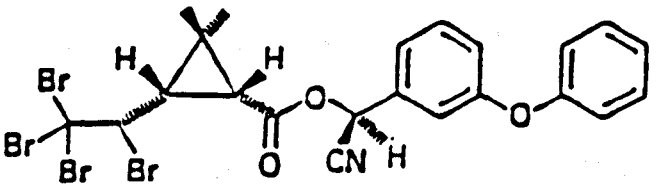
(32) RU 15525 [1*R*–*cis*]



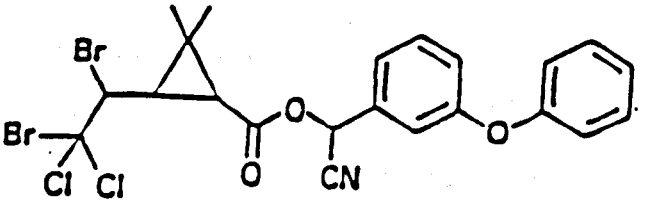
(33) cypothrin



(34) flucythrinate [2*S*, α*RS*]



(35) tralomethrin [1*R*–*cis*, α*S*]



(36) tralocythrin

Workers at American Cyanamid have investigated a series of spiro-substituted cyclopropanecarboxylic acids with 3-phenoxybenzyl alcohol and its α-cyano derivative[42]. Cypothrin (33) has acheived commercial status in animal health as a tickicide, whereas flucythrinate (34) acts as a broad spectrum insecticide[43].

Bromination of the double bond of both deltamethrin, to yield tralomethrin (35)[44], and cypermethrin[45] have been described. Bromination introduces a new centre of assymetry, tralomethrin consists of two isomers, while bromination of cypermethrin produces sixteen (36).

It can be seen that most recent work has resulted mainly in the synthesis of a number of compounds having biological properties very similar to those of the first four pyrethroids to find use as agricultural insecticides. The success of the newer pyrethroids will depend on their ability to match or surpass the performance of the older compounds, or to offer a broader, or different spectrum of biological activity.

1.2.4. Photochemical reactions of the pyrethroids.

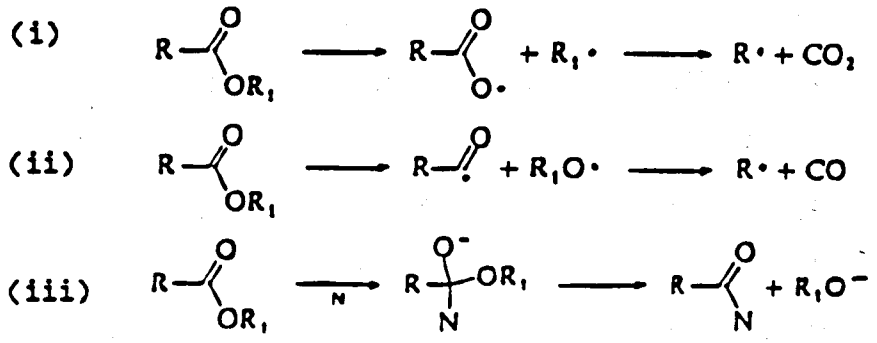
The photochemical breakdown of chemicals in the environment is a subject that merits discussion since it is in many cases the primary pathway for disposal of these chemicals. Much of what occurs after the application of a pesticide can be determined by its photoreactions mediated by sunlight. This is especially true of pyrethroids[46], which contain several light absorbing moieties and can thus be expected to yield considerable numbers of photoproducts.

The pyrethroids that are derivatives of chrysanthemic acid contain an isobutenyl group which is very susceptible to biological[47] and photochemical[48] oxidations. This photolabile moiety was replaced with dihalovinyl substituents in the insecticidally potent compounds

permethrin, cypermethrin and decamethrin. These compounds exhibit two major ultraviolet absorption bands; a relatively intense one at 210-230nm (ϵ>1000 $mol^{-1}dm^{-3}$) for the transition $\pi \rightarrow \pi^*$ transition of the unsaturated groups and another at 250-280nm (ϵ<100) corresponding to the carbonyls which is essentially $n \rightarrow \pi^*$ in charachter. It is the latter transition that is responsible for environmental photodegradation.

1.2.4.1. Photochemical ester cleavage.

There are three main mechanisms that can cleave ester bonds: (i) scission of the carboxylate-carbon bond yielding carbonyl and alkyl CO_2; (ii) cleavage of the carbonyl-oxygen bond and subsequent production of CO_2; (iii) photonucleophillic attack by solvent or other nucleophiles (N) at the excited ester carbonyl.



Cleavage of both *cis*- and *trans*-isomers of resmethrin upon exposure to sunlight wavelengths on silica gel and in aqueous solutions yields chrysanthemic acid but no corresponding alcohol i.e. 5-benzyl-3-furyl-methanol[48]. Ester cleavage however does not occur to any appreciable extent for pyrethrin I, allethrin, tetramethrin or dimethrin when irradiated as thin films on glass by sunlight wavelengths[50]. The pyrethroid s-bioallethrin yielded chrysanthemic acid under a variety of conditions[51], but the alcohol moiety photoproducts were not

characterised.

Photolysis of the ester bond is a major reaction in the newer pyrethroids such as decamethrin[52,53], permethrin[54] and fenvalerate[55]. When *trans*-permethrin is irradiated in hexane or water solution (λ>290nm.) the isometric dihalovinyl acid and 3-phenoxybenzyl alcohol are obtained: in methanol the corresponding ester and ether are formed (Figure 2). *Cis*-permethrin undergoes analogous reactions. Photolysis of decamethrin in hexane, alcohols and aqueous solutions results mainly in two modes of ester cleavage (eqns.(i) & (ii)) including decarboxylation as a minor pathway (Figure 3). The reaction rate decreases in the order methanol>ethanol>propan-2-ol; either because of decreased nucleophilicity or by increased viscosity.

Fenvalerate is rapidly decomposed in acetonitrile-water solutions, methanol and hexane upon irradiation (λ>290nm.). The major photoproduct (>60%) in all cases is the decarboxylated material (Figure 4).

1.2.4.2. Reactions involving the cyclopropyl group.

The insecticidal activity of pyrethroids largely depends upon the configuration at carbon 1 (adjacent to the carboxyl group) of the cyclopropyl ring[71], the most active having a (1R)-configuration. Any epimerisation at this site would therefore result in a dramatic loss of activity. Furthermore the *cis*- and *trans*-isomers (about C_1 and C_3) differ considerably in biostability and insecticidal activity[57,58]. These factors make photoisomerisation an important reaction of pyrethroids.

Early work on simple alkyl esters of chrysanthemic acid[59] reported the formation of a lactone and elimination of a carbene to yield a dimethyacrylate (Figure 4). Chrysanthemol was photoisomerised to 2-isopropenyl-5-methyl-4-hexen-1-ol by 1,4-proton migration of the initially formed diradical intermediate. Direct irradiation of the

Figure 2. Ester cleavage reactions of t-permethrin.

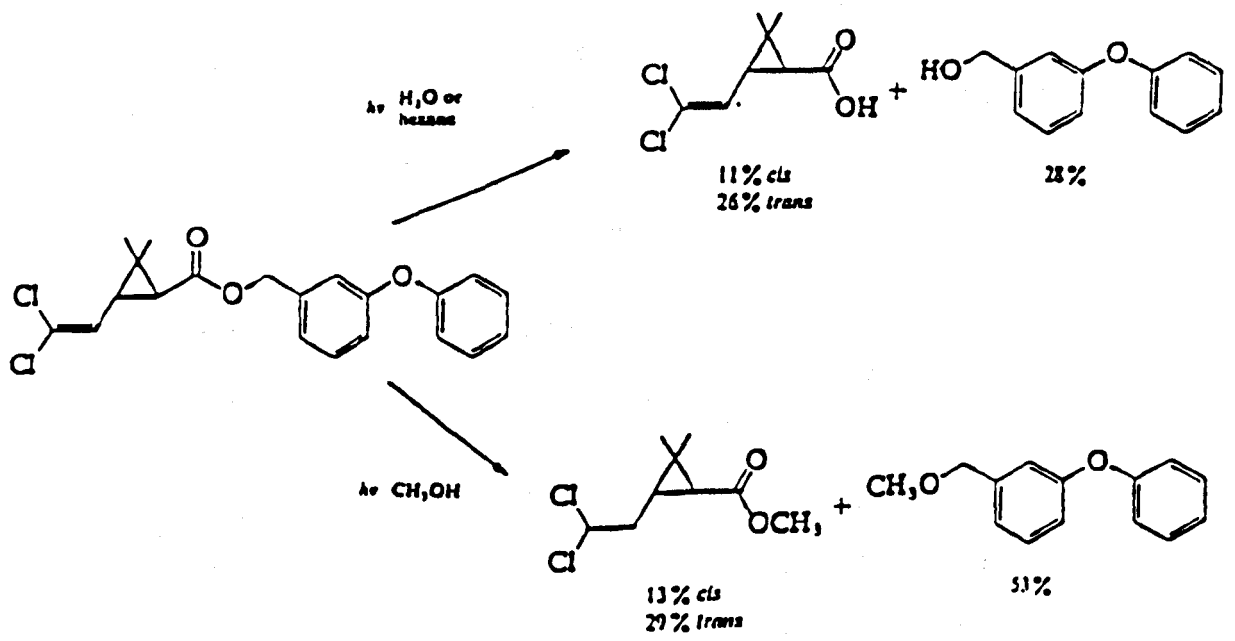


Figure 3. Ester cleavage reactions of decamethrin.

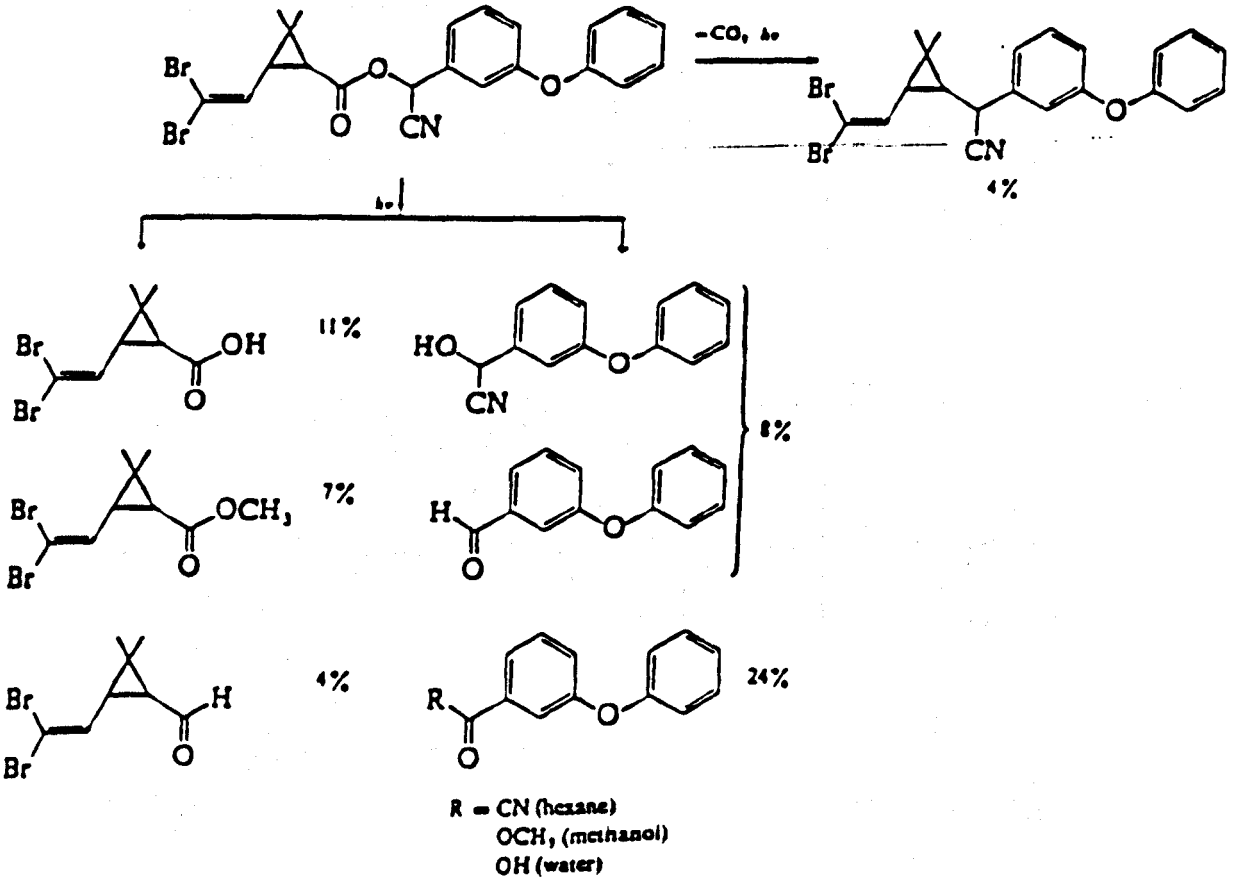


Figure 4. Ester cleavage reactions of fenvalerate.

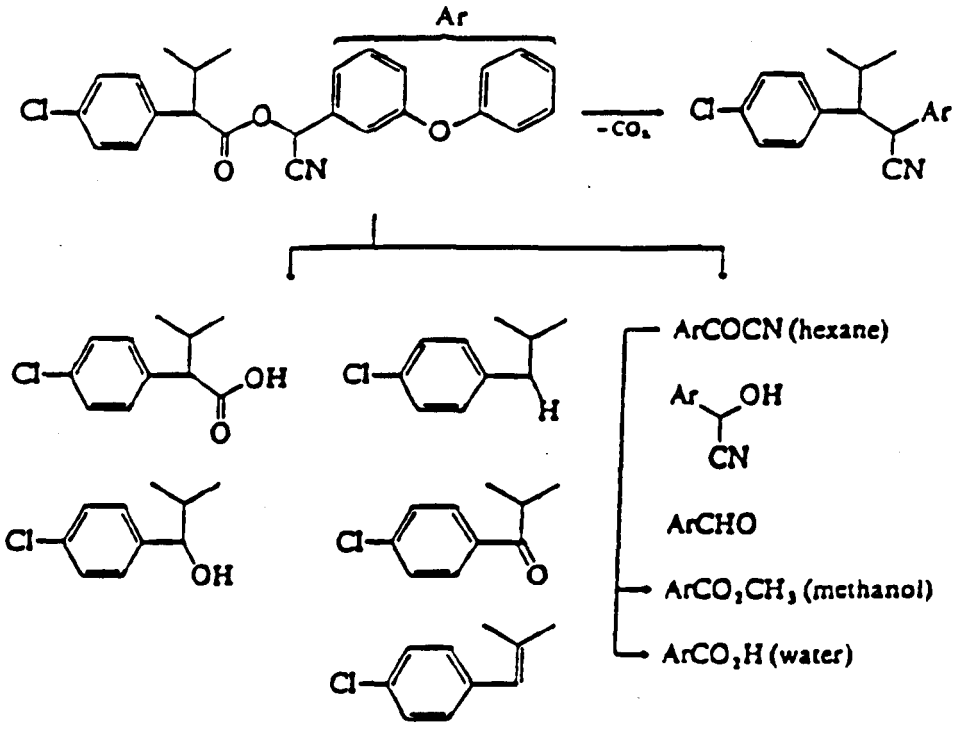


Figure 5. Isomeric products of kadethrin.

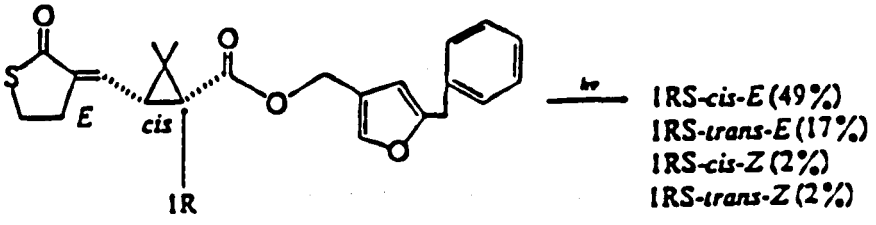
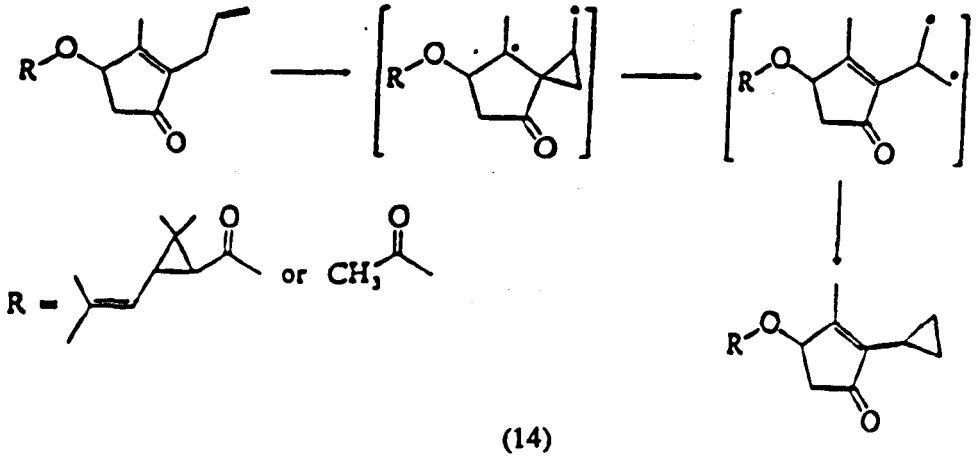


Figure 6. Di-π-methane rearrangement in allethrin and allethrolone acetate solutions.



trans-chrysanthemum dicarboxylic acid results in the formation of the *cis*-isomer, the process could be enhanced by addition of isobutyrophenone as a sensitiser. The abscence of *cis*-trans isomerisation process in thin-films of pyrethrin, allethrin, tetramethrin and dimethrin[80] and in resmethrin[81] suggests that absorption by the alcohol moiety predominates.

Kadethrin, which contains a thiolactone ring in conjugation with the vinyl side chain and thus resembles a pyrethrate, undergoes efficient *cis-trans* isomerisation of the cyclopropane ring as well as E-Z interconversion about the double bond[82] upon sunlight photolysis (Figure 5). These processes are also apparent from the ester cleavage products identified.

1.2.4.3. Isomerisation in the alcohol moiety.

Allethrin posesses a substituted cyclopentenone chromophore which undergoes photochemical rearrangements with wavelengths greater than 300nm in hexane solution to give the cyclopropyl derivative[83,84] (Figure 6). The chrysanthemate moiety is not involved in this reaction since allethrolone acetate undergoes the same process. The mechanism of conversion involves a di-π-methane rearrangement, sensitisation and quenching experiments suggest that the resulting vinylcyclopropane compound is formed via a triplet excited state. Jasmolin I (Figure 7) does not undergo the di-π-ethane rearrangement upon irradiation but yields instead the E-*trans*-isomer from the Z-*cis*-2-pentenyl group[85]. Neither allethrin nor jasmolin I have been found to yield lactones or dimethyl acrylates upon irradiation.

1.2.4.4. Reductive dehalogenation.

Many halogenated pesticides undergo dehalogenation reactions readily at low wavelengths[88] but not under sunlight irradiation

because of their low absorption at $\lambda > 290$nm. The dihalovinyl side chain in the newer pyrethroid is a special case since the double bond is probably conjugated with the ester carbonyl via the the "bent" cyclopropane bonds which resemble an sp^2 system. Thus, *cis-trans* isomerisation and reductive dehalogenation are competitive processes in the acid moiety of decamethrin [67,68] at 254 and 300nm. Cleavage of the carbon-halogen bond does not appear to proceed from a triplet state since the reaction cannot be quenched. Such processes are usually the result of bond homolysis which yields a free radical pair in a solvent cage, a further step may include electron transfer from halide and vinyl cations[69,70] (Figure 8). The free radical can then abstract from a proton donor (DH), the vinyl cation may react with a neucleophile (N) to give substitution products (eqn.(iv)).

Photoysis of permethrin in methanol, hexane or aqueous solutions yields the monochlorinated derivative of the parent ester and the acid moiety, but only as minor products (Figure 9). Decamethrin[71] debromination to the E and Z isomers is more efficient because of the decreased bond strength of the C-Br bond relative to that of the C-Cl bond. Only the free radical products are observed in all solvents, *trans*-debromination being preferred by a factor of four, over *cis*-debromination in methanol[72].

1.2.4.5. Debromination.

Photolysis of tralomethrin and tralocythrin yield debrominated and dehydrobrominated compounds, *trans*-decamethrin and *trans*-cypermethrin and ester cleavage products similar to those obtained from their precursers[73]. The debromination mechanism involves cleavage of a C-Br bond from the most highly halogenated site yielding a radical

Figure 7. Isomerisation of jasmolin I in hexane solution.

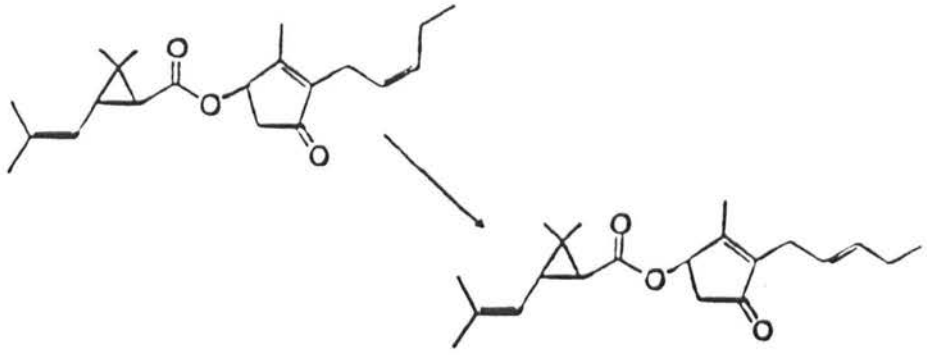


Figure 8. Reductive debalogenation.

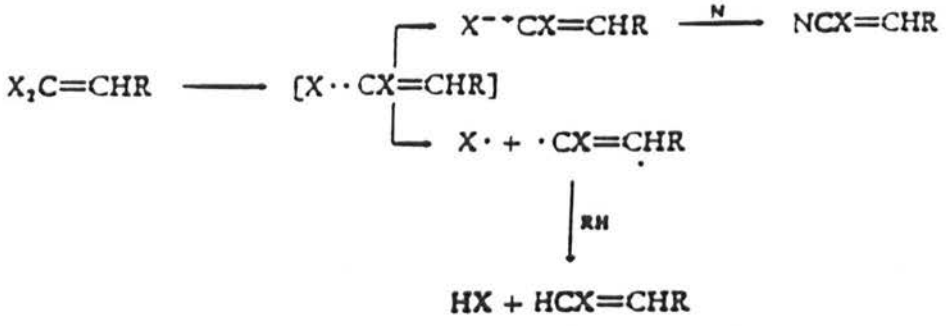
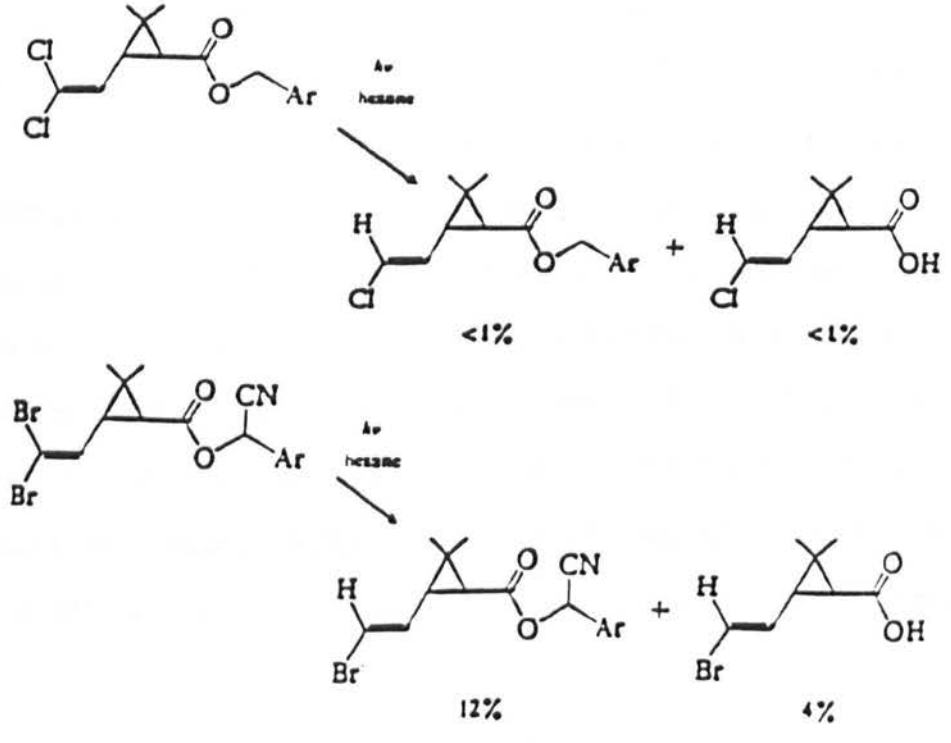


Figure 9. Reductive debalogenation of permethrin and decamethrin.



pair which can either recombine or separate by abstraction of a proton from the solvent; collapse of the resulting trihaloethyl radical by extrusion of a second bromine atom yields decamethrin or *cis*-cypermethrin respectively (Figure 10). The yield of debrominated material is directly proportional to the proton-donating ability of the solvent, irradiation in solvent containing no abstractable protons leads to a complex mixture of polar or polymeric materials and decreased yields of debrominated products.

1.2.4.6. Photooxidation of chrysanthemates.

Pyrethroids possessing the chrysanthemic acid moiety are very susceptable to oxidaton when photolysed in the presence of oxygen[74]. Several mechanisms operate resulting in oxidised products that resemble those obtained from metabolic systems (Figure 11). A recent study of the photolysis of S-bioallethrin[75] confirmed these findings and identified additional products arising from the epoxidation of the isobutenyl side chain, in analogy with the oxidation of tetramethrin and other chrysanthemates in mammals[76]. When S-bioallethrin is irradiated in solution or in the solid phase (360nm) inthe presence of oxygen, consierable amounts of epoxides from the substrate and its products are formed (Figure 12). Hydroxylation of the *t*-methyl group on the isobutenyl moiety also takes place. Formation of the epoxides upon irradiation is greater in benzene (33%) than in hexane (12%) or aqueous solutions (8%), they are not detected in methanol. The reactions of S-bioallethrin can be sensitised by energy transfer from benzophenone, thus increasing the yields of triplet products, but the effect of benzophenone goes beyond that of a sensitiser. Benzophenone is a source of radicals in solution (Figure 13) which can abstract protons from the isobutenyl methyl groups to

Figure 10. Major photoprocesses of tralomethrin (X=Br) and tralocythrin (X=Cl) in the presence of hydrogen donors (DH).

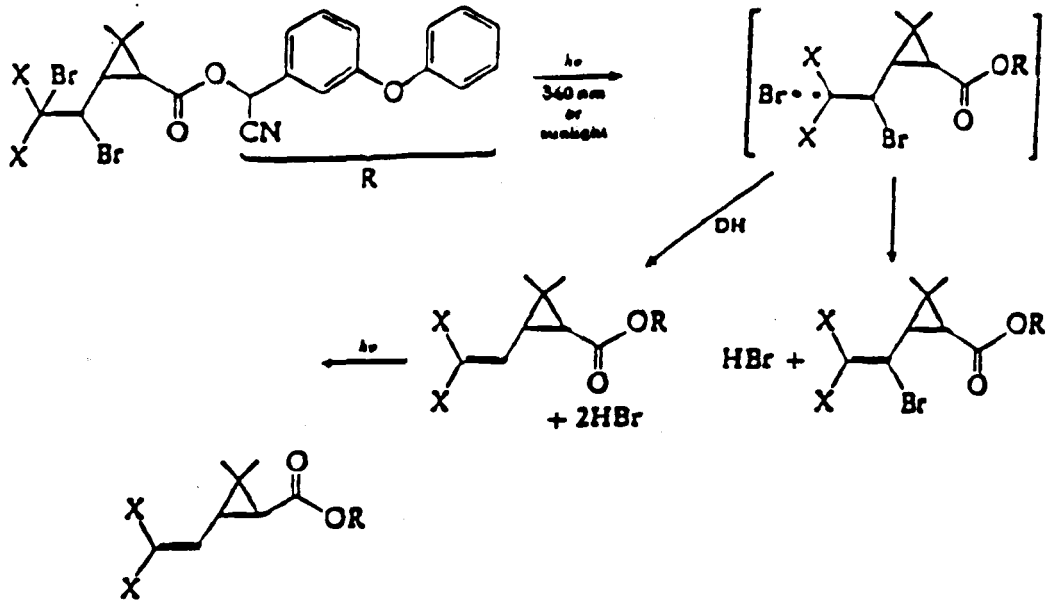


Figure 11. Partial pathways involved in photodecomposition of the acid moiety of chrysanthemates.

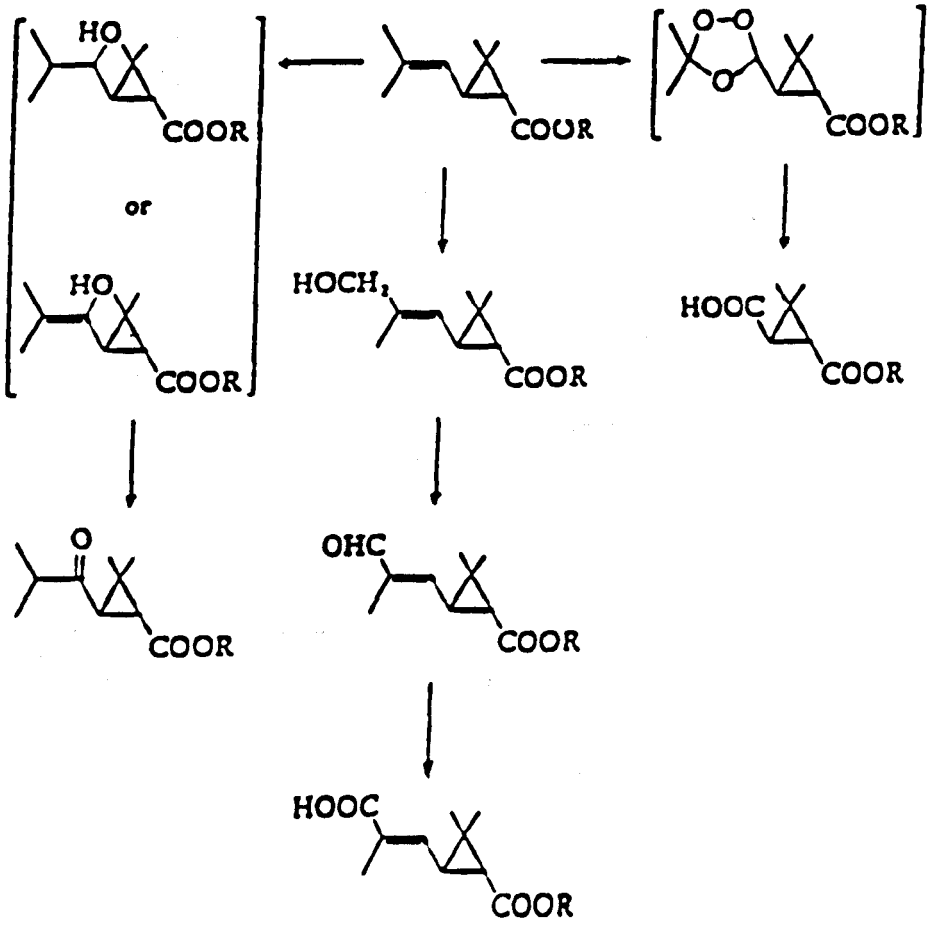


Figure 12. Photo-oxidation of S-bioallethrin.

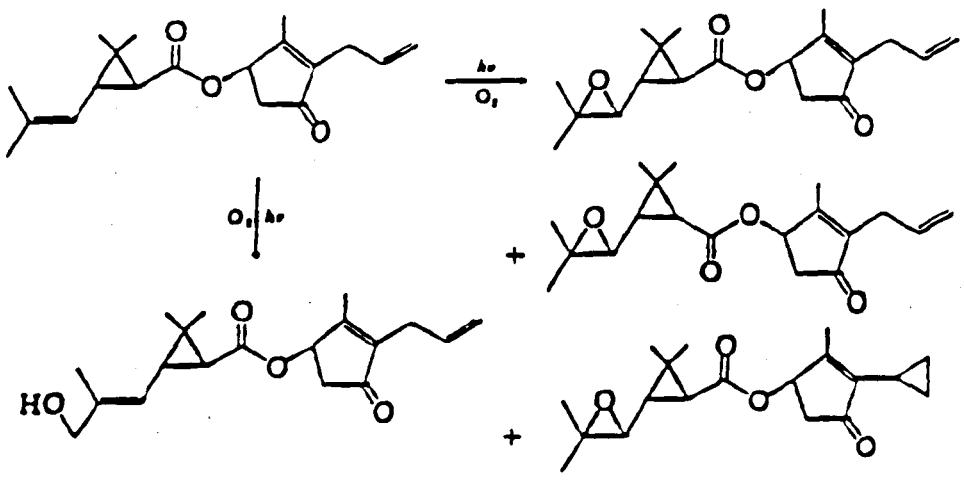
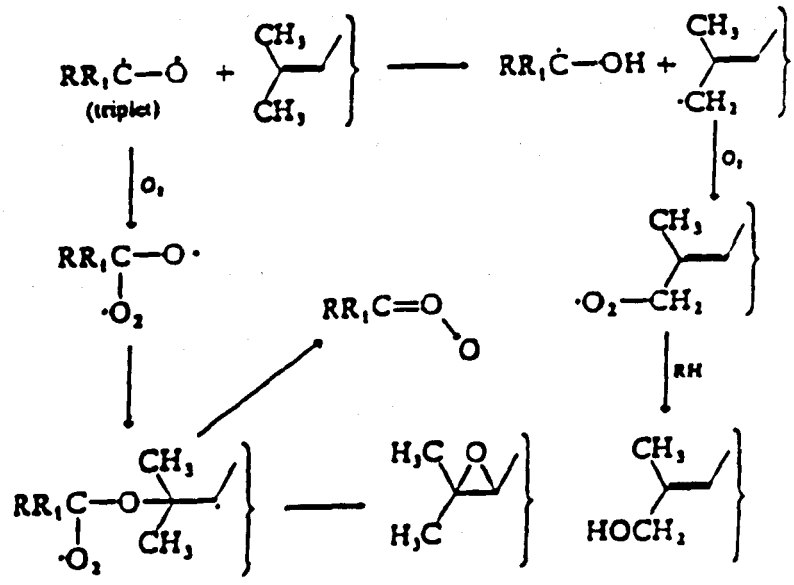


Figure 13. Photoreactions of benzophenone or benzil (RR$_1$C=O) with the isobutenyl substituents of S-bioallethrin.



yield the allylic alcohol, or transfer oxygen to form epoxides.

Epoxidation and allylic oxidations also take place in the absence of sensitisers presumably via radical reactions with triplet oxygen, since these processes are not detected in methanol or 1,3-cyclohexadiene solutions where readily abstractable hydrogen is available to terminate radicals, or in the presence of singlet oxygen. It has been proposed that kadethrin[77] and resmethrin[78] also undergo epoxidation in the acid moiety. However the major oxidative reaction in these processes involves degradation of the furan ring to yield a cyclic ozonideperoxide by addition of oxygen across the unsaturated system (Figure 14) similar to those postulated as intermediates in the photochemistry of furans[79]. Migration of the benzyl cation or radical would give the benzyloxylactone; migration of a proton from the position symmetrical to the benzyl group would yield the hydroxylactone. The hyroxy-cyclopentenolone, obtained as a major product only from resmethrin, may be formed by reduction of the cyclic peroxide to the diol, followed by rearrangement.

The photo-oxidation of the furan ring is probably mediated by singlet oxygen[80,81] since Rose Bengal sensitisation in methanol yields a methoxy-hydropeoxide (Figure 15) by reaction of the solvent with the endoperoxide.

1.2.4.7. Photooxidation of dihalovinylpropanecarboxylates.

Permethrin and monochloropermethrin do not undrgo photo-oxidation within a week of irradiation in methanol containing singlet oxygen. Permethrin does not react with excess *m*-chlorobenzoic acid or trifluoro-peroxyacetic acid in dichloromethane at 298K[82]. The epoxide of monochloropermethrin is, however, obtained with an excess of oxidant. Decamethrin is also resistant to epoxidation[83] but its

Figure 14. Photo-oxidation of the kadethrin and resmethrin moiety.

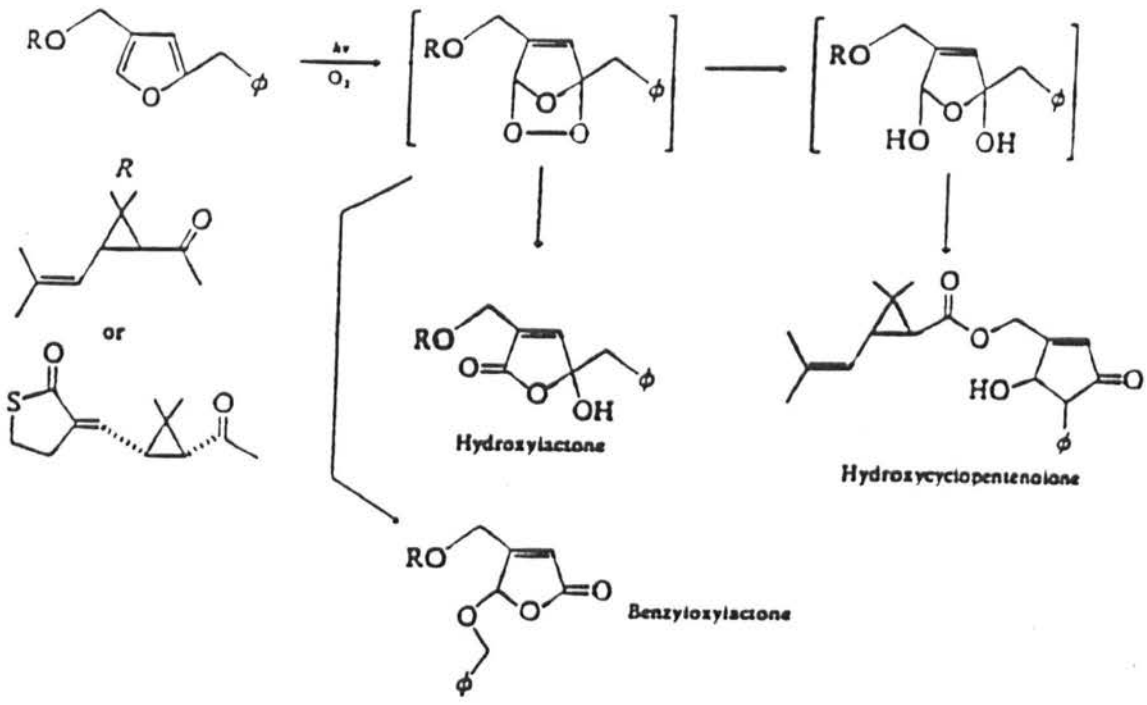


Figure 15. Addition of singlet oxygen to the furyl group of resmethrin.

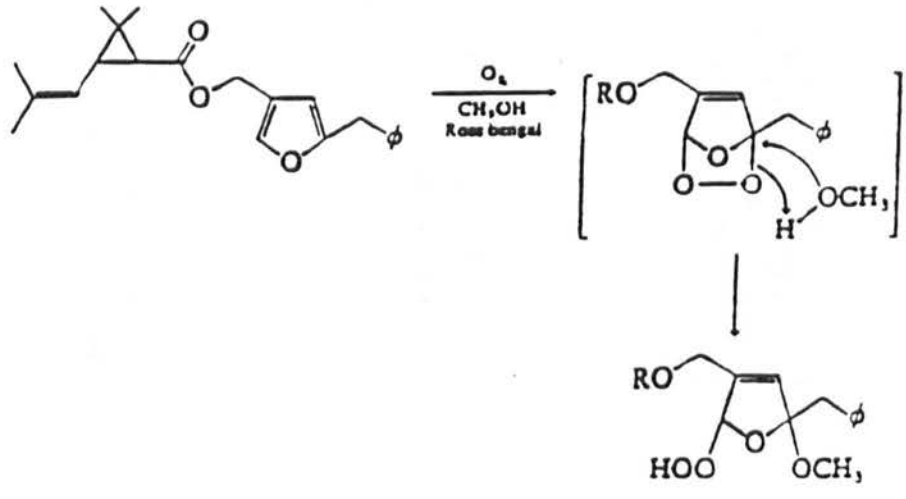
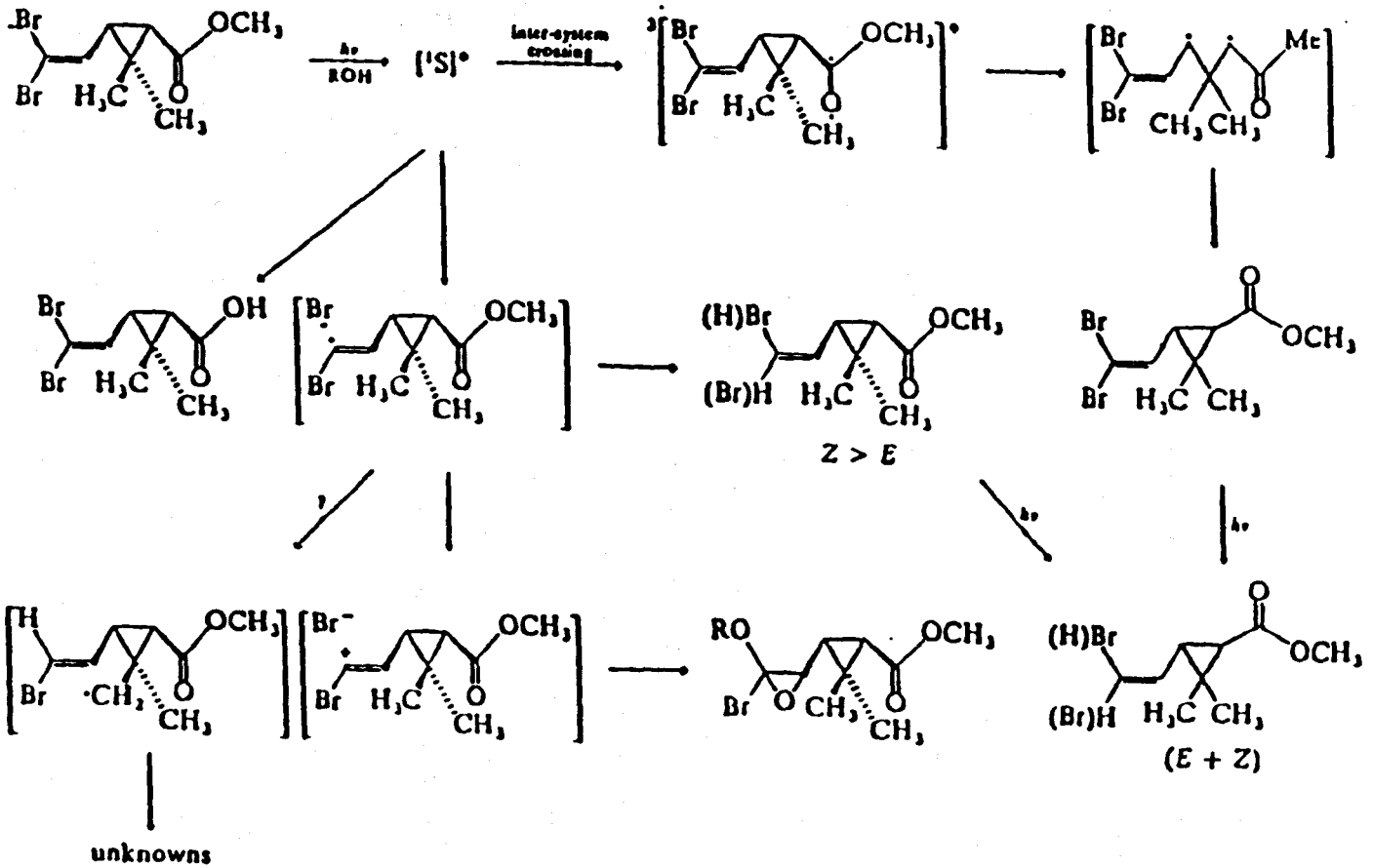


Figure 16. Reactions of cis-2,2-dimethyl-3-(2,2-dibromovinyl)-cyclopropanecarboxylate.



methyl ester yields oxidation products lacking one bromine constituent[84] (Figure 16). Oxidation of the dihalovinyl moiety may be possible under different photolysis conditions since other deactivated alkenes, such as tri- and tetrachloroethylene are epoxidised by irradiation at high temperatures[85].

1.3. Singlet Oxygen.

A brief history.

Mulliken, in 1928[88], studying the absorption bands of atmospheric oxygen established the electronic states of oxygen. There were three low lying states, the triplet ground state $^3\Sigma_g^-$, and two excited singlet states $^1\Delta_g^+$ and $^1\Sigma_g^+$. The chemical species singlet oxygen , the $^1\Delta_g^+$ state , was discovered soon afterwards by Kautsky[87] in 1931 where he described it as "a short-lived, very reactive type of oxygen molecule, that is generated via the transfer of absorbed photon energy to the ground state oxygen molecule". However singlet oxygen remained in the realms of atmospheric spectroscopy until the mid 1960's when it began to attract the attention of organic chemists and biologists as a chemical species of some importance.

1.3.1. The Electronic structure of Singlet Oxygen.

Molecular orbital theory predicts three low lying electronic states as proposed by Mulliken, *vide infra*, and this is borne out by the calculated potential energy curves of molecular oxygen (Figure 17). Information on the electronic structure and behaviour of molecular oxygen may be obtained from these curves. The three low lying states $^3\Sigma_g^-$, $^1\Delta_g^+$ and $^1\Sigma_g^+$ have nearly identical equilibrium inter-nuclear distance separations for their minima and dissociate to the same products in the limit of zero binding. These similarities must stem from a fundamental base and arise from the fact that the same initial electronic

Figure 17. Potential energy curves for the lowest electronic states of molecular oxygen.

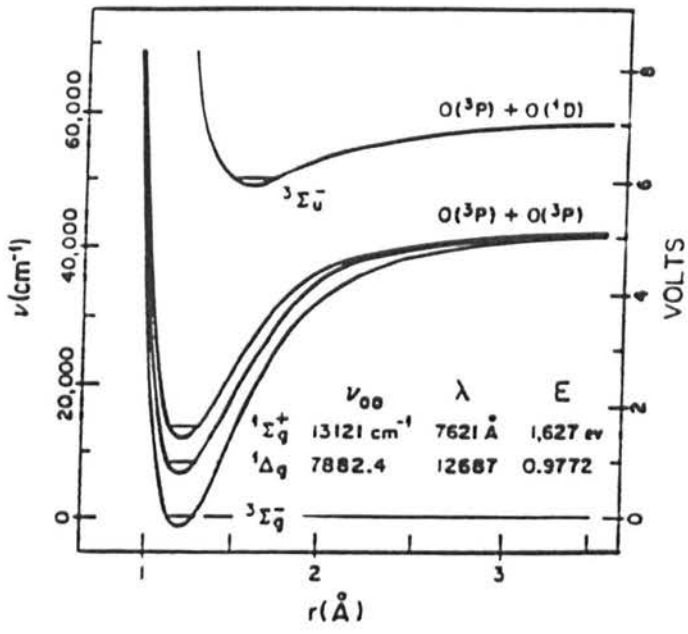


Figure 18. A simplified model of the lowest electronic states of molecular oxygen.

STATE	ORBITAL ASSIGNMENT	LEWIS STRUCTURE	WAVE FUNCTION
$^1\Sigma_g^+$	$\uparrow_{\pi_x}\ \uparrow_{\pi_y}$	$:\ddot{O}:\ \ddot{O}:$	$\pi_x(1)\ \alpha(1)\ \pi_y(2)\ \beta(2)$
$^1\Delta_g$	$\uparrow\downarrow_{\pi_x}\ \bigcirc_{\pi_y}$	$:\ddot{O}:\ \ddot{O}:$	$\pi_x(1)\ \alpha(1)\ \pi_x(2)\ \beta(2)$
$^3\Sigma_g^-$	$\uparrow_{\pi_x}\ \uparrow_{\pi_y}$	$:\ddot{O}:\ \ddot{O}:$	$\pi_x(1)\ \alpha(1)\ \pi_y(2)\ \alpha(2)$

configuration.

$$O_2(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$$

gives rise to the three lowest energy states. This electronic configuration shows how the six valency electrons are disposed among the available molecular orbitals. Since all of the orbitals up to the last two are filled the differences between the three states must be directly attributed to the distribution of these last two electrons in the $1\pi_g$ orbitals.

Using the simplest of models one may highlight the main differences in the electronic structure of the electronic states; though it should be made clear that this model is fraught with many inaccuracies upon rigorous inspection. The two outermost electrons are required to fill the two dgenerate $1\pi_g$ antibonding orbitals. The combination of two indistinguishable electrons and two degenerate orbitals results in a total of six sub-states, each having different electron distributions, energies and magnetic properties. The six electronic sub-states consist of three degenerate $^3\Sigma_g^-$states, two degenerate $^1\Delta_g^+$states and a single $^1\Sigma_g^+$state (Figure 18).

According to Hund's Rule the electronic state of highest multiplicity is the one of lowest energy, therefore $^3\Sigma_g^-$is the ground state of molecular oxygen and $^1\Delta_g^+$and $^1\Sigma_g^+$the first and second excited states respectively.

1.3.2. The Physical Properties of Singlet Oxygen.

The most important properties of singlet oxygen arise as a direct consequence of its electronic structure. The relatively long lifetime of the two excited states arise from the fact that the singlet-triplet transitions $^1\Delta_g^+$and $^1\Sigma_g^-$-$^3\Sigma_g^-$are "spin-forbidden" according to Pauli's Exclusion Principle. This fact is borne out by the extremely

long lifetimes in the gaseous state. Excluding any intermolecular collisions the lifetimes of the $^1\Sigma_g^+$ and the $^1\Delta_g^+$ states were estimated at 7.1 secs. and 45 mins. respectively[88]. In the liquid phase, however, the lifetimes are considerably shorter, due to interaction with the vibrational levels of the solvent, the order of 10^{-6} and 10^{-3}s. respectively, depending on the solvent used[88,89].

1.3.2.1. Quenching of Singlet Oxygen.

The term "quenching" may be used to encompass both the "chemical" and "physical" deactivation of the $^1O_2$ state.

$$Q + {}^1O_2 \begin{cases} \xrightarrow{(1)} Q + {}^3O_2 \\ \xrightarrow{(2)} QO_2 \end{cases}$$

Process (1) is usually referred to as the purely "physical" quenching of the excited state, with no oxygen consumption or products formed (from now on termed quenching). The "chemical" quenching (2), involves the reaction of the quencher, Q, with singlet oxygen and the production of a product or intermediate QO_2 (from now on termed reaction). If both processes occur simultaneously then the whole process is termed "total quenching".

There are 2 major mechanisms of singlet oxygen quenching: charge-transfer and energy-transfer. Both mechanisms are major deactivation pathways of $^1O_2$ but the energy-transfer mechanism appears to be marginally more efficient ($2\times10^{10}M^{-1}sec^{-1}$ vs. $10^6M^{-1}sec^{-1}$) under most circumstances.

A. Energy-Transfer Quenching.

Originally proposed in 1968[91], this mechanism is the reverse of the dye-sensitisation mechanism as proposed earlier by Golnick[82]. A triplet quencher and ground state oxygen are formed when the triplet state of the quencher is equal to or below the energy of the $^1O_2$ ($^1\Delta_g^+$).

state of 22 kcal.mol.$^{-1}$.

This mechanism has been documented for β-carotene[93-98] and is probably also the same for many other conjugated systems[99]. It should be noted that charge-transfer would also be a feasible mechanism for singlet oxygen quenching in these systems.

B.Charge-Transfer Quenching.

Charge-transfer quenching is much more general than energy-transfer and involves the interaction of the "electrophilic"singlet oxygen molecule with an electron donor to form a charge-transfer complex, where the intersystem crossing restrictions are relaxed, finally dissociating into donor and ground state oxygen[100-103]:

$$D + {}^1O_2 = [D...O_2]^1 = [D...O_2]^3 = D + {}^3O_2$$

The rate has been shown to be proportional to the oxidation potential of the donor, the reduction potential of the acceptor and the excitation energy of the excited species[104].

Some compounds that quench by this mechanism also react with singlet oxygen. The proportion of reaction versus quenching is dependant on structure and on the solvent. It is likely that the charge-transfer complex which results can either transfer the electron back, giving ground state oxygen, or combine to give product (DO_2):

$$D + {}^1O_2 \rightarrow [D...O_2] \begin{cases} \rightarrow D + {}^3O_2 \\ \rightarrow DO_2 \end{cases}$$

The ratio of reaction to quenching varies with structure[120] and probably on solvent.

Although there is no single definition of a singlet oxygen quencher, a likely compound must fulfill at least two basic criteria: (a) It should accelerate the deactivation of the singlet state in a given system without reacting with singlet oxygen.

(b) The rate of singlet oxygen deactivation by the quencher should be geater than the solvent dependant decay of singlet oxygen.

If we assume a biological system contains water, then the rate of quenching action, k_q, must be greater than the solvent deactivation rate for water ($k_d=5x10^5s^{-1}$). Assuming concentrations of the quencher to be $\simeq 10^{-2}$ to $10^{-3}M$, kq would have to have a minimum value of $\simeq 5x10^7$ - $5x10^8M^{-1}s^{-1}$ to be effective. Many naturally occurring compounds have values far in excess of this value and some even quench singlet oxygen reactions with rates approaching diffusion controlled reactions ($3x10^{10}M^{-1}s^{-1}$)<108>. It has been proposed that one of the principal functions of these compounds is to quench potential singlet oxygen reactions. Below are examples of some of the reported singlet oxygen quenchers:

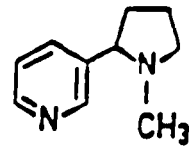
Carotenoids.

The carotenoids are the most extensive class of compounds recognised as singlet oxygen quenchers - an estimated 10^8 tons are produced in nature every year<107>. Most of this staggering output is in the form of four major carotenoids (fucoxanthin, lutein, violanthin and neoxanthin) containing conjugated systems of at least nine double bonds each. All of these pigments quench singlet oxygen reactions with rates approaching diffusion controlled reactions<108,109>,via an energy-transfer mechanism<110>.

Carotenes, although they quench singlet oxygen reactions very efficiently, are not very stable to oxidation - especially in the presence of light. This factor limits their usefulness as photo-stabilisers. The nature of the oxidation products is not completely certain but some progress has been made in this field<111,112>.

Amines.

Although less efficient at quenching singlet oxygen reactions than carotenoids, aliphatic and cycloaliphatic amines have kq values from 10^5 to $4x10^7 M^{-1}s^{-1}$ and aromatic amines; $5x10^8$ to $1.5x10^9 M^{-1}s^{-1}$; as determined by Ogryzlo and co-workers[113,114]. Nicotine(37) was the



(37)

(38)

first amine reported to quench singlet oxygen[115], at a rate of 5.4 times as fast as it is oxidised by singlet oxygen. DABCO (1,4-Diazabicyclo-2.2.2.-octane)(38) does not react with singlet oxygen[118], as does (37), but quenches singlet oxygen seven times as fast.

DABCO, although more efficient than (37), is still only moderately effective as a singlet oxygen quencher ($kq \approx 2.4x10^7 M^{-1}s^{-1}$) having an efficiency of about 1000 times less than β-carotene. Because of its wide spectral absorption and oxidative stability, DABCO has been widely used as a diagnostic tool for a singlet oxygen mechanism[117-126].

Amines of low ionisation potential are better quenchers i.e. tertiary > secondary > primary amines. This result would infer a charge-transfer intermediate being formed. A small spin-orbit coupling between the singlet and triplet states in the intermediate would allow a spin flip to occur and hence a facile inter-sytem crossing from $^1O_2 \rightarrow {}^3O_2$:

$$^1O_2 + NR_3 \Rightarrow [^1O_2 - NR_3] \leftrightarrow [^3O_2 - NR_3] \rightarrow {}^3O_2 + NR_3$$

The results of Young *et al.*[118] suggests only a partial charge-transfer complex and therefore maybe the reaction with singlet oxygen should be written thus:

$$^1O_2 + NR_3 \Rightarrow [^1O_2 \ldots . NR_3] \rightarrow {}^3O_2 + NR_3$$

Other amines react to a greater or lesser extent; the products are complex and often arise from secondary reactions. One of the major processes is oxidation of alkyl groups at the α-position to the aldehyde level. Abstractable protons α- to the amine are a requirement for the reaction to occur; in their abscence, amines are pure quenchers for singlet oxygen[127]. N-Methyl groups in particular are readily oxidised, leading to de-methylation[128,129].

Davidson and Tretheway[130,131] studying the dye-sensitised photo-oxidation of triethylamine and other amines, found that at high amine concentration the dye triplet is quenched by the amine - whereas at low concentration, the reaction proceeds by a singlet oxygen mechanism. They also showed that the amine oxidation rate can either be promoted or inhibited by an increase in the oxygen or amine concentration, depending on the conditions.

Sulphides.

Sulphides are known to both react and quench singlet oxygen, depending upon the conditions, via a persulphoxide intermediate.

$$R_2S + {}^1O_2 \rightarrow [R_2S\text{-}OO^-] \begin{cases} \rightarrow 2\ R_2SO & (a) \\ \rightarrow R_2S + {}^3O_2 & (b) \\ \rightarrow R_2SO_2 & (c) \end{cases}$$

The following experimental conditions are favoured[132]:

Reaction (a) - room temperature, protic solvents

Reaction (b) - room temperature, aprotic solvents

Reaction(c) - low temperature (198K), aprotic solvents and high dilution

Phenols

In a similar manner to amines and sulphides, it appears that phenols are capable of both quenching and reacting with singlet oxygen

under suitable conditions. Thomas[173] has made a detailed study of the reactions rates of 2,4,6-tri-substituted phenols. Further evidence [125] corroborates these findings, suggesting that the phenolic hydrogen does not take part in the rate-determining step and also proposes the intermediacy of phenoxy radicals in at least one of the reactions. Solvent and temperature effects were similar to those encountered with the sulphides[133-138].

Metal Complexes.

Many metal complexes, primarily Ni(II)chelates, have been studied as possible singlet oxygen quenchers. The k_q values for these range up to diffusion controlled rates, with many being employed as commercial photostabilisers for polymers[137-139]. Some of these photostabilisers work by mechanisms other than singlet oxygen quenching i.e.decomposing peroxides without initialising radical chain reactions and the ability to quench excited states other than singlet oxygen.

The exact mechanism for singlet oxygen quenching is not certain,but it appears likely to be that of energy-transfer, however a charge-transfer mechanism would also be possible for some. In general, the quenching ability of the complexes decreases in the order:

Ni(II) > Co > Cu, Pt, Pd, Zn

Inorganic Cations.

This field of study has not had the attention as that of the other compounds - in fact there has only been four reported k_q values, and those being in 1976[140,141]. These range from the rather inefficient Br^- anion ($k_q = 1.2 \times 10^6 M^{-1}s^{-1}$), to the quite efficient O_2^- anion ($k_q = 7 \times 10^8 M^{-1}s^{-1}$). The relative order of quenching of singlet oxygen is:

$I^- > N_3^- > Br^- > Cl^-$

1.3.3. Chemical and Physical Sources of Singlet Oxygen.

The studies of singlet oxygen behaviour and its chemical significance have been intrinsically related to the research on its generation. Thus the impetus for finding new sources of singlet oxygen was prompted not only by the need for better and more efficient producers of singlet oxygen for synthetic purposes, but also by the desire to understand its potential role and mechanisms of formation in biology, organic chemistry, atmospheric chemistry and various complex systems.

At present, there is an impressive variety of sources of singlet oxygen available. These can be conveniently divided into the following categories:-

1. Photosensitisation
2. Gaseous discharge
3. Decomposition of hydrogen peroxide
4. Thermal decomposition of organic ozonides
5. Thermal decomposition of photoperoxides
6. Miscellaneous sources

1.3.3.1. Photosensitisation.

It was Kautsky[142] in 1939 who first noted that the combined effect of light, sensitiser and oxygen could lead to the oxidation of a substrate physically separated from the sensitiser. Kautsky correctly proposed that the light excited the sensitiser which in turn excited the oxygen to his newly discovered singlet oxygen species, which in turn reacted and therefore oxidised the substrate.

It has been proved[142] that the triplet state of the sensitiser, being the longest living state - with respect to the singlet states - reacts with the ground state oxygen molecule to form a collision complex which decays to form the ground state sensitiser

molecule and singlet oxygen through energy transfer.

Because of the inherent proximity of the substrate to the sensitiser in the photosensitisation reaction there is a possibility of the excited state sensitiser molecules interacting with the ground state substrate molecules. These side reactions are classified as 'Type I'[144] to distinguish them from 'Type II' mechanisms that yield singlet oxygen. A Type I process involves the production of free radicals and radical ions by interaction of the sensitiser triplet with a reducing substrate (RH) via hydrogen or electron transfer:

$$^3S_1 + RH \longrightarrow \cdot SH + R\cdot$$

$$^3S_1 + RH \longrightarrow S^{\cdot -} + RH^{\cdot +}$$

Both transients ($R^{\cdot}$ and $RH^{\cdot +}$) produced can react directly with ground state oxygen, leading to photooxidation products or can initiate free radical chain autooxidation. The reduced sensitiser $S^{\cdot -}$ or $SH\cdot$ is further oxidised by oxygen to produce O_2 or its conjugate acid $HO_2^{\cdot}$, which can react further to produce a complex variety of side reaction products.

The factor that determines whether a Type I or Type II reaction occurs is the competition between the substrate and oxygen for the triplet sensitiser. The chemical structures of the sensitiser and the substrate determine the extent of their interaction. In general, sensitisers of ketonic structure (ketones, quinones and quinone-type dyes) with low lying triplet states are powerful abstractors of hydrogen from organic molecules, and react as such.

Substrates that favour a Type I mechanism are those that are readily oxidised (phenols, amines etc.), readily reduced quinones etc.), or prone to hydrogen abstraction (paraffins). Conversely sensitisers of fairly high energy triplet states (fluorescein- and phenothiazine-type dyes, aromatic compounds) react more often by a

singlet oxygen mode.

In general, the less reactive the acceptor is towards singlet oxygen, the more significant the side reactions will be.

Not suprisingly, the oxygen and substrate concentrations in solution can also dictate the occurence of Type I or Type II reactions with tendancy to Type I reactions in solvents of low oxygen concentration e.g. organic solvents, other things being equal. Singlet oxygen lifetimes also vary according to solvent, with the shortest lifetimes in hydroxylic solvents e.g. water: τ = 3 μs., and the longest lifetimes in perfluorinated hydrocarbons and deuterated solvents e.g. D_2O: τ = 52.5 μs, and C_2Cl_4: τ = 1200 μs etc.).

1.3.3.2. Gaseous discharge.

A stream of oxygen gas is subjected to electrodeless disharge thus exciting the molecules to higher electronic states, before they are deactivated both physically and chemically, usually with some fluorescence. Using this procedure concentrations of up to 10% of singlet oxygen can be reached.

Concentrations of singlet oxygen in the gas stream can be monitored by the intensities of the light emission bands corresponding to its decays. Since the major relaxation path for the $^1\Sigma g^+$ state is the more stable $^1\Delta g^+$ state the majority of reactions in the gaseous state are by $^1O_2$ photooxidation.

The least desirable contaminants in this system are oxygen atoms and ozone. The formation of ozone is easily avoided by operating the discharge at a low pressure of a few torr.

The oxygen atoms in the discharged stream can be supressed by a film of mercuric oxide deposited inside the reactor tube immediately after discharge[145]. This film removes the oxygen atoms from the

stream without affecting the singlet oxygen molecules. The presence of oxygen molecules in the gas stream can be detected by the weak yellow air glow that can be viewed in darkness. This glow is the chemiluminescent result of the reaction between nitric oxide and atomic oxygen:

$$NO + O \longrightarrow NO_2 + h\nu$$

The small amounts of NO are formed in the discharge from the contaminant traces of N_2 in the O_2 cylinders, the discharge appearing red from the $^1O_2$ emission in the absence of atomic oxygen. By purposely injecting NO into the system, oxygen atoms can be accurately titrated spectroscopically.

This method of $^1O_2$ generation is ideally suited for studying gas phase reactions and the gas stream may be bubbled through a reaction solution to produce a relatively 'clean' supply of $^1O_2$ without Type I side reactions interfering.

1.3.3.3. Decomposition of Hydrogen Peroxide.

The decomposition of hydrogen peroxide using NaOCl is the oldest method of generating $^1O_2$ with the original reaction performed in 1927[148]. It was not until 1963 that Kahn and Kasha[147] recorded and resolved the emission bands from the reaction and proposed $^1O_2$ as the species responsible for the chemiluminescence. The NaOCl - H_2O_2 reaction was used in 1964 for the first time as a chemical reagent for the preparative peroxidation of unsaturated compounds[148]. The reaction can be performed by adding either NaOCl solution to a solution of H_2O_2 or by passing Cl_2 gas through an alkaline solution of H_2O_2.

The mechanism and kinetics of the two electron oxidation of H_2O_2 by hypochlorous acid have been studied in detail[148,150]. Using radio-

labelled oxygen it was concluded that the molecular oxygen originates from the H_2O_2 and not from ClO or H_2O[151].

The main mechanisms for the reaction have been shown to be:

$$H_2O_2 + OCl^- \longrightarrow HOCl + HO_2^-$$

$$HO_2^- + HOCl \longrightarrow HOOCl + OH^-$$

$$HOOCl + OH \longrightarrow H_2O + ClOO^-$$

$$ClOO^- \longrightarrow {}^1O_2 + Cl^-$$

with the rate determining intermediate in the reaction being the chloroperoxy ion, $ClOO^-$. The yield of $^1O_2$, based on hypochlorite, varies from 60% in methanol and ethanol to 40% in isopropanol, and below 10% in other water-miscible solvents such as THF, dioxane and acetonitrile[152].

1.3.3.4. Thermal decomposition of organic ozonides.

In 1964 Corey and Taylor[153] proposed that singlet oxygen was likely to be formed during the thermal decomposition of ozone-phosphite adducts, and this was confirmed from experimental data of Murray and Kaplan[154] in 1969, using the triphenyl phosphite ozonide.

$$(C_6H_5)_3\text{-}P\langle^{O}_{O}\rangle O \longrightarrow (C_6H_5)_3\text{-}P{=}O + {}^1O_2$$

The triphenyl phosphite ozonide could oxidise typical singlet oxygen acceptors to give the same products as those formed during dye-sensitised photo-oxidation. Additional confirmation of singlet oxygen involvement was provided by its chemical trapping in the gas phase[154] and by spectroscopic detection using E.S.R.[155].

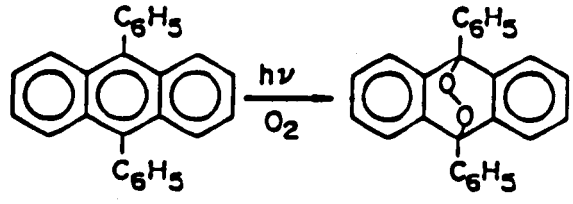
Subsequently, Bartlett and Mendenhall[158] provided experimental evidence for a direct reaction between the aryl phosphite ozonide and some singlet oxygen acceptors, to yield typical singlet

oxygen products at temperatures far less than that required to yield $^1O_2$ fom the adduct.

Because of this direct reaction, the ozonide cannot serve as a thermal source for singlet oxygen at temperatures below 248K. However, the use of pyridine in methanol as the reaction medium facilitates the smooth liberation of singlet oxygen at temperatures as low as 173K to yield similar yields of singlet oxygen as dye-sensitised photooxidation under the same conditions[157].

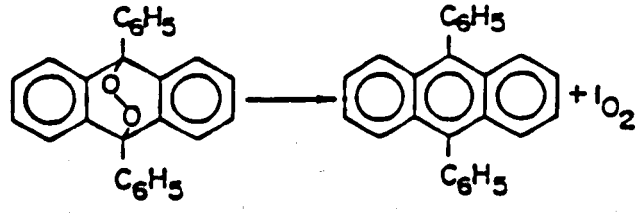
1.3.3.5. Thermal decomposition of photoperoxides.

Many polycyclic aromatic transannular peroxides undergo loss of molecular singlet oxygen upon thermolysis accompanied by regeneration of the parent hydrocarbon[158]. Studies[158] performed using 9,10-diphenylanthracene peroxide propose the following mechanism:



(iv)

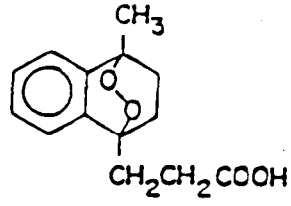
The photoperoxide is generated by the dye-sensitised photooxidation of the hydrocarbon in carbon disulphide at 273K (iv). The resulting peroxide is stable at 273-278K in the solid state, dissociating rapidly as the temperature is increased to full dissociation at 353K (v).



(v)

This method of singlet oxygen formation can be used to oxidise a wide variety of acceptors in aprotic solvents but alcoholic solvents are not suitable media as they react directly with the peroxide. There have

also been reports that the peroxides of other aromatics also release singlet oxygen including alkyl napthalenes[180] and a copolymer 9,10-di,p-styryl-anthracene-styrene[181]. For water-soluble singlet oxygen sources the endoperoxide of 3-(4-methyl-1-napthyl)propionic acid(39) and 9,10-diphenylanthracene-2,3-dicarboxylic acid methyl ester[182](40) may be used.



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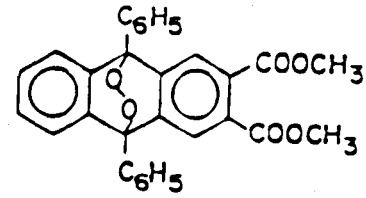


(40)

1.3.3.6. Miscellaneous sources of singlet oxygen.

Even though the direct excitation of ground state molecular oxygen to the singlet state is spin-forbidden a small proportion may be excited with either (a) a He-Ne or Nd-YAG laser at high pressures in Freon 113 [183,184] or (b) a K^+ pumped dye laser with molecular oxygen in gaseous form at 8-10 torr preessure.

The direct photolysis of oxygen in vacuum by U.V. radiation of 147nm. has also been found to yield a small concentration of singlet oxygen[185].

Numerous other methods of generating singlet oxygen have been reported[186-188],each yielding only small concentrations of singlet oxygen.

1.3.4. Chemical Reactions of Singlet Oxygen.

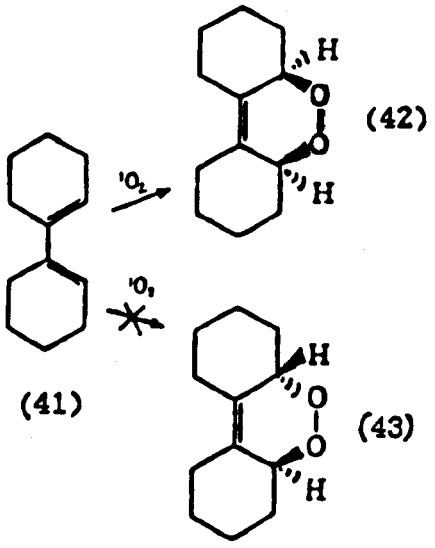
It has been mentioned that the quenching of singlet oxygen may be physical or chemical in nature. For many compounds with a π-system, which can react chemically with electrophilic singlet oxygen, physical quenching is thought to be unimportant in the majority of cases. There

are many factors affecting the rate and mechanism of singlet oxygen reactions, but one may gain an insight into this plethora of reactions by selecting a few examples from groups of compounds possessing similar chemical environments about the reactive π-system.

1.3.4.1. The Reaction of Singlet Oxygen with Dienes and Aromatic Hydrocarbons.

With acceptors such as *cis*-dienes or aromatic hydrocarbons singlet oxygen appears to behave as a good dienophile as some of the following examples show. The similarities of the reactions shown to the more familiar Diels-Alder reaction is obvious, and in fact, the parallels between the two are quite good(188). In general, those molecules which are more reactive in the Diels-Alder reaction are also more reactive towards singlet oxygen. Thus, while anthracene reacts well, both with singlet oxygen and with other good dienophiles, napthalene appears to be unreactive towards singlet oxygen and all but the most potent dienophiles (170).

The concerted character of the addition reaction is indicated by examination of the reaction of the *cisoid* conformation of 1,1'-bi-cyclohexenyl(41). The reaction leads exclusively to the *cis*-



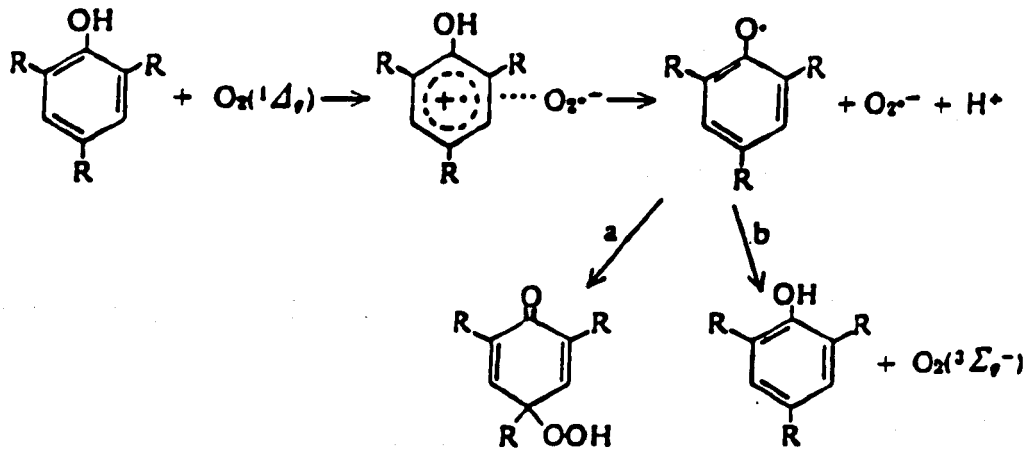
(42)

(41)

(43)

peroxide (42) as the only product. The *trans* product could be formed in a non-concerted two-step reaction involving the formation of an intermediate diradical, but this is ruled out experimentally[171]. To account for these and other experimental observations, it is suggested that the addition of singlet oxygen proceeds via a 6-membered ring transition state, analagous to the Diels-Alder reaction[172].

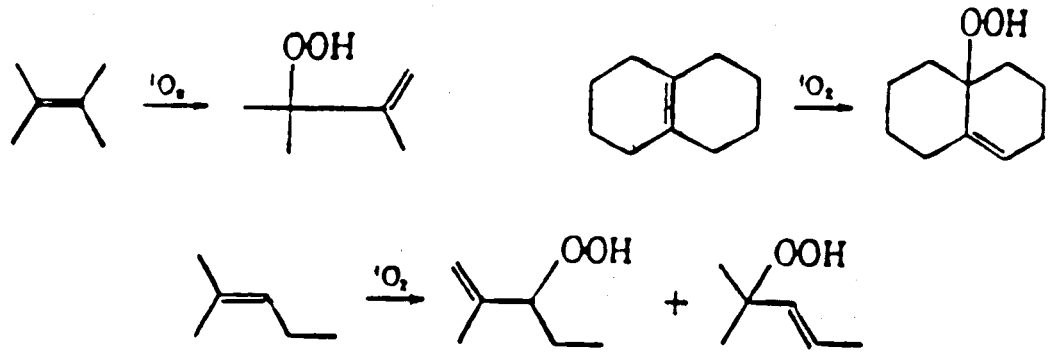
In contrast to the polyaromatics, phenols quench singlet oxygen by a combination of physical and chemical processes. It has been shown for a series of 2,4,6-tri-substituted phenols that the logarithm of the quenching rate constant is a linear function of the half-wave oxidation potential[173] and that both phenols and the corresponding ethers fit the same plot[174]. From these studies the 2,4,6-triphenyl phenoxy



radical is proposed as an intermediate in the quenching of singlet oxygen.

1.3.4.2. Reactions of Singlet Oxygen with Olefins. Formation of Allylic Hydroperoxides.

Perhaps the most thoroughly studied of all singlet oxygen reactions is the "ene" reaction in which singlet oxygen adds to olefins to form allylic hydroperoxides. Some examples of this mode of reaction are summarised below:



There have been numerous intermediates proposed for this mode of reaction, and these are summarised in Figure 19 .

'Ene' Mechanism - It would appear from initial considerations that this classic intermediate is the most probable mechanism by which this reaction proceeds. For instance, it accounts for the stereochemistry of the reaction, the absence of any evidence of radical intermediates, the lack of solvent and substituent effects and excellent correlation between photo-oxidation and rates of peracid oxidation(174,175).

Radical Intermediates- Known radical traps have been shown to have no effect on singlet oxygen reactions thus dismissing this intermediate (174).

Ionic Intermediates- If ionic intermediates were present then one would expect solvent effects to strongly influence the rates of reaction. There is some solvent effect but no correlation with solvent polarity(177,178).

Peroxirane Intermediates- This mechanism appears to correlate well with all experimental observations. The similarity between the rates of peracid oxidation of olefins and their rates of reaction with singlet oxygen can only be expected due to their mechanistic similarities, as illustrated below.

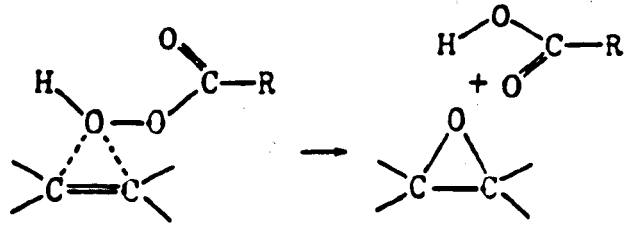
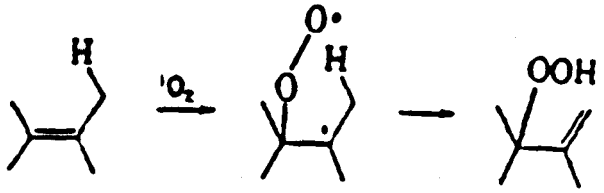


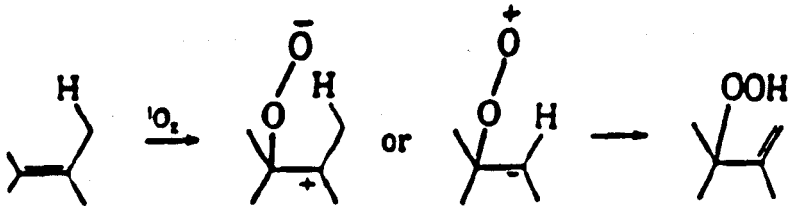
Figure 19. A Summary of the Intermediates Proposed for the Formation of Allylic Hydroperoxides.

"Ene" Mechanism

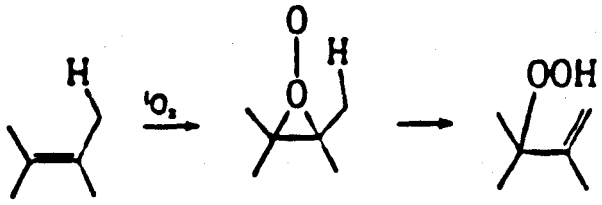
Radical Intermediate



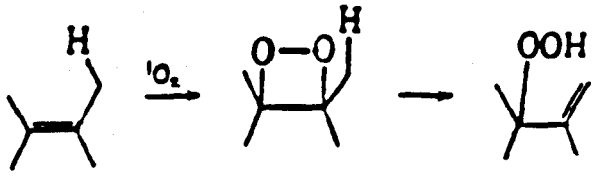
Ionic Intermediates

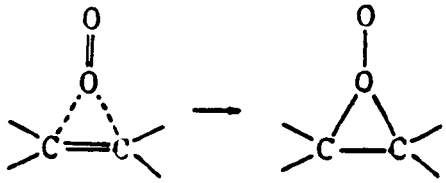


Peroxirane Intermediate



Dioxetane Intermediate

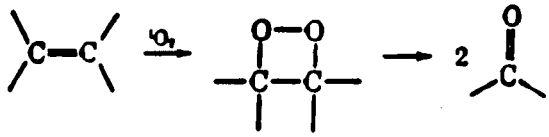




Dioxetane Intermediates- Although dioxetanes have been shown to be formed in the reaction of singlet oxygen with certain olefins[188,178], it is clear that the dioxetanes are not intermediates in the formation of allylic hydroperoxides. It has been shown[180,181] that tetramethylethyne thermally decomposes to yield only acetone, but no allylic hydroperoxide. Other experimental observations such as the lack of substitution effects [181], the stereochemistry and the absence of Makovnikov directing effects[177,178] are all consistent with this mechanism.

1.3.4.3. Reaction of Singlet Oxygen with Olefins. Formation of Dioxetanes.

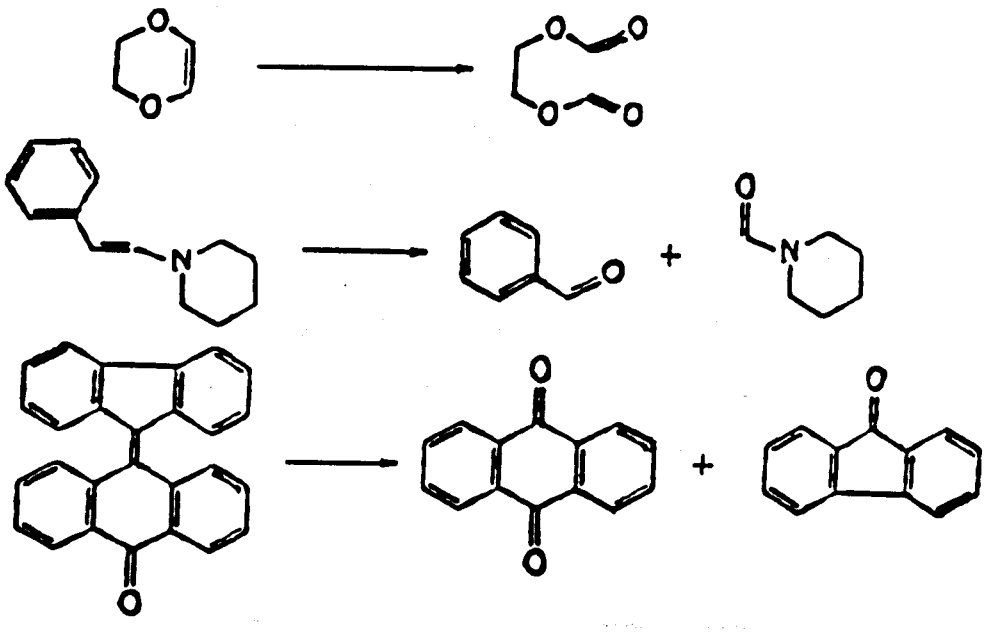
A further mode of reaction between singlet oxygen and olefins is a 1,2-cycloaddition to form relatively unstable dioxetanes which may cleave to yield carbonyl fragments:



The appearance of carbonyl fragments in singlet oxygen mechanisms during early investigations was often attributed to secondary oxidation reactions, and it was not until 1968 when the first stable dioxetane was isolated that this mechanism gained true acknowledgement[182]. The general significance of dioxetanes as intermediates in singlet oxygen reactions with electron-rich olefins becomes clear when it is shown that a dialdehyde, the sole product from the sensitised photo-oxidation of indene, does not arise from the unstable allylic hydroperoxide[178].

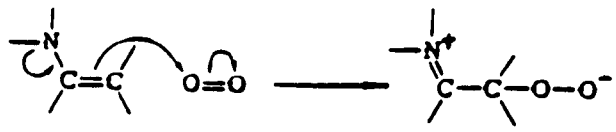
Studies performed since these discoveries have have further invoked the intermediacy of dioxetanes in singlet oxygen reactions with electron-rich olefins. Some of these reactions are illustrated below:

Reactant. Photoproducts.



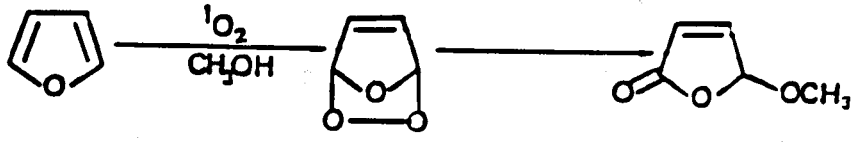
1.3.4.4. Reactions of Singlet Oxygen with Heterocyclic Compounds.

Addition of singlet oxygen to a heterocyclic system usually occurs by one of three methods:(a) 1,4-addition to the 1,3-diene system as frequently encountered in furans, pyroles, oxazoles, thiazoles, imidazoles and purines; (b) dioxetane formation, often encountered in benzofurans, certain imidazoles and purines; (c) hydroperoxide formation by atypical ene-type reaction. These processes may be preceded by the initial formation of a zwitterionic species in which the heteroatom releases elecrons to the electrophilic singlet oxygen through an adjacent double bond as shown in the enamine-like reaction below:

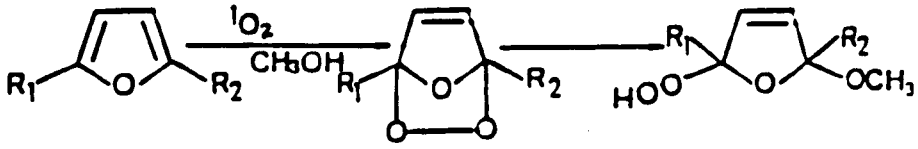


The great diversity among the products formed in the reactions between singlet oxygen and heterocycles is due more to the wide variety of routes to peroxidic intermediates than the mode of degradation following singlet oxygen attack on the heterocyclic system. In these subsequent reactions it is the effect of solvent, temperature, geometry and substituents that determines the nature of the products obtained.

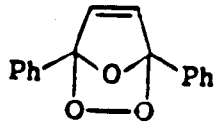
One of the most studied groups of all heterocycles are the furans, undergoing distinctive 1,4-addition to the furan ring, with the formation of a transannular-(2,5)-endoperoxide, which may be detected at low temperatures[183].



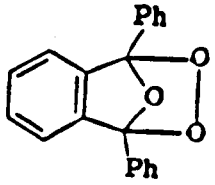
Allylic furans yield hydroperoxides as shown below for 2,5-dimethyl furan[184].



Whilst the transannular allylic hydroperoxides have been difficult to isolate and study due to their instability, a number of aryl furan adducts have been reported including those of 2,5-diphenylfuran [185] and 1,3-diphenylisobenzofuran[186]

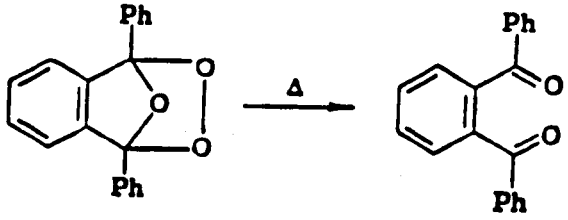


(47)



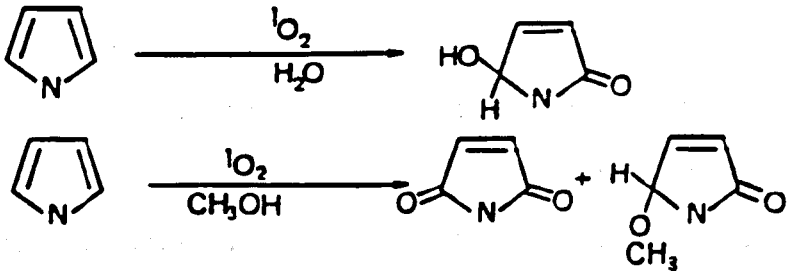
(48)

The endoperoxide (47) can be used to generate the parent furan by warming to room temperature. If the endoperoxide (48), once isolated and separated at temperatures lower than 200K, is warmed to room temperature it would explode. Warming in solution would yield the expected o-dibenzoylbenzene (49).



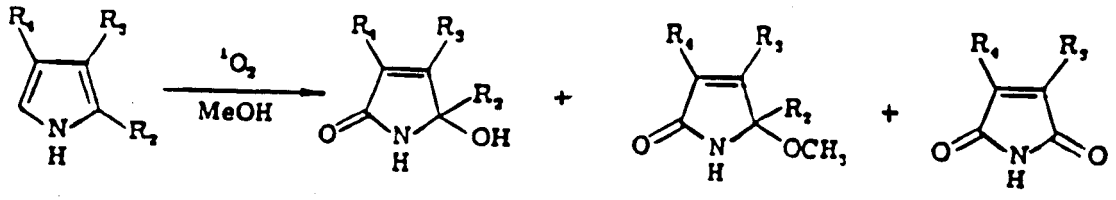
(49)

The reaction of pyrroles with singlet oxygen closely parallels that of the furans. The photo-oxidation of pyrrole in water yields the hydroxy derivative, whereas in methanol a maleimide and methoxy derivative are formed[187,188].



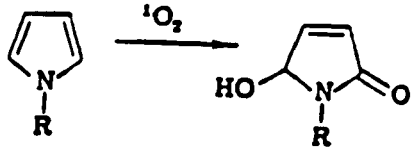
The reaction of singlet oxygen with alkyl pyrroles has been studied[189] resulting in the conclusion that they react to yield

only three different products as shown below:



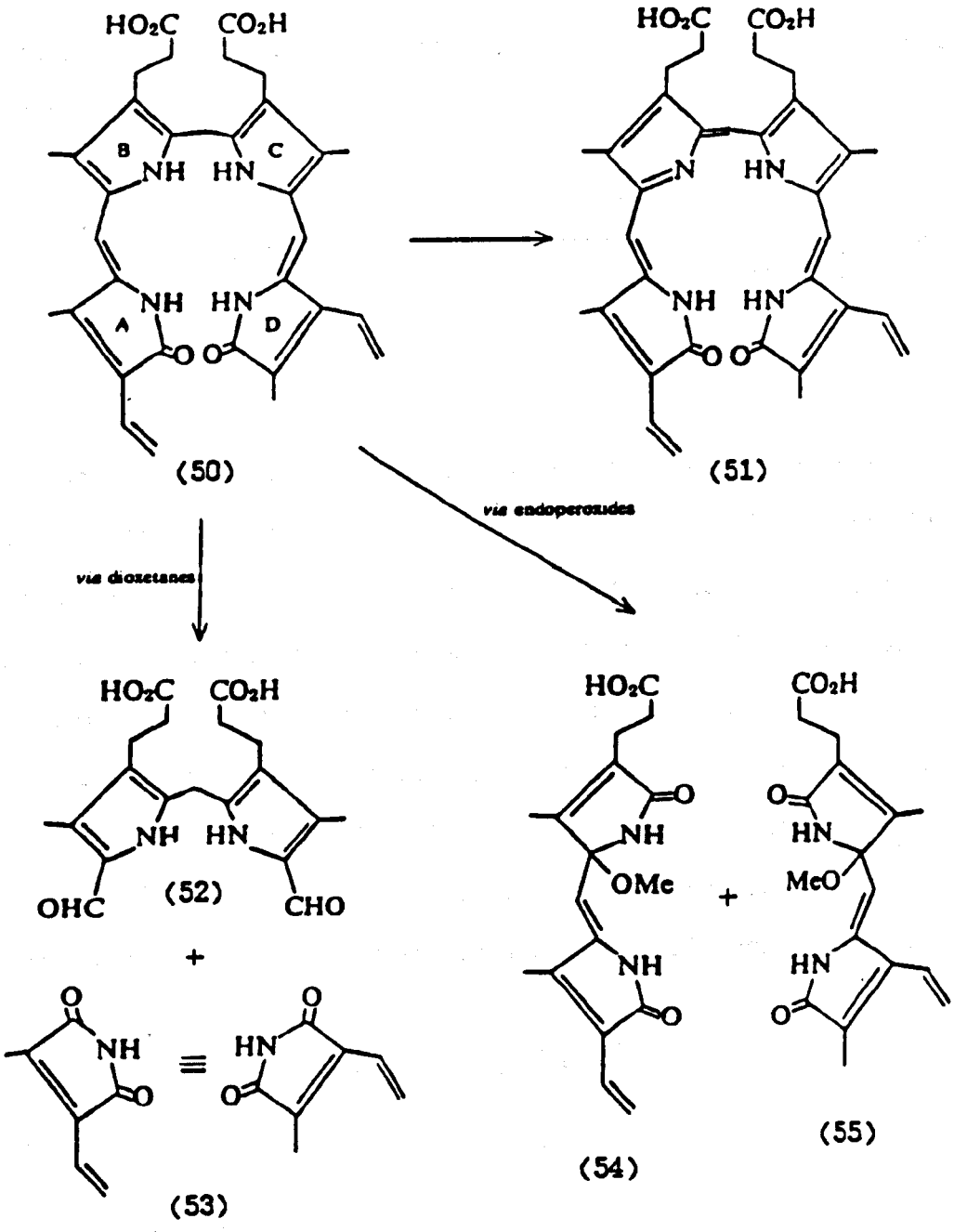
The proportion of each photoproduct is very much dependant on the nature of the alkyl group substituents. Similar to that of pyrrole, the mechanism proposed is that of a Diels-Alder addition of singlet oxygen to form a transannular endoperoxide intermediate.

The formation of hydroxylactams has been shown to occur when N-substituted pyrroles are reacted with singlet oxygen, as shown below[180].



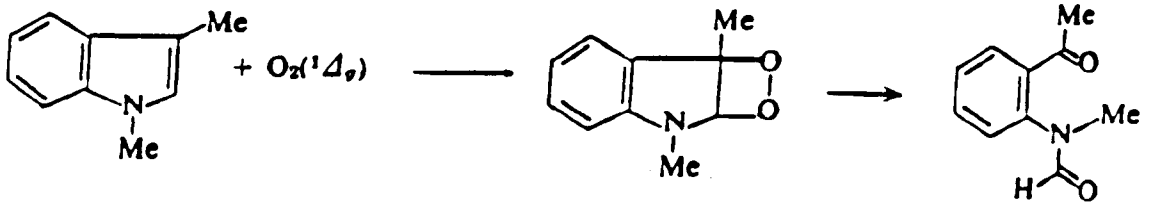
Most of the research undertaken into the reactions of singlet oxygen with pyrroles has been closely linked to the role of light in the breakdown of bilirubin; of great importance in the treatment of neonatal jaundice in prematurely born babies (re. 1.3.5.2.). If artificial light is not used to aid in the breakdown of the excess bilirubin motor development is retarded, or in some cases death. The breakdown of bilirubin in the blood serum to form water-soluble derivatives, which can be excreted from the body in the urine, is shown in Figure 20. Bilirubin (50) when reacted with singlet oxygen in methanol produces biliverdin (51) and photoproducts (52)-(55). Both bilirubin and biliverdin quench singlet oxygen reactions very efficiently with rates

Figure 20. The Degradation of Bilirubin by Singlet oxygen.



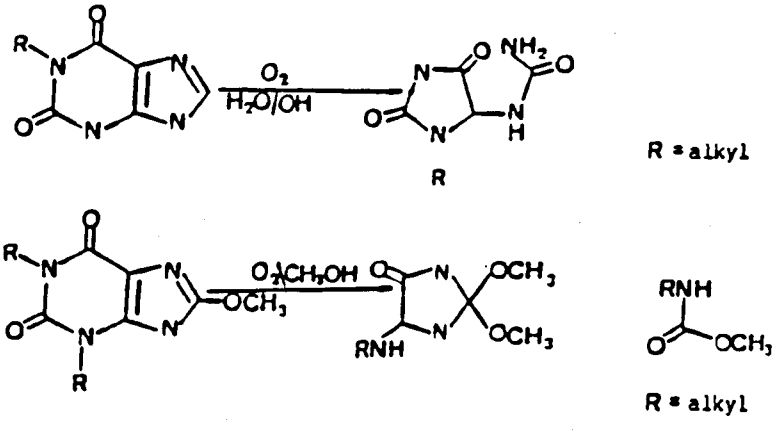
of $\approx 10^{8} mol^{-1} dm^{3} s^{-1}$.

The reactivity of indoles towards singlet oxygen is essentially characteristic of electron-rich compounds, the principal products at room temperature being those resulting from the dioxetane fragmentation as shown below:



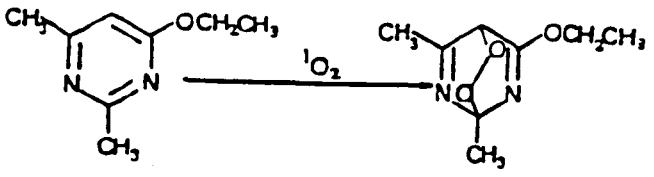
Indole derivatives and their reactions with singlet oxygen are of particular interest in connection with the photodynamic degradation of tryptophan residues in proteins, and the possibility that these oxidations may represent model reactions for the biological oxidation of tryptophan catalysed by monooxygenases and dioxygenases.

Studies have also been performed on purine and pyrimidine compounds similar to those contained in RNA and DNA. Purines containing the imidazole nucleus react with a similar mechanism to form photoproducts via endoperoxide or dioxetane intermediates, as illustrated below[181]:



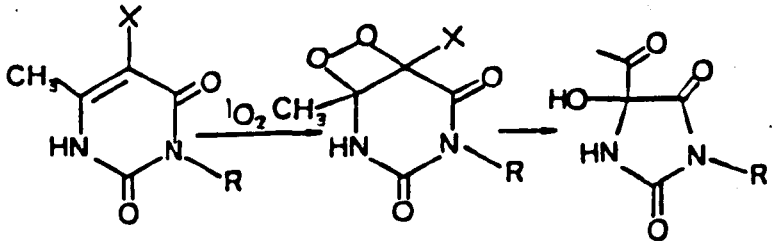
This type of reaction has been studied for a large number of purines including xanthine and uric acid[182].

The pyrimidine nucleus is generally unreactive towards electrophiles, such as singlet oxygen, due to the destabilising effect of the electronegative nitrogen atoms on any transition state which might arise from the electrophilic attack. However, electron donating substituents increase reactivity, and the substituted pyrimidine (55) was found to react with singlet oxygen to produce the unstable crystalline endoperoxide shown below[183].



(55)

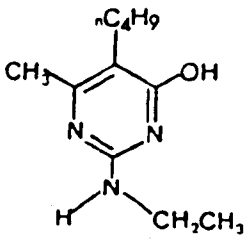
The herbicide terbacil (56)[184] and bromacil (57)[185] have both been shown to react with singlet oxygen to give several products, as detailed below, via dioxetane intermediates.



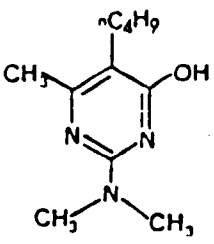
(56) (X=Cl R=C_4H_9)

(57) (X=Br R=C_4H_9)

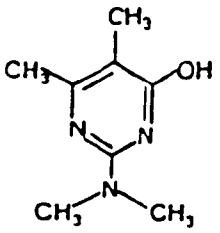
Two similar compounds ethirimol (58) and dimethirimol (59), used as systemic fungicides, and a product (60) arising from the hydrolysis of the insecticide pirimicarb are thought to react efficiently with singlet oxygen[186], with rates of $\approx 10^7 mol^{-1}dm^3s^{-1}$. The intermediate in these reactions is thought to be solvent dependant - a charge transfer type leading to a dioxetane type intermediate in polar solvents; and a zwitterionic type (61) and/or hydroperoxide intermediate leading to an ene type mechanism in non-polar solvents[188,187].



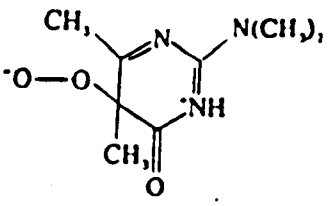
(58)



(59)



(60)



(61)

1.3.5. Singlet oxygen and its applications.

1.3.5.1. Environmental aspects of singlet oxygen

Singlet oxygen has gained importance in the realm of pollution studies over the last three decades with the discovery that singlet oxygen may be formed in many ways, and once formed it can be involved in processes that may be detrimental to various aspects of life.

Among the more important ways that singlet oxygen may be generated in the environment is through the direct photolysis of ozone with short wavelength ultraviolet radiation which exists in solar radiation. Singlet oxygen generated by this method is thought to explain some of the ultraviolet absorption anomalies in the upper atmosphere[198-200]. Evidence is accumulating that a wide variety of pollutants[201-203] may act as sensitisers. Thus compounds such as phosphite esters[204], ethers and alcohols[205] react with ozone to yield singlet oxygen, as may sulphides, sulphoxides, amines and phosphines.

Studies have been performed to ascertain whether singlet oxygen has a sufficiently long lifetime in order to react with other compounds in the environment[206]. Complex reaction mechanisms have been proposed for the photo-oxidation of gaseous nitric oxide[207] and the photodegradation of polyethylene, to name but a few.

The photodegradation of polymer surfaces has received great attention once it was realised that gaseous singlet oxygen could oxidise the surface of *cis*-polybutadiene films in a heterogeneous reaction[208]. Oxidations of this kind have been found to promote modification, chain

degradation or cross-linking which change the physical and mechanical properties of the polymer. It is because of these drastic changes that much work has been performed on the oxidation of polymers by singlet oxygen - resulting in an enormous quantity of published work[208,210].

Singlet oxygen has also been shown to be produced by natural substances such as chlorophylls a and b[211] in plants; haems [238], and fulvic and humic acids in various soils and natural waters [212-213]. It appears that singlet oxygen, along with other excited species of oxygen, is of fundamental importance in the day-to-day multitude of natural processes that make up our fragile ecosystem. Most of these processes still remain shrouded in mystery due to their incredibly complex nature, but singlet oxygen is being invoked in an ever increasing number of these processes as more and more research is being undertaken.

In addition to naturally occuring sensitisers there exists a number of natural quenchers, one could propose that their role is to limit the effect that the powerful singlet oxygen species has on natural systems. The most readily available of this group of natural singlet oxygen quenchers is the carotenoids, which readily quench singlet oxygen reactions at concentrations as low as 10^{-4}M[218]. It is even thought that the physiological function of carotenoids is to protect enzymes, nucleic acids and membrane lipids against damage caused by singlet oxygen[200].

In the environment evidence is accumulating that a wide variety of pollutants may act as sensitisers i.e. olefins, aromatic and poly-aromatic compounds from exhaust fumes[201,202] and oil-spillages[203]. Suprisingly, other pollutants have been found to be susceptible to singlet oxygen attack and are rapidly degraded in the environment by natural sensitisers e.g. humic and fulvic acids[217,218].

1.3.5.2. The biological and biochemical aspects of singlet oxygen.

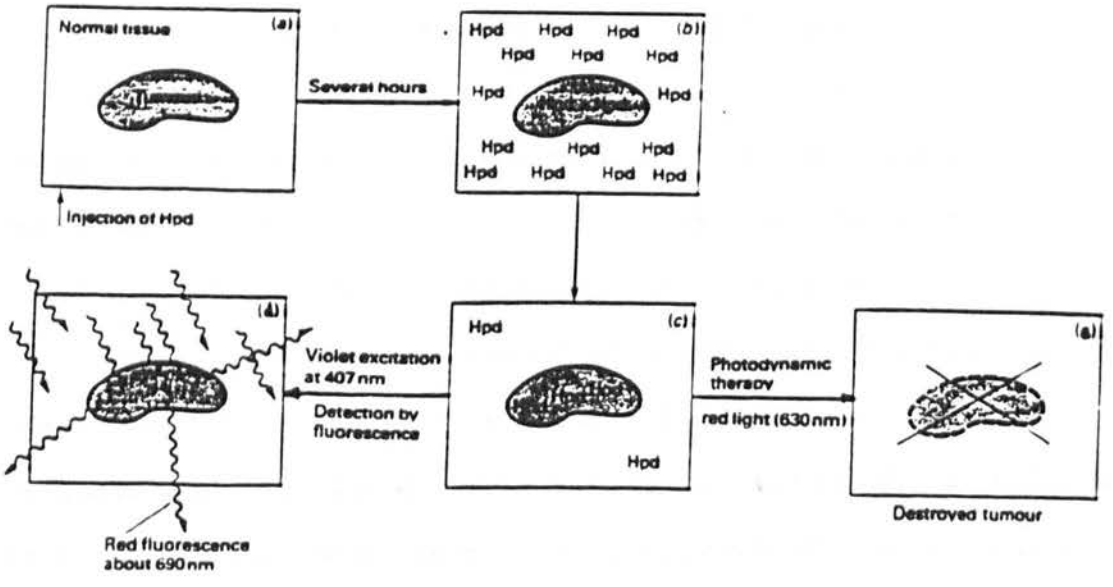
Oxidation processes are of paramount importance in cellular systems. Many aspects of metabolic change rely on oxidation steps for their proper functions; other oxidation events induced by exogeneous or adventitious initiators can be severely damaging to organisms. The known reactions of singlet oxygen with heterocyclic compounds have lead many authors[231,232] to the suggestion that biological systems containing these groups could be destroyed by singlet oxygen. It is possible to categorize the effects under two major headings:

(1) Oxidations induced by the presence of light, a sensitiser (extrinsic or intrinsic), and oxygen - Photodynamic Effects.

(2) Naturally occurring metabolic processes that proceed via oxidation without assistance from radiant energy.

A. Photodynamic Effects.

A great deal of work has been published over the last 15-20 years on the great potential to treat some forms of malignant tumours with light and sensitisers i.e. *in vivo* generation of singlet oxygen. In its simplest form the patient is treated as shown below.



(a) The patient is injected with a porphyrin sensitiser (Haematoporphyrin derivative - Hpd) and this is allowed to translocate within the body.

(b)-(c) Naturally occurring sensitisers, and Hpd, have been known for some time to naturally accumulate in neoplastic (cancerous) tissues[234] and after a few hours this accumulation has been completed.

(d) It is only now that the true extent of the tumour can be seen for the tumour cells can have a very similar appearance to ordinary cells. Fortunately, Hpd has the property to fluoresce at 690nm (Red) when irradiated with light of wavelength 407nm (Violet) therefore a three-dimensional picture of the tumour can be generated.

(e) Once the tumour has been assessed it may be destroyed by irradiation with light of wavelength 630nm, usually generated by a laser.

The rate of tumour necrosis (death) may be monitored periodically by the same fluorescence method. This method of treatment has great potential for future development providing that operating parameters can be optimised and the purity of the sensitiser can be raised to limit side reactions encountered with the present work.

There is a disorder called Erythropoietic protoporphyria (EPP) which occurs in susceptible patients on exposure to sunlight and is characterised by swelling.. The photosensitivity of EPP patients can be reduced by oral administration of β-carotene[235], a well known

singlet oxygen quencher. The red blood cells of EPP patients contain large amounts of free protoporphyrin, similar in sensitising efficieny to Hpd. These cells are haemolysed upon irradiation with visible light via photo-oxidation of membrane components. Further evidence for singlet oxygen participation in this reacion arises from the protection afforded by Vitamin E[238] and the detection of 3-hydroxy-5-hydro-peroxycholestene (the photo-oxidation product of cholesterol[237]), using red blood cells from EPP patients.

At the biochemical level there is clear evidence that some amino-acids, particularly histidine, methionine, tyrosine and tryptophan, are photo-oxidised via a singlet oxygen mechanism[238]. Leading on from this the deactivation of the enzymes alcohol dehydrogenase[239] and tryptophan residues in several enzymes (lysozyme and papain) [240,241] have been attributed to singlet oxygen mechanisms.

In all of the biological photo-oxidations examined so far in which singlet oxygen is invoked, nowhere has its intervention been directly demonstrated. All the evidence relies on the correlation of oxidation products with those of established singlet oxygen reactions, the effects of D_2O and quencher on the reaction, and on the identification of specific reaction products from added reactive substrates. Further work is desired to close the gap and offset the need for the long extrapolation from chemical properties to biological processes.

B. Polymorphonuclear Leukocytes.

Scientists have long been intrigued by the body's defensive system whereby foreign bodies, and in particular microbes, are repelled by the many complex cells that make up this system. Both intra- and extra-cellular processes give rise to microbial action.

Intracellular microbiocidal activity is carried out by a variety

of phagocytic cells and higher organisms possessing two circulating phagocytic cells, the polymorphonuclear leukocyte and the mononuclear leukocyte, the latter eventually becoming tissue macrophages. Work performed on polymorphonuclear leukocytes has shown that many of the processes which occur in these cells are also applicable to other types of phagocytic cells and may serve as examples of a general type of intracellular microbial action.

The process whereby invading micro-organisms are recognised and investigated by phagocytic cells has been described in several reviews (242,243). Following the recognition of the opsonised micro-organism, phagocytosis is initiated by the formation of pseudopodia from the surface of the phagocytic cell. These pseudopodia gradually surround the invading micro-organism and ultimately will totally enclose it in a membrane-bound vesicle called a phagosome. It is during this process that the metabolic activity of the phagocytic cell alters - a respiratory burst of 10- to 20-fold increase in the rate of oxygen consumption! The products of the reaction are initially the superoxide radical, $O_2^{\cdot-}$, and its breakdown product, H_2O_2. The production of H_2O_2 from the radical can occur either spontaneously (1) or when catalysed by the enzyme superoxide dismutase (2).

$$O_2^{\cdot-} + O_2 \xrightarrow{\text{SPONTANEOUS}} H_2O_2 + O_2 \qquad (1)$$

$$O_2^{\cdot-} + O_2 \xrightarrow{\text{SOD}} H_2O_2 + O_2 \qquad (2)$$

It was Howes and Steele(246) who first noted the appearance of chemiluminescence during the metabolism of liver microsomes and correctly attributing this to to the generation of singlet oxygen. Co-workers subsequently proposed the generation of singlet oxygen from phagocytosing polymorphonuclear leukocytes based on similarly observed

chemiluminescence.

Myeloperoxidase (MPO)[245] is an example of that class of enzyme which, in the presence of H_2O_2, catalyses the oxidation of a number of substrates. It was proposed by Howes and Steele[248] that the chemiluminescence produced during the oxidation of NADPH was due to the generation of singlet oxygen, as shown in (3).

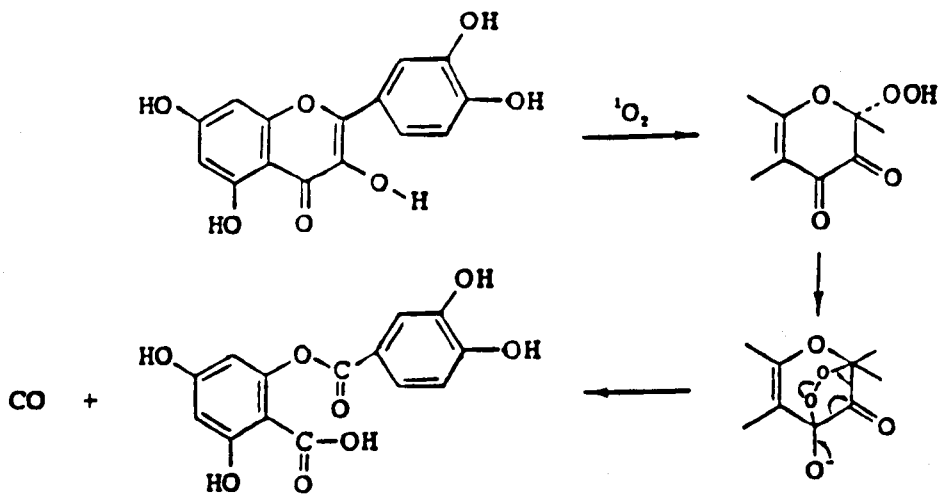
$$O_2 \text{ and/or } H_2O_2 \xrightarrow{MPO} {}^1O_2 \text{ Chemiluminescence} \qquad (3)$$

The presence of Cl^- or any halide ion is an important co-factor in the reaction. Singlet oxygen was confirmed by the use of two strains of *s.lutea*, one containing carotenoid pigments and the other one without. The one with the pigment afforded protection against singlet oxygen to the polymorphonuclear leukocytes, whilst the other afforded no protection and was killed[247].

C.Enzyme systems.

One of the earliest suggestions that singlet oxygen might be involved in an enzymatic reaction was made by Krishnamuty & Simpson in 1970[248]. They were working with the fungus *Aspergillus flavus*, which produces an inducible oxygenase quercitin. Through $^1{}^8O_2$ studies quercitin was found to be a dioxygenase. Matsuura[249] obtained the same depside following the photosensitised oxidation of quercitin, thus concluding that the enzyme utilises an "activated" oxygen molecule to form a cyclic peroxide intermediate which decomposes to produce the depside.

It was Stauff[250,251] who repeated that xanthine oxidase when incubated with one of its substrates, xanthine, gave rise to chemiluminescence. It was first thought that this was due to singlet oxygen being generated by the spontaneous disproportionation of O_2 but more recently[252] it has been suggested that the chemilumin-



escence is from the recombination of carbonate and bicarbonate radicals.

Pederson and Aust[253] using xanthine oxidase to study the effects of O_2 on rat liver microsomal lipids found that the presence of solubilised iron markedly increased the effect of lipid peroxidation. The peroxidation could be inhibited by the addition of either superoxide dismutase (SOD) or by adding diphenylisobenzofuran (DPBF). The addition of DPBF did not affect the rate of O_2 production but did yield DBB when it inhibited lipid peroxidation. Although DPBF can be converted to DBB by reactions that do not involve singlet oxygen, this evidence was used to support their mechanism that O_2, generated by the action of xanthine oxidase, could decompose to yield singlet oxygen which would then initiate lipid peroxidation.

D.Miscellaneous oxygen effects.

There are a number of other systems in which there is indirect evidence that singlet oxygen may be involved.

(a) Red blood cell damage - many examples exist whereby red blood cells can be damaged by singlet oxygen, but the majority involve the use of exogeneous or endogeneous sensitisers. It has been proposed however[254] that red blood cells associated with oxidative hemolytic diseases are

susceptible to damage. The Haber-Weiss reaction[255] was also invoked as generating either singlet oxygen or hydroxyradical (OH•) which can subsequently lead to denaturation of haemoglobin and damage to the red blood cell membrane, both effects culminating in a haemolytic condition.

(b) Cytotoxic agents - agents such as hydroxy- and amino- substituted dopamines have been studied[258] and are suspected of producig both O_2 and H_2O_2 during auto-oxidation. In addition Cohen and Heikkila [258] were able to demonstrate, through the formation of ethylene from methonal , that ·OH was also produced during the auto-oxidation of these compounds. Since both catalase and SOD inhibited ethylene production, it was concluded that the Haber-Weiss reaction was responsible for the production of ·OH radicals.

As with all systems that invoke this reaction, the possibility exists that singlet oxygen is either formed directly or may result from the associated reaction involving quenching of the O_2 by ·OH.

$$O_2 + \cdot OH \longrightarrow {}^1O_2 + \cdot OH$$

CHAPTER 2.

Apparatus & Materials.

2.1. Photolysis apparatus.

2.1.1. The oxygen electrode.

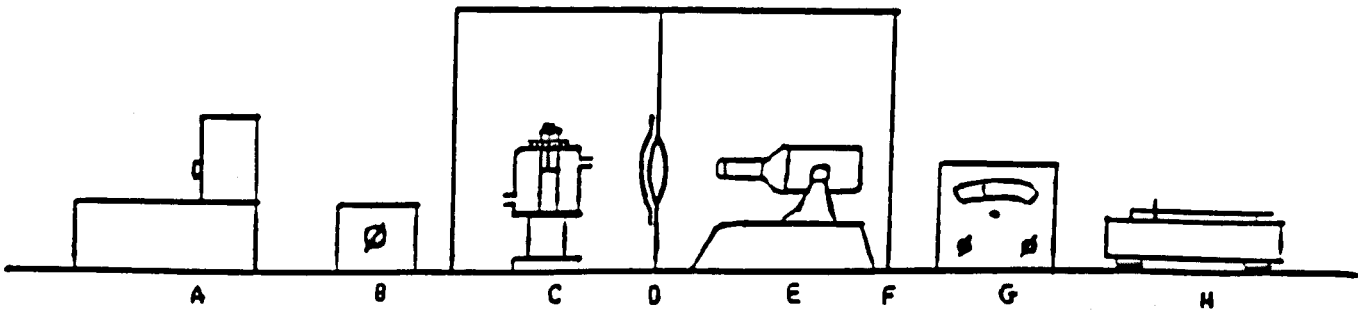
An oxygen electrode was used to follow the rate of removal of oxygen from the solutions in photolysis experiments. The oxygen electrode (Rank Bros. of Bottisham, Cambridge) shown in Figure 21 measures the dissolved oxygen concentration in a solution placed within its sample chamber. In this apparatus an Ag/AgCl electrode is connected to a platinum electrode via a paper membrane saturated with molar KCl solution to form a salt bridge. The reaction solution is separated from the platinum electrode by a thin (0.2mm) square of teflon. It is through this teflon square that oxygen dissolved in the reaction solution diffuses and is reduced by the following cell reactions:

$$O_2 + 2e^- + 2H^+ \longrightarrow H_2O_2$$

$$2H_2O_2 + 2e^- \longrightarrow 2H^+ + 2H_2O$$

The current flowing in the cell is directly proportional to the concentration of oxygen in the reaction solution. The reaction solution is kept at a specific predetermined temperature by a circulating pump that feeds water from the water bath through the circulating jacket, around the sample chamber and back to the bath. The bath was either heated, by means of the bath heater, or cooled, by immersion of a cooling probe, to within 0.5K of the desired temperature.

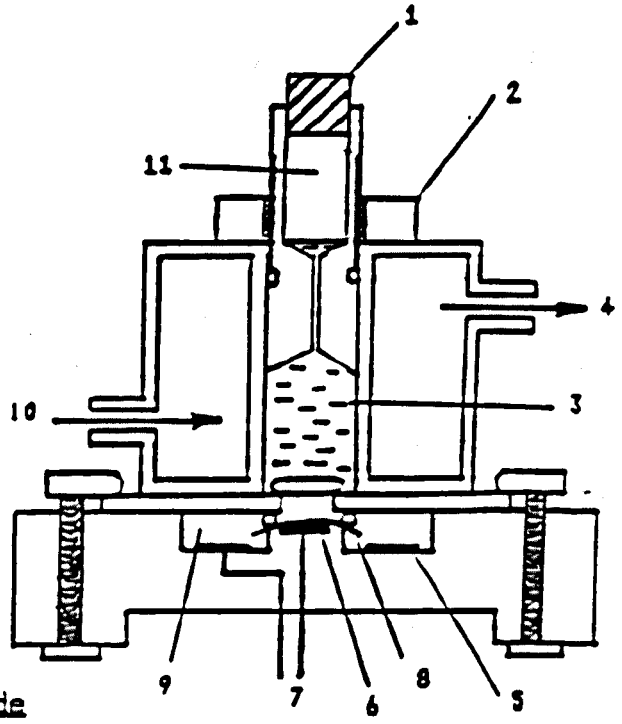
After the sample solution was inserted into the chamber an air-tight stopper was capped on the vessel along with a "nitrogen blanket" above the solution to prevent oxygen from the atmosphere diffusing into the solution to replace that lost when photolysis takes place. The magnetically-stirred reaction solution was irradiated through a Wratten filter using a 40W microscope lamp via a magnifying lens, used to focus the light on the solution. At the back of the oxygen electrode



Apparatus

A. thermostatted water bath
B. magnetic stirrer control
C. oxygen electrode on stirrer mount
D. magnifying lens with gelatine filter
E. microscope lamp
F. light proof box
G. oxygen meter
H. X - Y plotter

Fig. 23 - Oxygen electrode apparatus.



Oxygen Electrode

1. rubber cork
2. locking nut
3. reaction mixture
4. water to bath
5. circular Ag anode
6. central Pt cathode
7. connections to oxygen meter
8. 'Teflon' membrane held with 'O' ring
9. saturated KCl solution
10. water from bath
11. nitrogen atmosphere

on the outside of the water jacket was attached a strip of aluminium foil to reflect any stray light back into the sample chamber to gain maximum absorption efficiencies from the sensitiser in solution. To exclude light of wavelengths other than those that can pass through the filter the whole of the apparatus was enclosed in a light-tight box as detailed in Figure 23.

The signal from the cell is amplified and plotted as a function of time on an X-Y plotter. A typical trace showing the change in oxygen concentration with time is shown in Figure 24. The initial rate of oxygen consumption, $-d[O_2]/dt$, was determined using the expression

$$\text{Gradient} = -\frac{d[O_2]}{dt} = \frac{(Y_2-Y_1) \,.\, [O_2] \,.\, S}{(X_2-X_1) \,.\, Y_1}$$

where $[O_2]$ represents the initial concentration of oxygen in the solution, expresed in mol dm^{-3}, S is the chart speed in mm sec^{-1} and Y and X values are used to calculate the gradient of the line, and are expressed in mm.

2.1.2. Quantitative photochemical reactor.

The use of equation (20) (re. page 81) to determine the rate constant, k_{ov}, for the overall interaction of singlet oxygen with a substrate requires that a set of sample solutions absorb the same amount of photon radiation. This was acheived using the 'merry-go-round' apparatus shown in Figure 28.

This quantitative photochemical reactor was designed by Moses et al.[143] and a copy built in Kingston Polytechnic workshops. Sample solutions were prepared in a darkroom and placed in the sample wells of the reactor. The reactor was immersed in a thermostatted water bath so

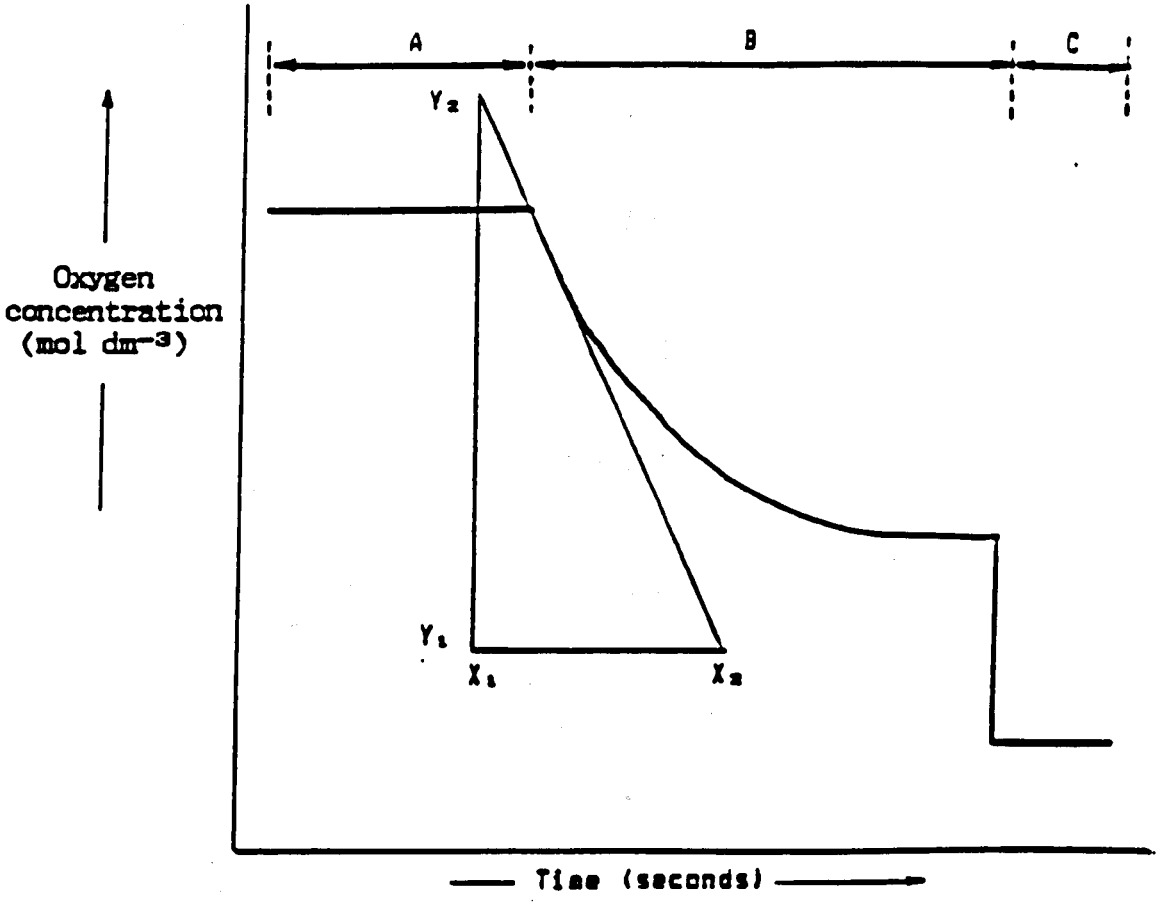


Figure 24. A Typical Output Trace From the Oxygen Electrode Apparatus.

KEY:

A. Equipment switched on, trace left to stabilise.
B. Light switched on, oxygen in solution is converted into singlet oxygen - which reacts with the substrate and therefore the free oxygen concentration decreases.
C. Both the light source and oxygen meter are switched off to obtain the 'zero' oxygen concentration in the system - as confirmed by a sodium dithionite calibration solution.

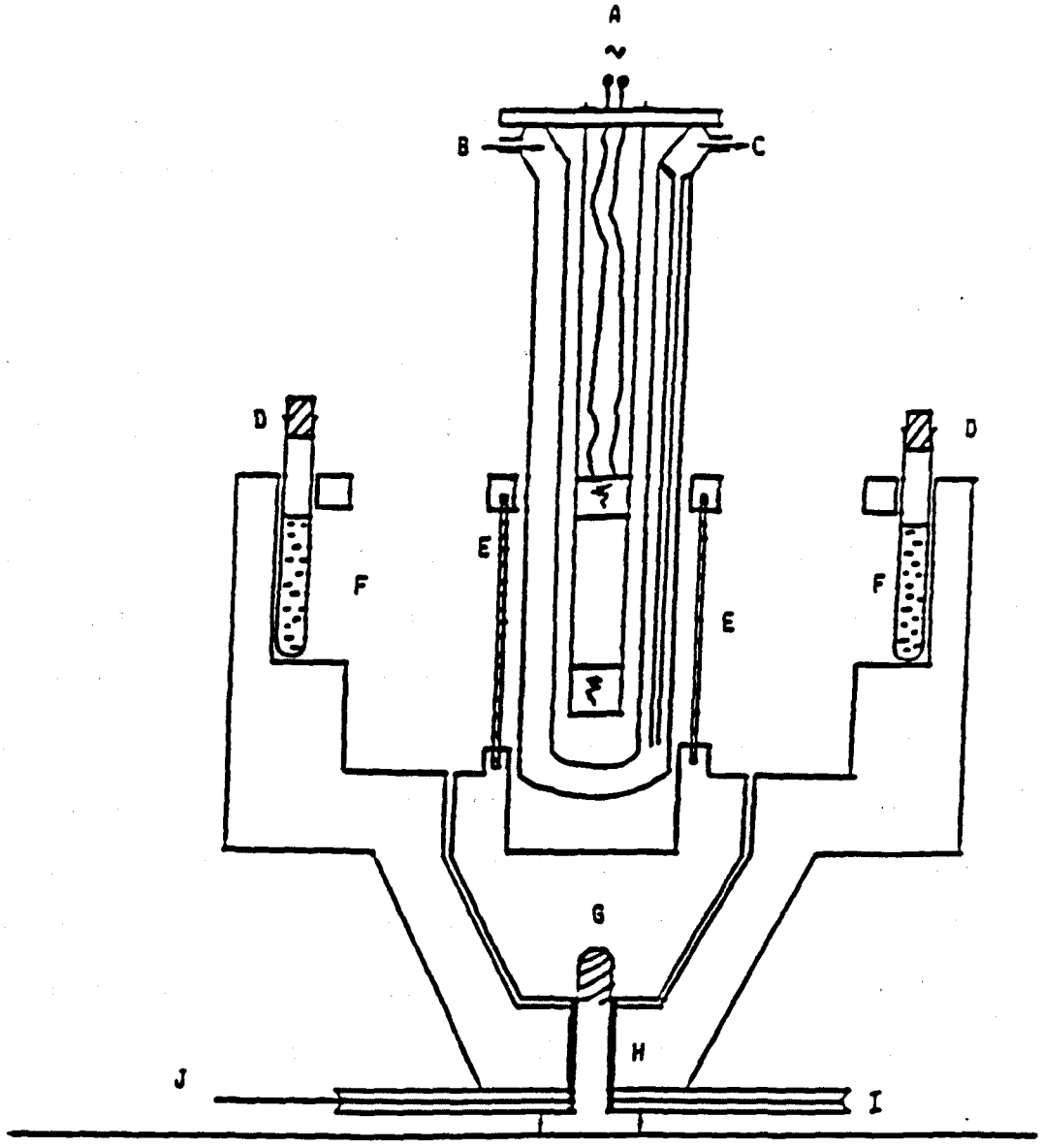


Figure 26 - Merry go round Apparatus.

A. Hg - vapour discharge lamp
B. lamp cooling solution in
C. lamp cooling solution out
D. sample tubes
E. glass filters
F. machined windows
G. phosphour - bronze spindle
H. 'Teflon' bearing
I. chain drive
J. to stirrer motor

that reactions may be performed at a variety of temperatures, this system was then placed within a light proof box to exclude stray light.

2.1.3. Preparative photochemical reactor.

The preparative photochemical reactor is shown in Figure 27. The reactor consists of a central compartment where a magnetic stirrer and glass reaction vessel could be sited, surrounded by a thin metal frame to support the desired light filters. Outside of the frame was a composite light source of 6 x 100W standard pearl light bulbs mounted radially and equidistant around the central sample well. The bulbs were so aligned that light from them would pass through the filters and into the sample solution. The light bulbs were surrounded by a circular metal outer wall to reflect light inwards and the components all mounted on a circular wooden base. The samples were shielded from extraneous light by enclosing the whole apparatus with a heat resistant wooden lid.

Low temperature photolyses were performed in a 5mm diameter borosilcate nmr tube that was situated in the cooling vessel as illustrated in Figure 28. A slurry of 'cardice'(solid carbon dioxide) and acetone was used to keep the temperature of the tube at approximately 200K, whilst the water-filled beaker was used to balance the slurry bath and aid heat dissipation. An air bleed was inserted into the photolysis solution and compressed air gently bubbled through the system so that oxygen consumed in the reaction could be quickly replaced.

2.1.4. Surface-separated-reactor.

The surface-separated-reactor is shown in Figure 29. The reactor is of the same design as that reported in the literature[20-30]. In the reactor light from the radiation source impinges on the sensitiser which is adsorbed on a silica gel plate positioned ≈1mm above the surface of the substrate solution which is contained in up to eight

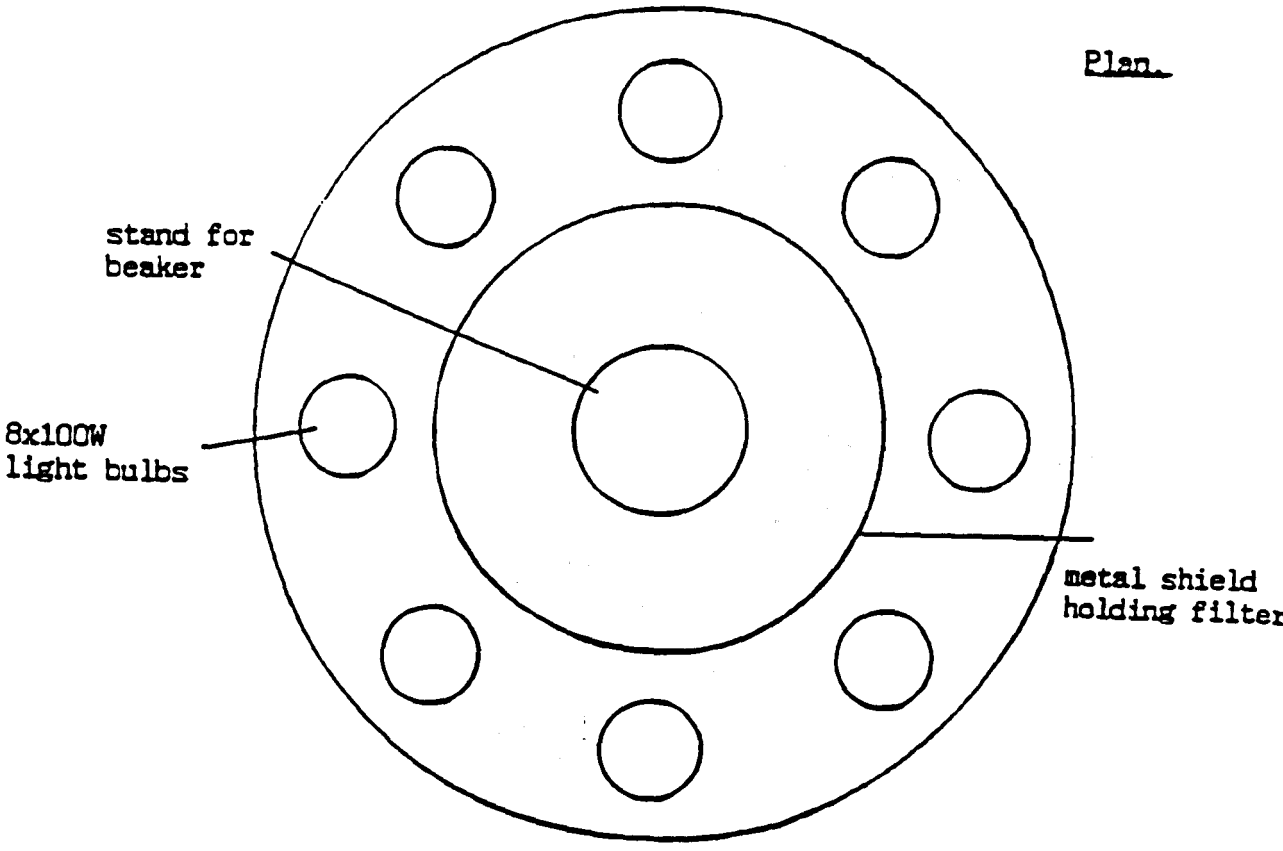
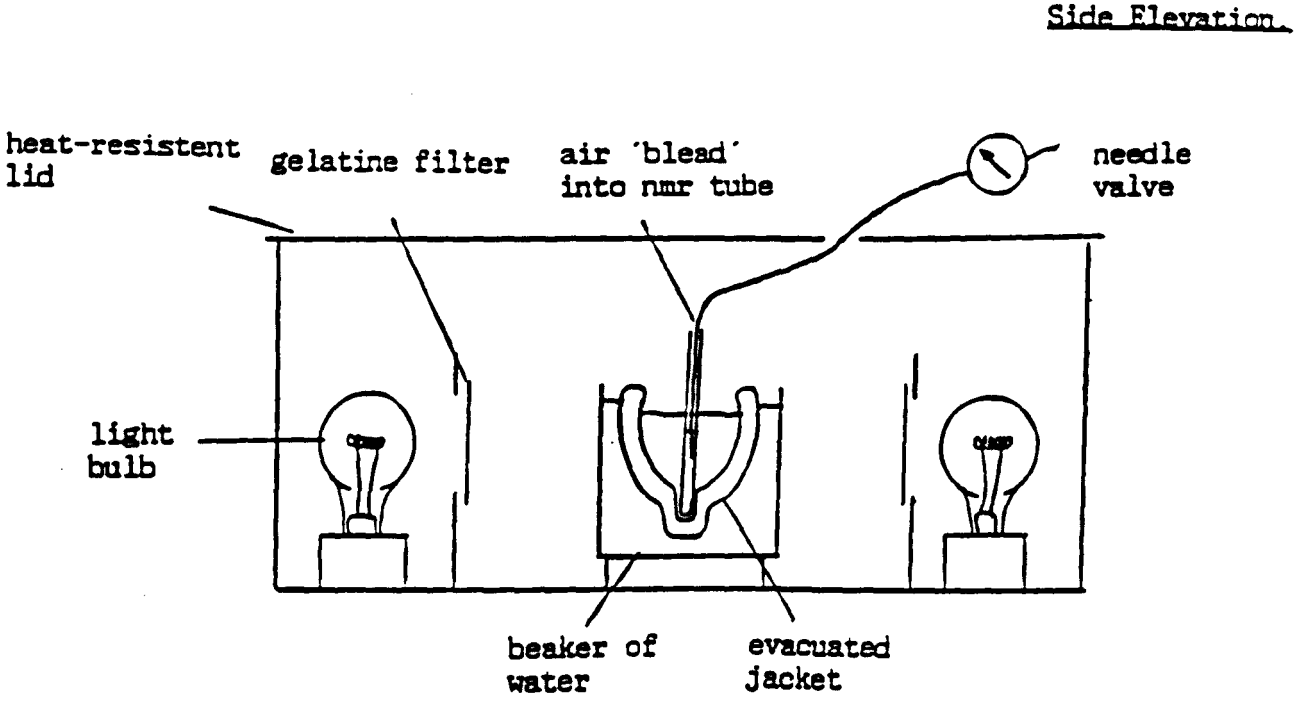


Figure 27. The Preparative Photochemical Reactor System.



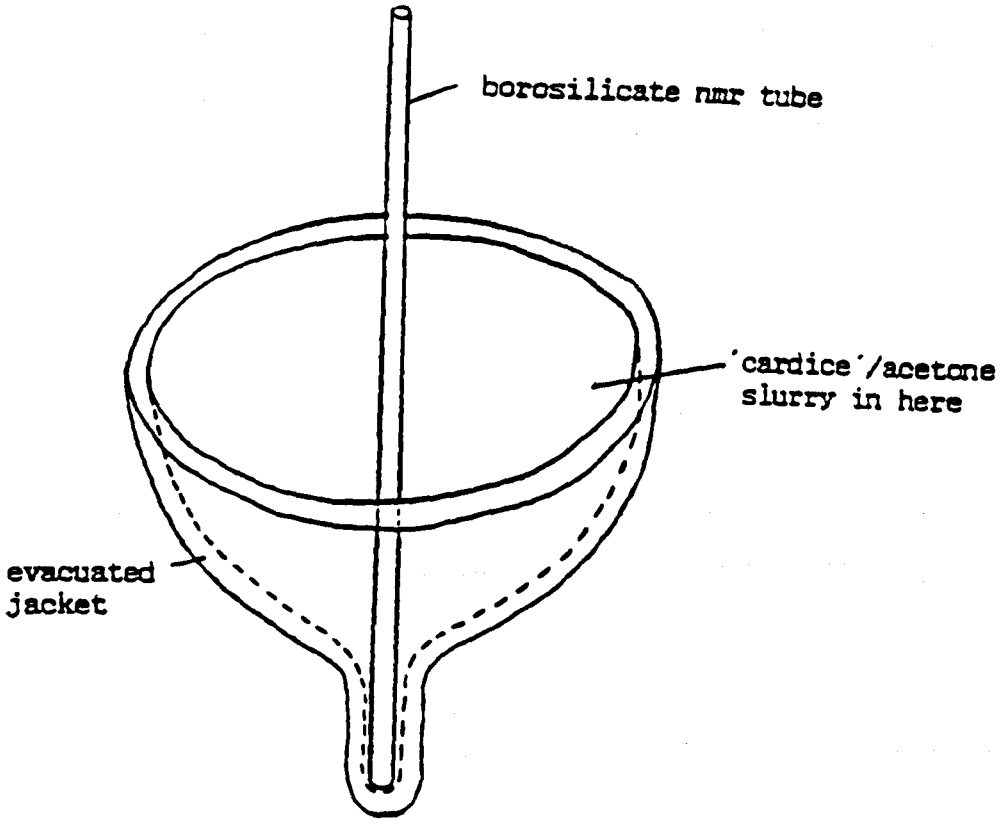


Figure 28. Cooling Vessel for Low Temperature Photolysis.

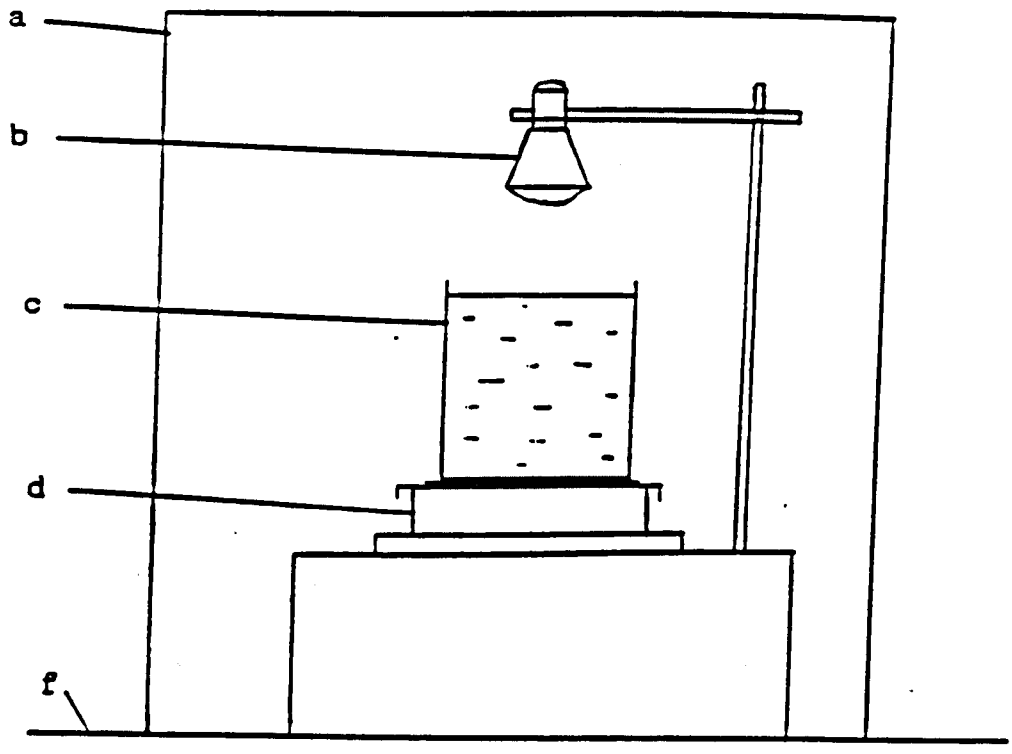
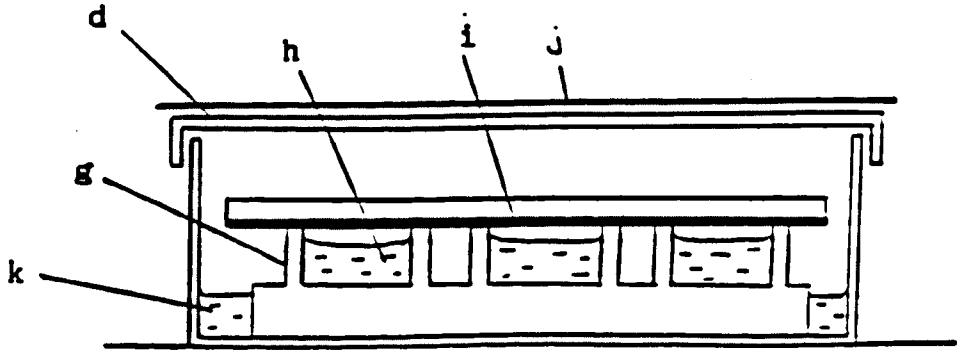
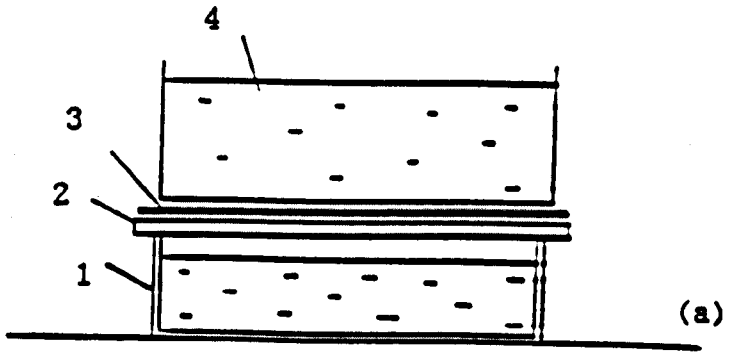
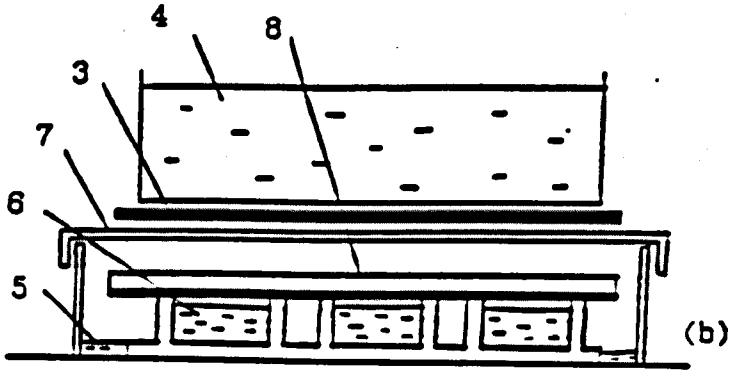


Figure 29. The Surface-separated reactor and associated apparatus.

a. light-tight box
b. light source
c. water vessel for heat-sink purposes
d. petri dish
e. cold plate
f. bench
g. Boerner slide fitted with glass collars
h. substrate solution
i. sensitiser adsorbed onto silica plate
j. gelatine filter
k. solvent







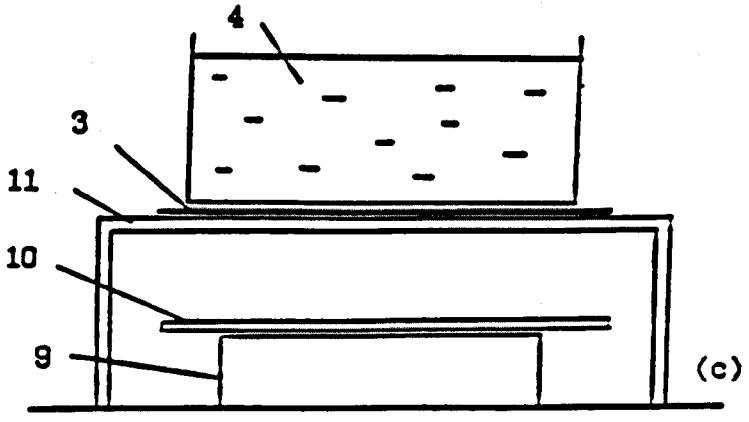


Figure 30. Arrangement for the Disposition of Sensitiser and Substrate in Product Studies.

KEY:

1. Petri dish containing substrate & sensitiser in solution.
2. Plain glass plate to cover petri dish.
3. Wratten gelatine filter.
4. Beaker of water to absorb heat from the light source.
5. Solvent.
6. Substrate in solution.
7. Lid of large petri dish.
8. Sensitiser absorbed onto silice gel plate.
9. Inverted petri dish.
10. TLC plate spotted with reactants.
11. Glass supports for filter & beaker.

wells on a Boerner slide. The sensitiser plate and Boerner slide are within a covered petri dish containing solvent and the petri dish is in contact with a cold plate to prevent solvent evaporation during irradiation. After irradiation the Boerner slide was removed and the substrate solution analysed spectrophotometrically or by hplc.

The sensitiser (Rose Bengal, Methylene Blue or Chlorophyll) was coated onto the tlc plate by immersion into a saturated solution of the appropriate sensitiser; i.e. methanolic solutions of Rose Bengal and Chlorophyll or ethanolic solutions of Methylene Blue. The tlc plate was left immersed for approximately 10 minutes and then retrieved and placed in a vacuum oven at ambient temperature and under a partial vacuum of 100mbar for 30 minutes. The tlc plate was finally inspected and any loose particles were blown from the surface by a high pressure stream of nitrogen.

The light source was either a 120W Wotan spotlight bulb or a 400W medium pressure mercury discharge lamp. The former was used when either Rose Bengal, Methylene Blue or Chlorophyll was employed as sensitiser and the light was filtered through a Wratten gelatine filter to remove radiation of wavelength less than 420nm. The latter source was used when soil samples were acting as sensitisers, but in such cases the light filter was not used.

Kinetic studies were performed using the reactor as described above. Studies on the products formed in different systems were carried out with one of the arrangements (a)-(c) described below and depicted in Figure 30.

In system (a) the sensitiser and substrate are in solution, along with a quencher when required. In system (b) the sensitiser and substrate are separated as described above. In system (c) both

sensitiser and substrate are applied as acetone solutions to a tlc plate as a single spot i.e. the substrate is first applied, followed by the quencher (if required), and finally the chosen sensitiser is applied to the spot. The tlc plate is rested on a small petri dish and this combination replaced the large petri dish atop the cooling plate. The vessel of water and filter are retained above the new combination by a supported glass sheet to allow air to circulate above the tlc plate.

2.1.5. Filters.

The filter used in the quantitative photochemical reactor was a Wratten gelatine filter (No.12) which absorbed radiation of wavelength greater than 355 nm. The filter used in the other apparatus was a Wratten gelatine filter (No.8) which absorbed radiation of wavelength greater than 420nm.

2.2. Analytical instrumentation.

Ultraviolet-visible spectra were recorded on a Kontron Uvikon 860 spectrophotometer equipped with a printer. Absorbance measurements at a fixed wavelength were recorded on a Perkin Elmer Coleman 55 digital spectrophotometer. For all absorbance measurements the solutions were held in silica glass cells.

Low temperature proton magnetic resonance spectra were measured using a Brucker AM250 Fourier Transform instrument equipped with a temporary low temperature unit consiting of a copper tube coil immersed in a vat of liquid nitrogen, which in turn was connected to the nitrogen inlet for the probe. A stream of dried nitrogen was passed through the coil into the probe unit at a sufficient rate to decrease the probe temperature to below 243K (estimated by measuring the inlet and outlet temperatures of the nitrogen stream). The instrument was run at 250.1Mhz using a $^{1}H/^{13}C$ dual probe unit. Data was analysed using a

Standard Fourier Transform algorithm after a Lawrencian to Gaussian transformation.

Purity and identity checks of reagents, products and stable intermediates measurements were performed on a Perkin-Elmer R32 continuous-wave spectrometer. In all measurements involving the R32 the internal locking reference was from a trace quantity of tetramethylsilane (TMS) that was injected into the sample. For low temperature work the internal reference was that of deuterium from the deuterochloroform solvent.

High performance liquid chromatography was employed to determine compound (I) and (III) concentrations in reaction mixtures.
The system used was a simple modular one consisting of the following parameters:-

Pump:	Applied Chromatography Services hplc pump
Detector:	Cecil Instruments CE212A variable wavelength uv monitor set at 240nm.
Integrator:	Shimadzu C-R3A
Column:	5µ nitrile spherisorb (20 x 4.6mm)
Column temp:	Ambient
Injection volume:	10µL
Eluent:	Hexane + 0.5% Propan-2-ol

Retention times: for compound (I) was found to be ≃5 mins. whilst that for compound (III) was ≃12 mins.

Autoradiography was used to detect degredates in the product distribution studies (re.3.4.). Determinations of the (^{14}C) activity of solutions were made using a portable radiation monitor with the radiation probe close to the surface of the liquid. The (^{14}C)

activity of compound (I) which was absorbed on tlc plates was measured using a Geiger-Muller tube (22mm dia.) placed with its thin mica window touching the tlc plate. The G-M tube (Mullard ZP/481, operating at 450 volts) was connected to a rate counter.

Total organic carbon content of the soils used as sensitisers were obtained from Butterworth Laboratories Ltd. of Teddington, Middlesex.

2.3. Chromatography.

2.3.1. Thin layer chromatography.

Merck Silica Gel F254 plates (thickness 0.2mm, size 10cm x 10cm) were used. The most common elution mixture was of dichloromethane/ether (3:1).

Autoradiographic plates were developed using a solvent mixture of chloroform/acetonitrile/hexane (8:1:1).

2.3.2. Column chromatography.

Column chromatography was carried out using Merck Silica Gel F254 (70-200 mesh). A slurry of the silica gel was made up in the solvent system to be used for the development of the column. The slurry was packed into a glass column (100 x 3 cm) and solvent was eluted through the column for at least 30 minutes to ensure the silica gel was evenly packed throughout the column. The sample mixture was dissolved in a small quantity of the solvent ($\approx 20cm^3$) before being added to the top of the column. Elution of the various fractions of the sample from the column were monitored by thin layer chromatography of the collected samples.

Column chromatography was used for the separation of chlorophylls a and b[224]. This process required the use of a DEAE sepharose column, with acetone followed by an acetone/methanol (10:3) mixture as the eluents.

2.3.3. High performance liquid chromatography (HPLC).

This technique was used for the detection of compound (I) at low concentration levels before, during, and after photolysis in various systems. Normal-phase chromatography was employed using a 5µ nitrile column (20 x 4.6mm) and a mobile phase of hexane + 0.5% propan-2-ol. Column temperature was ambient with detection being made at 240nm using a uv detecter.

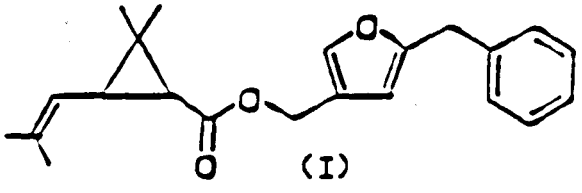
2.3.4. Autoradiography.

Autoradiography was performed on radioactive samples that had been developed on thin layer chromatography (tlc) plates. The plate was positioned in a specially constructed holder and an X-ray film (Kodak NS.59T) was placed directly on the silica gel. A piece of opaque glass was placed on the film and held by clips on the holder. The complete system was wrapped in black polythene system and placed in a light-proof wooden box. After exposure, typically 72 hrs for an initial count rate of 10 counts per second (cps), the film was developed and fixed using Ilford photographic chemicals. The entire operation was performed in a darkroom fitted with Kodak 6B safelights.

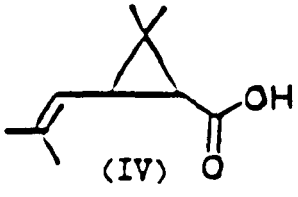
2.4. Chemicals.

2.4.1. Substrates.

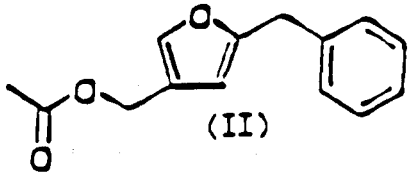
The structures of the chemicals used in this study are shown below.



(I)

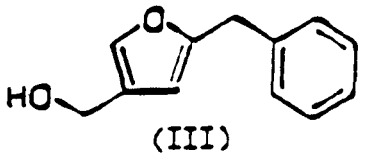


(IV)



(II)

(V)



(III)

The compounds are labelled with the numerals (I)-(V) for identification purposes at different points in later text.

Compounds (I), (III) and (IV) were gifts from the Rothamsted Experimental Station, supplied as 'Technical' grade and were purified by preparative column chromatography before use. Compound (II) was made by simple esterification of compound (III) with acetic acid, followed by recrystalisation at 273K with hexane. Compound(V) was purchased from Aldrich Chemical Co. Ltd., of a purity at least of 99%, and used without further purification. Confirmation of structure was proved by nmr analysis of the compounds in deuterochloroform solutions.

Anthracene-9,10-diethanol was synthesised using the method prescribed by Evans[118] for the preparation of Anthracene-9,10-diethane sulphonate, but was curtailed once the diethanol intermediate had been prepared. This intermediate was recrystallised from ethanol at 273K and its identity confirmed by nmr.

2.4.2. Sensitisers and quenchers.

Rose Bengal (4,5,6,7-tetrachloro-2',4',5',7'-tetraiodo-fluorescein sodium salt), Methylene Blue (methylthionine chloride), sodium azide (NaN_3) and *trans*-β-carotene were obtained from Aldrich Chemical Co.Ltd. and were used as supplied.

Chlorophyll was prepared by extraction, at low temperature (273K), from spinach leaves into acetone[134]. Separation of chlorophylls a and b, from the oligosacharides, was achieved by column chromatography.

Soil samples were kindly donated by the School of Geography, Kingston Polytechnic. The soils were dried under vaccum overnight at 353K and sieved through a 250μm mesh to obtain a sterilised sample.

Soils were categorised by their relative pH, as defined by a soil testing kit. Three soil samples were used, the pH and total organic carbon content of each sample is given below:

Sample	(1)	(2)	(3)
pH	4.2	5.5	7.5
Organic C content (%)	2.9	1.8	3.1

2.4.3. Solvents.

The solvent systems used throughout the initial kinetic studies of the photo-oxidation of compounds (I)-(V) are given in Table 2 below:

Solvent	Compounds Studied
Methanol/Water (1:1 v/v)	(II), (III), (IV), (V)
Methanol	(I), (II), (III), (V)

In order to study the effect of pH on the photo-oxidation of compounds (II)-(V) in Methanol/Water (1:1) the water portion of the solvent mixture was substituted for a buffered solution of the desired pH, the Methanol portion remaining unaltered. To study the effect of solvent deuteration on the rate of photo-oxidation of compounds (III) and (IV) H_2O was exchanged for D_2O and CH_3OH exchanged for CD_3OD, both of at least 99.9% deuterium isotope.

Solvents for recrystallisations, sample, and standard preparations, general chromatography and spectroscopy were of "AnalaR" quality, whilst solvents for HPLC studies were of "Hypersolv" quality (BDH Chemicals). Solvents used for nmr spectroscopy studies were of '100%' isotopic purity and were obtained from Amersham International.

CHAPTER 3.

Experimental & Results.

3.1. Kinetic Equations used in Conjunction With Experimental Results.

Of all the many methods that have been used to generate singlet oxygen, dye sensitisation was chosen in the present study for its consistency of operation and high quantum yields of generation of singlet oxygen. Three systems have been used with the sensitiser and substrate in various physical states as shown below:

		substrate	
		liquid	solid
sensitiser	liquid	(a)	----
	solid	(b)	(c)

(a) sensitiser and substrate both dissolved in solution - homogeneous.
(b) singlet oxygen exogeneously generated from solid phase sensitiser, substrate in solution.
(c) both substrate and sensitiser in solid state absorbed onto silica plate.

Kinetics have been performed on systems (a) and (b) and the results analysed using the equations derived in the following sections.

3.1.1. Measurement of the Rate Constant for the Reaction of Singlet Oxygen With a Substrate.

Since the excited states of oxygen cannot be directly generated in any appreciable quantity, they have to be generated by energy transfer from a donor molecule[184,185]. The donor, usually a dye such as Rose Bengal or Methylene Blue, transfers absorbed energy to the ground state oxygen molecule thus returning to its own ground state but promoting the oxygen molecule to a higher energy state.

In homogeneous solution the following processes[186,187] occur in the dye sensitised formation of singlet oxygen:

$$\text{Dye } (S_0) \xrightarrow{I_a} \text{Dye } (S_1) \qquad (3)$$

$$\text{Dye } (S_1) \xrightarrow{k_r} \text{Dye } (S_0) + h\nu \qquad (4)$$

$$\text{Dye } (S_1) \xrightarrow{k_{10}} \text{Dye } (S_0) \qquad (5)$$

$$\text{Dye } (S_1) \xrightarrow{k_{isc}} \text{Dye } (T_1) \qquad (6)$$

$$\text{Dye } (T_1) \xrightarrow{\quad k_d' \quad} \text{Dye } (S_0) \qquad (7)$$

$$\text{Dye } (T_1) + {}^3O_2 \xrightarrow{\quad k_{oxy} \quad} \text{Dye } (S_1) + {}^1O_2 \qquad (8)$$

where Ia represents the intensity of the absorbed irradiation, S_0. S_1, T_1 represent respectively the ground and first singlet states and the first triplet state of the dye molecule. The prefix "k" denotes the respective rate constant for the proccess with the suffixes "f,ic,isc,d'" and "oxy" representing respectively fluorescence, internal conversion, intersystem crossing, deactivation of the triplet excited state and the quenching of the excited dye by the ground state oxygen molecule. Applying the steady state principle to the above reaction scheme gives rise to the following expression for the rate of singlet oxygen production

$$\frac{d\,[{}^1O_2]}{d\,t} = \frac{Ia \,.\, \Phi r \,.\, k_{oxy}\,[{}^3O_2]}{k_d' + k_{oxy}\,[{}^3O_2]} \qquad (9)$$

where Φr is the quantum yield for formation of the dye triplet state

$$\Phi r = k_{isc} / (k_f + k_{ic} + k_{isc}) \qquad (10)$$

Since k_{oxy} is normally $\simeq 2 \times 10^9 M^{-1}s^{-1}$ and k_d' is normally $\simeq 10^4\ s^{-1}$ equation (9) simplifies to

$$\frac{d\,[{}^1O_2]}{d\,t} = Ia \,.\, \Phi r \qquad (11)$$

If a substrate, (A), is present which reacts with singlet oxygen the following further processes have to be taken into account

$$^1O_2 \xrightarrow{\quad k_d \quad} {}^3O_2 \qquad (12)$$

$$^1O_2 + A \xrightarrow{\quad k_r \quad} \text{Products} \qquad (13)$$

where k_d represents the rate constant for physical quenching, and k_r the rate constant for chemical quenching of singlet oxygen. This assumes that there is no significant interactions between the singlet and triplet dye states and that the species, A, reacts exclusively with singlet oxygen.

The rate of removal of singlet oxygen by reactions (12) and (13)

is represented by

$$-\frac{d[^1O_2]}{dt} = \left[k_d + k_r\,[A]\right][^1O_2] \qquad (14)$$

Assuming that there is no build up of singlet oxygen in the reaction system equations (9) and (14) can be combined to give the steady state concentration of singlet oxygen as

$$[^1O_2] = \frac{I_a \,.\, \Phi_r}{k_d + k_r \,.\, [A]} \qquad (15)$$

The rate of removal of oxygen from the system is equal to the rate of reaction of singlet oxygen, as represented by equation (13) and is given by

$$-\frac{d\,[O_2]}{dt} = k_r.[A].[^1O_2] \qquad (16)$$

Combining equations (15) and (16) gives

$$-\frac{d\,[O_2]}{dt} = \frac{k_r\,[A] \,.\, I_a \,.\, \Phi_r}{k_d + k_r \,.\, [A]} \qquad (17)$$

Inversion of equation (17) results in equation (18)

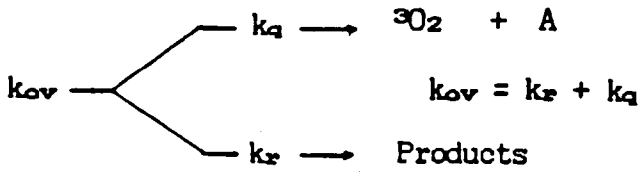
$$\left[-\frac{d\,[O_2]}{dt}\right]^{-1} = \frac{1}{I_a.\Phi_r} \cdot \frac{1}{I_a.\Phi_r} \cdot \frac{k_d}{k_r} \cdot \frac{1}{[A]} \qquad (18)$$

If the above mechanism represents that for the dye-sensitised photo-oxidation of a substrate then a plot according to equation (18) of the reciprocal of the rate of oxygen consumption versus the reciprocal of the substrate concentration, should yield a straight line plot. The ratio of slope/intercept is equal to the ratio k_d/k_r and as k_d is known for a variety of solvents[108], the value for k_r can be determined.

3.1.2. Measurement of the Overall Rate Constant, k_{ov}, for the Interaction of Singlet Oxygen with Compound (I).

The interaction of singlet oxygen with a substrate, A, can have outcomes, either physical quenching of singlet oxygen to produce ground state triplet oxygen or chemical reaction with the resultant formation

of products. These processes are depicted schematically below, along with the rates constants, k, for these processes:



$$k_{ov} = k_r + k_q \qquad (19)$$

If the substrate A is added to a system in which $^1O_2$ reacts with another substrate, A′, then the rate of removal of A′ from the system will be reduced relative to that when no substrate A is added, because of competition between A and A′ for $^1O_2$. It has been shown[229] that if two solutions of equal volume, one containing substrate A and one without A and each having the same initial concentrations of A′, are each exposed to the same amount of $^1O_2$, then k_{ov} can be calculated from the equation:

$$k_{ov} = \frac{k_{ox}\left([A']_f^0 - [A']_f^e\right) + k_d \cdot \ln\frac{[A']_f^0}{[A']_f^e}}{[A] \cdot \ln\frac{[A']}{[A']_f^e}} \qquad (20)$$

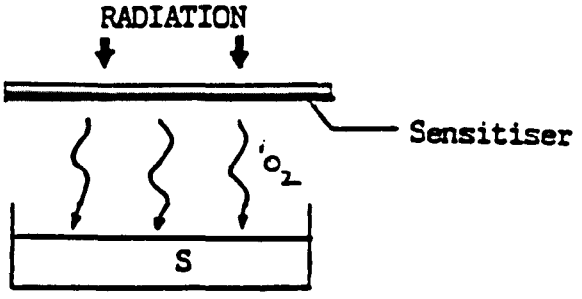
in which $[A']$ is the initial concentration of A′, $[A']_f^e$ the final concentration of A′ in the solution not containing substrate A, and $[A]_f^0$ the concentration of substrate A, k_{ox} is the rate constant for the reaction of singlet oxygen with A′, and k_d is the rate constant for the deactivation of singlet oxygen.

It can be seen from equation (19) that $k_{ov} = k_q + k_r$. Thus if the value of k_{ov} is determined for any system, the value of k_q can be calculated using the value of k_r determined by the method given in the previous section.

In our system the substrate A was compounds (I)-(V) and the substrate A′ was Anthracene-9,10-diethanol(ADE).

3.1.3. The Order of Reaction for the Reaction of Singlet Oxygen with Substrate in Solution (Singlet Oxygen Generated Exogeneously.)

The diffusion of singlet oxygen across the air gap between the sensitiser and the solution containing a substrate, S, in a surface-separated reactor is depicted schematically below:



Once the singlet oxygen reaches the solution it may react with the substrate, S, and the reaction may be written as:

$$^1O_2 + S \xrightarrow{k} \text{Products}$$

where k is the rate constant for the reaction.

The rate of reaction w.r.t. the consumption of S during the reaction is given by

$$-\frac{dS}{dt} = k \cdot [^1O_2]^a \cdot [S]^b$$

where a and b represent the order of reaction w.r.t. singlet oxygen and the substrate S respectively.

If the intensity of radiation is kept constant so as to maintain the concentration of singlet oxygen, $[^1O_2]$, constant at the surface of the solution then the above rate equation reduces to

$$-\frac{dS}{dt} = (\text{constant})_1 \cdot [S]^b$$

If b=1, then the rate equation becomes that of a first order reaction for which the following expression holds:

$$\log \frac{[S]_0}{[S]_t} = (\text{constant})_2 \cdot t$$

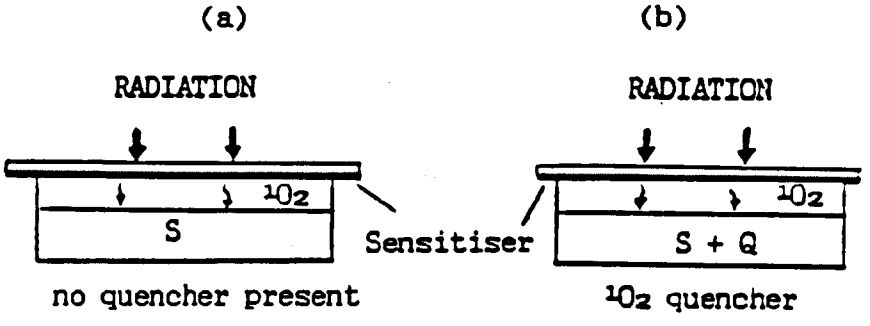
where $[S]_0$, $[S]_t$ represent the initial concentration of S and

the concentration at time t, respectively.

If b=0 or 2, then either the standard zero order or second order rate equations would describe the reaction.

3.1.4. Measurement of the rate constant for the reaction of exogeneously generated singlet oxygen with a substrate (Method I).

Consider a surface-separated reactor as shown below in which there are two wells containing an equal volume of solution with a substrate, S, of known concentration, and in which in system (a) there is no quencher present but in system (b) there is a quencher, Q, present.



The processes involving singlet oxygen in the two systems are depicted below:

System (a)	System (b)
$^1O_2 \xrightarrow{k_d} {}^3O_2$	$^1O_2 \xrightarrow{k_d} {}^3O_2$
$^1O_2 + S \xrightarrow{k_r}$ products	$^1O_2 + S \xrightarrow{k_r}$ products
	$^1O_2 + Q \xrightarrow{k_q} {}^3O_2 + Q$

Assuming a steady state concentration of singlet oxygen in each solution

Rate of diffusion of $^1O_2$ into solution = Rate of removal of $^1O_2$

Thus the following expression can be written for system (a)

$$R_{diff} = k_d.[^1O_2] + k_r.[^1O_2][S] \quad (21)$$

Likewise for system (b):

$$R_{diff} = k_d.[^1O_2] + k_r[^1O_2][S] + k_q.[^1O_2].[Q] \quad (22)$$

Equations (21) and (22) can be rearranged to give equations (23) and (24) respectively

$$^1O_2 = \frac{R_{diff}}{k_d + k_r . [S]} \quad (23) \qquad ^1O_2 = \frac{R_{diff}}{k_d + k_r.[S] + k_q.[Q]} \quad (24)$$

The rate of removal of substrate, S, in each solution is given by the expression

$$- \frac{d[S]}{dt} = k_r.[^1O_2].[S] \quad (25)$$

Substitution of equations (23) and (24) into equation (25) gives equations (26) and (27) respectively

$$- \frac{d[S]}{dt} = \frac{k_r . R_{diff}}{k_d + k_r [S]} \quad (26)$$

$$- \frac{d[S]}{dt} = \frac{k_r . R_{diff}}{k_d + k_r [S] + k_q Q} \quad (27)$$

Dividing equation (26) by equation (27) gives the following expression

$$\frac{(- d S / dt)_a}{(- d S / dt)_b} = 1 + \frac{k_q}{k_d + k_r [S]} . [Q] \quad (28)$$

The terms on the LHS of equation (28) can be written in the form shown in equation (29)

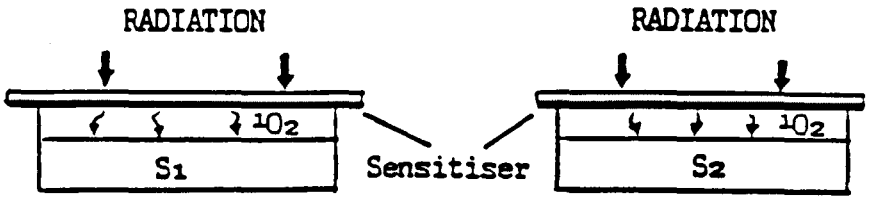
$$\frac{[S]_{t=0} - [S]_{t=t}}{[S]_{t=0} - [S]_{t=t}} = 1 + \frac{k_q}{k_d + k_r [S]} . [Q] \quad (29)$$

where $[S]_{t=0}$, $[S]_{t=t}$, $[S]_{t=0}$, $[S]_{t=t}$ represent the respective initial concentrations of S in system (a), the concentration of S at time t in system (a), the initial concentration of S in system (b), the concentration of S at time t in system (b). If these concentrations can be determined experimentally then equation (29) shows that a plot of the LHS of equation (29) against [Q] should yield a straight line with an intercept of one and a slope equal to $k_q/k_d + k_r [S]$.

Thus if k_q, k_d and [S] are known, the value of the rate constant, k_r, for the reaction of $^1O_2$ with the substrate can be determined.

3.1.5. Measurement of the Rate Constant for the Reaction of Exogeneously Generated Singlet Oxygen with a Substrate (Method II).

Consider a surface-separated reactor as shown below in which there are two wells containing an equal volume of solution with one containing a substrate, S_1, and the other containing substrate, S_2.



The reactions of $^1O_2$ which lead to the removal of the substrates are depicted below:

$$^1O_2 + S_1 \xrightarrow{k_1} \text{Products} \qquad (30)$$

$$^1O_2 + S_2 \xrightarrow{k_2} \text{Products} \qquad (31)$$

The rate of removal of substrate in each system can be expressed as

$$-d[S_1]/dt = k_1 [^1O_2] . [S_1] \qquad (32)$$

$$-d[S_2]/dt = k_2 [^1O_2] . [S_2] \qquad (33)$$

The rate of diffusion of singlet oxygen into solution will be the same for each system and as the steady state concentration of singlet oxygen, $^1O_2$, is determined by this rate of diffusion so this concentration will be the same in each system. Thus dividing equation (32) by equation (33) results in the expression

$$\frac{-d[S_1]/dt}{-d[S_2]/dt} = \frac{k_1}{k_2} . \frac{[S_1]}{[S_2]} \qquad (34)$$

It can be seen from equation (34) that if the rates of removal of substrates S_1 and S_2 can be measured at known values of $[S_1]$ and $[S_2]$ then the ratio of k_1/k_2 can be determined. If the value of k_1 is known for the substrate S_1, then the value of

the rate constant, k_2, for the reaction of singlet oxygen with any other substrate S_2 can be determined.

3.2. Kinetic Experiments using the Oxygen Electrode.

The rate of removal of oxygen from reaction systems was measured using the oxygen electrode (re. 2.1.1.). For each experiment a set of solutions of varying substrate concentration ($1x10^{-3}M$ to $1x10^{-2}M$) with constant dye sensitiser concentration ($2x10^{-5}M$) were photolysed. The photolyses were performed in triplicate for each substrate concentration. The substrate concentrations were chosen so that an acceptable distribution of points was obtained when the reciprocal of the observed rate of reaction against the reciprocal of substrate concentration was plotted.

Assuming the mechanism of dye sensitistion proposed by Davidson *et al.* [131](re. 3.1.1.), then a plot according to equation (18) should yield a straight line, from which the ratio of slope/intercept gives the ratio k_d/k_r, where k_r is the rate constant for the reaction of singlet oxygen with substrate, and k_d the inverse of the lifetime of singlet oxygen. The lifetime of singlet oxygen in water was reported by Merkel and Kearns[108] to be 2μs and in water/methanol 3.5μs. Knowing k_d the value of k_r can be determined from the ratio k_d/k_r.

3.2.1. The Effect of Temperature on the Rate of Dye sensitised Photo-oxidation of the Compounds (I)-(V) and Anthracene-9,10-diethanol (ADE).

Solutions of compounds (I)-(V) and (ADE) in water/methanol (1:1) and in methanol, of concentrations varying between 1 X $10^{-3}M$ and $10^{-2}M$ containing Rose Bengal (2 x $10^{-5}M$) were photolysed in

the oxygen electrode apparatus at different temperatures. Plots according to equation (18) (the inverse of the rate of oxygen removal against the inverse of substrate concentration) were obtained at each temperature. The results are given in Tables 3-22, Figures 31-50 for water/methanol was used as solvent, and Tables 23-47, Figures 51-75 for systems in which methanol was used as solvent.

The value of the rate constant ratio k_d/k_r for each system studied was obtained from the ratio of slope/intercept of Figures 31-75. Since the value for k_d is known to be $2.8 \times 10^5 s^{-1}$ in water/methanol[123] and $5.0 \times 10^5 s^{-1}$ in methanol the value of k_r for each system could be determined. These values are given in Tables 7, 12, 17, 22 and Tables 27, 32, 37, 42 & 47 respectively. The average % error in the value of k_r is $\pm$ 18%. The Arrhenius plots derived from the data are illustrated in Figures 35, 40, 45, 50 and Figures 55, 60, 65, 70 & 75 respectively. The energy and entropy of activation obtained from the Arrhenius plots are summarised in Tables 48 and 49.

3.2.2. The Effect of pH on the Rates of Dye-sensitised Photo-oxidation of Compounds (III) and (IV).

Standard solutions of compounds (III) and (IV) of concentration varying between 1×10^{-3}M and 1×10^{-2}M and having the same concentration of Rose Bengal (2×10^{-5}M) were prepared using water buffered to pH values of 4.0, 7.0 and 9.0. Samples of the solutions at the three pH values were then photolysed in the oxygen electrode apparatus. The kinetic data for the rate of oxygen removal i.e. the rate of photo-oxidation, is shown in Tables 50-55, and the plots according to equation (18) are given in Figures 76-81. The value of the rate constant, k_r, for the photo-oxidation of compounds (III)

and (IV) at the different pHs are given in Table 56.

3.2.3. The Effect of Solvent Deuteration on the Rates of Dye sensitised Photo-oxidation of Compounds (III) and (IV).

Individual solutions of compounds (III) and (IV) with concentrations varying between $5x10^{-4}M$ and $1x10^{-2}M$ containing Rose Bengal ($2x10^{-5}M$) in D_2O/CD_3OD (1:1 v/v) were photolysed in the oxygen electrode apparatus. The kinetic data for the rate of oxygen removal is shown in Tables 57 and 58, with plots according to equation (18) given in Figures 82 and 83. The rate constant, k_r, for the photo-oxidation of compounds (III) and (IV) derived from the plots in Figures 82 and 83 are given in Table 59, along with the corresponding values in the non-deuterated solvent. The ratio $k_{r(deuterated)} : k_{r(non-deuterated)}$ is also listed in Table 59 under the heading of isotope effect.

3.2.4. The Effect of Sodium Azide on the Rate of Photo-oxidation of Compounds (III) and (IV)

Two sets of methanolic solutions containing Rose Bengal ($2x10^{-5}M$) and compound (III) ($1.0x10^{-3}$-$1x10^{-2}M$) were pepared, with one of the sets containing sodium azide ($1x10^{-4}M$) in each solution. Samples of each solution were photolysed in the oxygen electrode apparatus. The rate of oxygen removal was determined in each case and plots obtained of the inverse of the rate against the inverse of the concentration of compound (III). The same procedure was used for compound (IV). The values of the rate constants, k_r, calculated from Figures 84 & 85 are given in Table 62,along with the values of the rate constants for non-quenched systems. The ratio of the rate constant, $k_{r\ (quenched)} : k_{r\ (non-quenched)}$, is also listed in Table 62 under the heading of quencher effect.

3.3. Kinetic Experiments Using the 'Merry-go-Round' Reactor.

3.3.1. Determination of the Rate Constant, k_{ov}, for the Dye sensitised Photo-oxidation of Compounds (I), (II), (III) & (V).

A set of solutions containing compounds (I), (II), (III) and (V) individually at concentrations of ($2x10^{-3}M$) and anthracene-9,10-diethanol (ADE) ($1.6x10^{-3}M$) were prepared in methanol, as was a control solution of ADE ($1.6x10^{-3}M$) in methanol. Two samples of each solution were photolysed in the 'Merry-go-Round' reactor for 15 hours at 298K. The concentration of ADE in each solution before and after irradiation was determined by measuring the absorbance of the solution at 440nm. All experimental readings were the average of six determinations, three measurements were taken for each of the two samples. In all procedures involving ADE, sample preparation and analysis were performed in a dark room fitted with Ilford F904 safelights.

Substitution of the values for the concentration of ADE into equation (20) (re. 3.1.2.), along with the values of the rate constant, k_r ($=k_{ox}$), for the photo-oxidation of ADE (re. Table 47), gave the value for the rate constant, k_{ov}. These values are listed in Table 63.

3.4. Kinetic experiments using the surface-separated-reactor.

In the surface-separated-reactor the sensitiser is physically removed from the substrate solution by an air gap of $\simeq$1mm, and singlet oxygen produced by the sensitiser has to traverse this gap before reacting with the substrate. Singlet oxygen produced in this way is referred to herein as exogeneously generated singlet oxygen.

3.4.1. Testing the surface-separated-reactor for its ability to generate singlet oxygen.

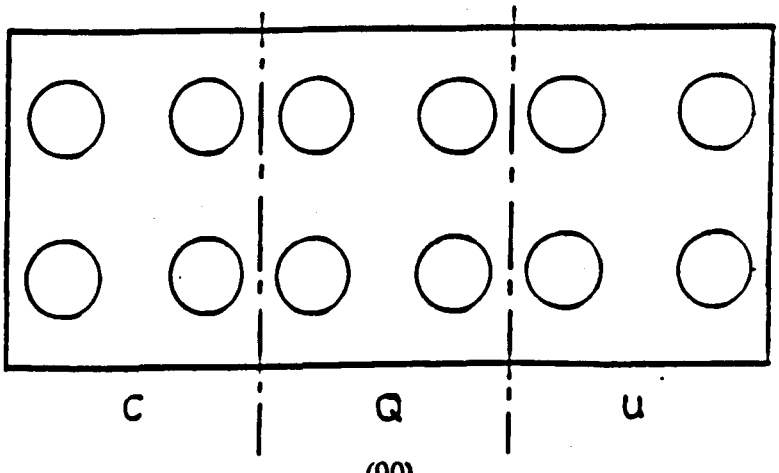
The surface-separated-reactor was tested for its ability to

generate singlet oxygen by using the well documented histidine/N,N-dimethyl-4-nitorosoaniline (RNO) reaction[183-185]. If singlet oxygen is formed in the apparatus the absorbance of RNO at 440nm would decrease proportionally with irradiation time.

Solutions of histidine (10^{-2}M) and RNO (10^{-5}M) in phosphate buffer (pH = 7.2, 0.02 M) were placed in the wells of a Boerner slide and covered with a silica gel tlc plate onto which chlorophyll had been adsorbed as a sensitiser. The chlorophyll was then irradiated with radiation of wavelength greater than 420nm. Samples of the reaction solutions were taken at regular intervals and the absorbance of RNO at 440nm was monitored with respect to irradiation time. The results are given in Table 84 and Figure 88.

3.4.2. <u>The effect of sensitiser on the rate of reaction of exogeneously generated singlet oxygen reaction with compounds (I) and (III).</u>

The reaction of exogeneously generated singlet oxygen with compounds (I) and (III) was studied using Rose Bengal and Chlorophyll as sensitisers. Solutions of compound (I) (10^{-2}M) were prepared in benzene, along with solutions of compound (I) (10^{-2}M) containing β-carotene (10^{-3}M). Samples of these solutions were placed in the wells of a Boerner slide as described below. The samples in section C did not contain β-carotene and were covered by the sensitiser plate with the sensitiser coated side uppermost. These solutions were the controls, C.



The samples in section U did not contain β-carotene and were covered by the sensitiser plate with the sensitiser coated side down. These solutions are referred to herein as unquenched, U. The samples in section Q contained β-carotene and were covered by the sensitiser plate with the sensitiser coated side down. These solutions are herein referred to as quenched, Q.

The sensitiser plates/Boerner slides were irradiated using a 150W spot lamp as radiation source. Samples from the sections C, U and Q were withdrawn at regular intervals and the concentration of compound (I) present in each sample was determined by hplc analysis. The same procedure was repeated for compound (III).

The experimental data showing the relative concentrations of compound (I) and compound (III) with respect to irradiation time is given in Tables 65-66 and Figures 87-90.

3.4.3. Investigation of Soil Samples as Sensitisers for the Reaction of Exogeneously Generated Singlet Oxygen with Compounds (I) and (III).

Three soil samples were kindly donated from the reference collection of the School of Geography, each of different pH. The soils were sterilised and sieved (re. 2.4.2.) to obtain a fine sample of even particle size. Double-sided adhesive tape was attached to one face of a pre-cut glass slide to form a thin semi-transparent film onto which the chosen soil sample was sprinkled. The soil surface was blown with a high pressure stream of nitrogen to remove any loose particles.

A solution of compound (I) (10^{-2}M) was prepared in benzene, as was a solution of this compound containing β-carotene (10^{-3}M). Samples of these solutions were placed in the wells of the Boerner slide using the scheme described in the previous section. The Boerner slide was covered by a sensitiser plate to which a soil sample was adhered

and irradiated in the reactor using a medium-pressure Hg vapour discharge lamp as light source. Samples from sections C, U and Q of the Boerner slide were withdrawn at regular intervals and the concentration of compound (I) present in each sample was determined by hplc analysis. The same procedure was repeated for compound (III).

The experimental data showing the relative concentrations of compounds (I) and (III) with respect to irradiation time is given in Tables 67-68 and Figures 91-96.

3.4.4. Determination of the Order of Reaction w.r.t. Compound (I) for the Reaction of Singlet Oxygen with Compound (I) in Homogeneous Solution (Singlet Oxygen Generated Exogeneously).

If the reaction of singlet oxygen with compound (I) was first-order w.r.t. compound (I) then according to the analysis given in section 3.1.3. the following equation would hold

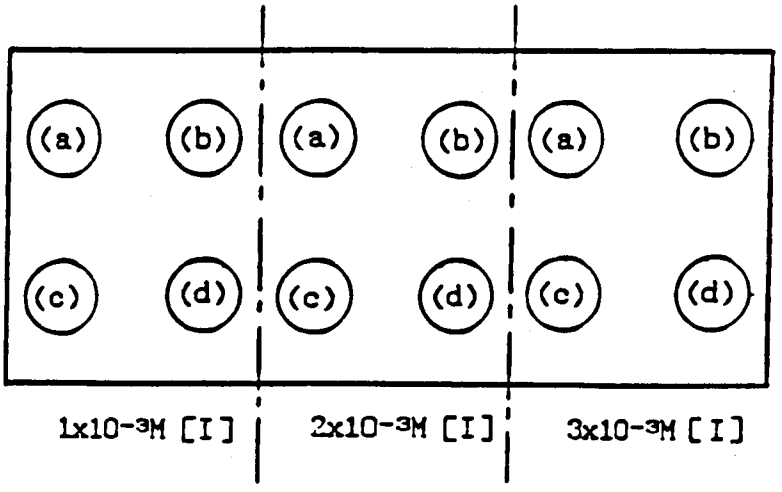
$$\log [I]_o / [I]_t = (\text{constant}) \cdot t \qquad (35)$$

where $[I]_o$, $[I]_t$ represents the initial concentration of compound (I) and the concentration at time t respectively. In such a case a plot of $\log [I]_o/[I]$ against time should yield a straight line passing through the origin.

A solution of compound (I) (10^{-2}M) was prepared in benzene, and samples of the solutions were placed in the wells of a Boerner slide. The Boerner slide was covered by a sensitiser plate on which Rose Bengal was adsorbed as the sensitiser, and the irradiated in the reactor using a 150W spot lamp as light source. Samples were withdrawn at regular intervals and the concentration of compound (I) in each sample was determined by hplc analysis. The relative concentration of compound (I) at each sample time is given in Table 69 as are the corresponding values for $\log [I]_o/[I]$. A plot according to equation (35) is shown in Figure 97.

3.4.5. Determination of the Rate Constant for the Reaction of Exogeneously Generated Singlet Oxygen with Compound (I) (Method I).

Three sets of solutions of Compound (I) were prepared in benzene, with concentrations of $1x10^{-3}M$, $2x10^{-3}M$ & $3x10^{-3}M$, and distributed between the wells of a Boerner slide as indicated below. Each well contained 100µl of the appropriate solution. To each of the wells was added a varying volume of β-carotene stock solution ($10^{-2}M$ in benzene) followed by a quantity of benzene so that the final volume in each well was 250µl. The Boerner slide was covered with a silica-coated plate, upon which Rose Bengal had been absorbed via a saturated methanolic solution; the silica-coated side facing downwards.



key:

(a) - $1x10^{-3}M$ β-carotene
(b) - $2x10^{-3}M$ β-carotene
(c) - $3x10^{-3}M$ β-carotene
(d) - $4x10^{-3}M$ β-carotene

After 5.5 hours of irradiation the samples were analysed by hplc analysis, concentrations of Compound (I) relative to that of the solution not containing quencher are given in Table 70. Plots of the data given in Table 70 according to equation (29) are shown in Figure 98. The gradient of each of the lines gives rise to a value for k_r - values for kd and kq being readily available in the literature;

k_d = 36900s-1 and k_q = 1.3 x $10^{10}M^{-1}s^{-1}$ [234]. The average value for kr is given in Table 72.

3.4.6. Determination of the Rate Constant for the Reaction of Exogeneously Generated Singlet Oxygen with Compound (I). (Method II).

Solutions of 2,5-Dimethylfuran (DMF) ($10^{-2}M$) and compound (I) in benzene were placed in the wells of the Boerner slide and a silica gel plate with absorbed Rose Bengal as sensitiser was placed over the slide. The system was irradiated with light from a "Wotan" spotlight lamp. Samples were withdrawn at hourly intervals and analysed by hplc to determine the relative concentration of DMF and of compound (I) remaining. The results are given in Table 71 and the data plotted in Figure 99.

Equation (34) as applied to the present system is given below

$$\frac{-d[DMF]/dt}{-d[I]/dt} = \frac{k_{DMF}}{k_r} \cdot \frac{[DMF]}{[I]}$$

where the rates of removal of DMF and compound (I) are given by the slopes of the plots of Figure 99, [DMF] and [I] are respectively the initial concentrations of 2,5-dimethylfuran and compound (I), k_{DMF} is the rate constant for the reaction of singlet oxygen with 2,5-dimethylfuran in benzene ($2.3x10^{-3}M$)[234], and k_r is the desired rate for the reaction of singlet oxygen with compound (I) in toluene. The calculation of the value of k_r is shown below:

$$\frac{14.88}{10.60} = \frac{1.4 \times 10^8}{k_r} \cdot \frac{10^{-3}}{10^{-3}}$$

$$k_r = 1.4 \times 10^8 / 1.4$$

$$k_r \simeq 1 \times 10^8 \ M^{-1}s^{-1}$$

This value is compared with that obtained from Method I and that obtained from the homogeneous generation of singlet oxygen using the oxygen electrode (cf.3.1.1.) in Table 72.

3.5. Product Studies.

3.5.1. A Comparison of the Product Distribution Arising from the Photo-oxidation of Compound (I) using Different Modes of Singlet Oxygen Generation.

(i) Homogeneously Generated Singlet Oxygen.

Two solutions were prepared in benzene containing Rose Bengal (10^{-2}M) and ^{14}C-labelled compound (I) (21 μc, 10^{-4}M), with one of the solutions containing β-carotene (10^{-4}M) as quencher. Samples of these solutions were photolysed for 2 hours with radiation of wavelength greater than 420 nm using the apparatus shown in Figure 3Ø(a).

(ii) Heterogeneously Generated Singlet Oxygen.

Two solutions were prepared in benzene containing ^{14}C-labelled compound (I) (21μc, 10^{-4}M), with one of the solutions containing β-carotene (10^{-4}M) as quencher. To each solution was added silica gel impregnated with Rose Bengal, and samples of the solutions were photolysed for 2 hours with radiation of wavelength greater than 420 nm using the apparatus shown in Figure 3Ø(a).

(iii) Exogeneously Generated Singlet Oxygen.

Two solutions were prepared in benzene containing ^{14}C-labelled compound (I) (21 μc, 10^{-4}M), with one of the solutions containing β-carotene (10^{-4}M) as quencher. Samples of these were placed in Boerner wells in the surface-separated reactor, covered with a Rose Bengal impregnated silica gel plate which was irradiated with radiation of wavelength greater than 420 nm (Figure 3Ø(b)), for 2 hours.

The photolysed samples produced were evaporated to dryness and then dissolved in acetone (≃ 2 ml). Each sample solution was spotted onto a silica plate such that each spot had an activity count of 10 counts per

second (±5%). The spots were allowed to dry. The tlc plate was developed in Chloroform/Acetonitrile/Hexane (80:10:10), dried, and an autoradiogram obtained as described in section 2.3.4. The autoradiogram is shown in Figure 100(A).

3.5.2. A Comparison of the Product Distribution Arising from the Photo-oxidation of Compound (I) using Rose Bengal and a Soil Sample as Sensitisers for the Exogeneous Formation of Singlet Oxygen.

Two solutions of ^{14}-C-labelled compound (I) (21 μc, 10^{-4}M), were prepared in benzene, with one of the solutions containing β-carotene (10^{-4}M) as quencher. Samples of the solutions were placed in Boerner wells in the surface-separated reactor, covered with a Rose Bengal impregnated silica gel plate which was irradiated with radiation of wavelength greater than 420 nm (Figure 30(b),, for 2 hours.

The experiment was repeated using similarly prepared solutions - but the Boerner wells were covered using a glass plate with a soil sample adhered to the underside (re. 2.3.4.). The solutions were then irradiated with a medium pressure mercury discharge tube for 2 hours.

Both sets of samples were evaporated to dryness and then dissolved in acetone (≃ 2 ml). These sample solutions were spotted onto a silica gel plate such that each spot had an activity count of 10 counts per second (±5%). The spots were allowed to dry. The tlc plate was developed in Chloroform/Acetonitrile/Hexane (80:10:10), dried and an autoradiogram obtained as described in section 2.3.4. The resulting autoradiogram is shown in Figure 100(B).

3.5.3. A Comparison of the Product Distribution Arising from the Heterogeneous Photo-oxidation of Compound (I) using various Sensitisers.

A solution of compound (I) (10^{-4}M) was prepared in acetone and spotted onto a silica gel plate such that each spot had an activity

count of 10 counts per second (±5%). The spots were allowed to dry. A saturated solution of β-carotene in acetone was prepared and 10 μL of this solution was spotted onto selected spots on the plate containing compound (I). The spots were allowed to dry. Each of the spots on the plate was further spotted with an acetone solution containing one of the sensitisers - Rose Bengal, Methylene Blue or Chlorophyll. The spots were allowed to dry. The tlc plate was then placed beneath a light source in the apparatus shown in Figure 30(c) and irradiated with radiation of wavelength greater than 420 nm, for 2 hours. The tlc plate was developed in Chloroform/Acetonitrile/Hexane (80:10:10), dried and an autoradiogram obtained as described in section 2.3.4. The resulting autoradiogram is shown in Figure 100(C).

3.6. Attempted Identification of Intermediates Resulting from the Dye Sensitised Photo-oxidation of Compound (I) at low Temperature.

A solution of Rose Bengal (10^{-4}M) and compound (I) (10^{-2}M) in a 1:1 deuteromethylene chloride:deuteroacetone mixture was aerated with oxygen and photolysed for 24 hours at 203 K in a borosilicate NMR tube, using the apparatus described in section 2.1.3. The ^{1}H NMR spectra of the solution, before and after photolysis, were obtained below 243K and are shown in Figures 101-104.

3.7. Estimation of Experimental Errors.

Errors in experimental measurements may be divided into two classes: (a) Random Errors and (b) Systematic Errors. The first class of errors, random errors, or accidental errors, is indicated by fluctuations in successive measurements and are random variations due to small errors beyond the control of the observer. Since the true value is generally unknown, this error may be minimised by using the mean of a series of determinations; the difference between the mean value and the observed

value being the residuals. Typically, instrument readings and experiments were performed so that the mean of at least three determinations could be calculated. The difference between the residuals and the mean was found to be acceptably low ($\leqslant$ 1.5%) for all techniques.

It is possible to correct for the second class of errors, and they are therefore designated corrigible or determinate errors. Many systematic errors may be eliminated by the application of familiar corrections or by determining corrections experimentally.

The main equation to determine the rate constant, k_r, using the oxygen electrode apparatus is given in Equation 18. This simplifies to:

$$k_r \qquad \frac{k_d}{[A]} \cdot \frac{d[O_2]}{dt}$$

Allowing for tolerances in glassware (pipettes and volumetric flasks) and fluctuations in temperature of the solutions it could be rationalised that the maximum inherent error encountered in the preparation of a solutions is $\simeq$ Ø.5%. The error asociated with measuring the rate of oxygen consumption was experimentally found to be $\pm$ 15%. The constant k_d, obtained from the mean of literature values, was found to have a maximum possible error of 2.5%. The limit of confidence in the overall result is then the sum of the constituent inherent errors. Thus, the error in the value of k_r derived from measurements using the oxygen electrode is taken as $\pm$ 18%.

The merry-go-round apparatus is used to determine the overall rate constant, k_{ov}, for a substrate and is governed by the equation:

$$k_{ov} = \frac{k_{ox}\left([A']_p^p - [A']_p^o\right) + k_d \cdot \ln\frac{[A']_p^p}{[A']_p^o}}{[A] \cdot \ln\frac{[A']}{[A']_p^o}}$$

Similar arguments may be used to assign inherent errors in the determination of k_{ox} and k_d - these will have errors of 3.1% and 2.5%

respectively associated with them. Concentrations of A' are determined by UV-visible absorbances and thus typically were found to deviate by ≃Ø.3%. The overall maximum error associated with this technique is a complex summation of substituent contributions, numerically equal to ≃ 13%.

Calculation of the exogeneous rate constant for a substrate is governed by the Stern-Volmer equation:

$$\frac{[S]_{t=0} - [S]_{t=t}}{[S]_{t=0} - [S]_{t=t}} = 1 + \frac{k_q}{k_d + k_r [S]} \cdot [Q]$$

The determination of the overall maximum inherent error with this technique is a compilation of the constituent errors. These have been calculated to be ≃15%,

Calculation of the rate constant for a substrate by comparison of its reaction rate with that of a documented singlet oxygen quencher involves the use of the following equation:

$$\frac{-d[S_1]/dt}{-d[S_2]/dt} = \frac{k_1}{k_2} \cdot \frac{[S_1]}{[S_2]}$$

Experimental results have shown that the error associated with the determination of the rates of quencher disappearance are in the order of ≃ 5% with determination of the substrate using hplc techniques possesing an error of ≃ 1Ø%. Assuming that k_1 has a maximum error of 5%, the overall maximum error can be taken as 2Ø%.

Summary.

Kinetic Technique	Max. Error (%)
Oxygen Electrode	18
Merry-Go-Round	15
Stern-Volmer	15
Rate comparison	2Ø

Table 3. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (II) in methanol/water (1:1) at 293 K.

10^{3}(II) (mol dm^{-3})	10^{6}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(II)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-5}Rate^{-1} ($mol^{-1}dm^{3}s$)
10.0	4.65	0.1	2.15
4.5	3.55	0.22	2.81
3.0	2.80	0.33	3.58
1.75	2.19	0.57	4.56
1.25	1.64	0.80	6.08
1.0	1.36	1.0	7.35

Figure 31. Plot According to Equation (18) of Above Data.

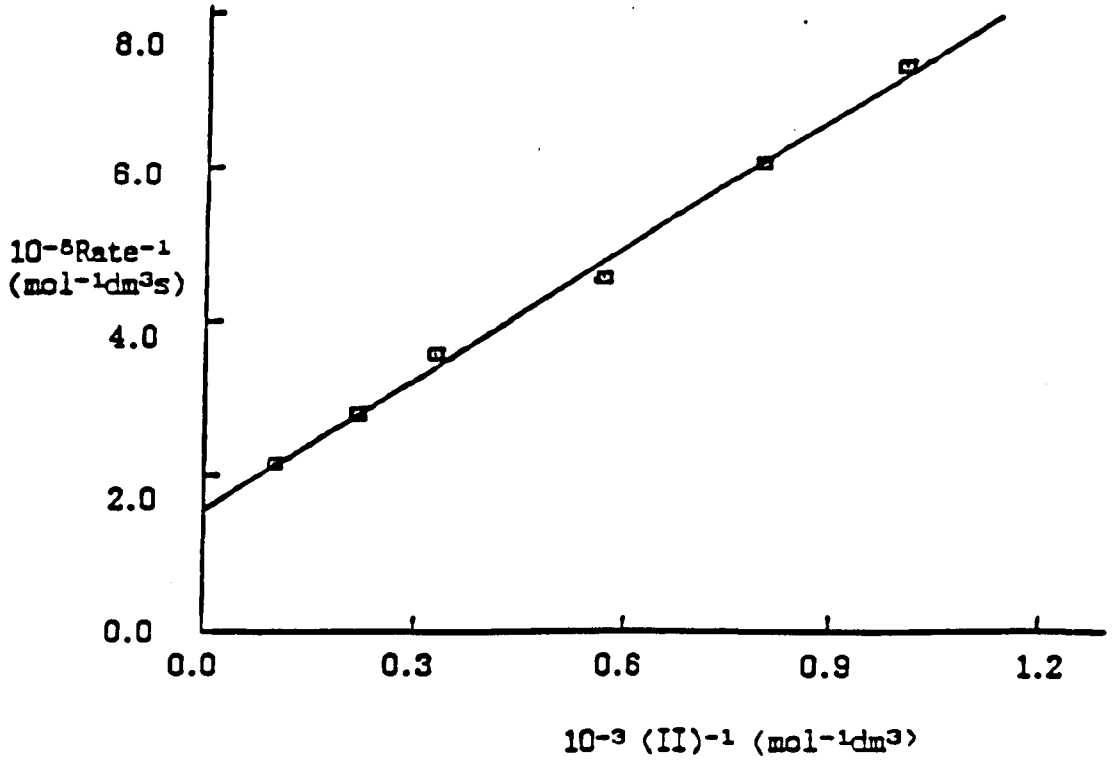


Table 4. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (II) in methanol/water (1:1) at 298 K.

10^{3}(II) (mol dm^{-3})	10^{6}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(II)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-5}Rate^{-1} ($mol^{-1}dm^{3}s$)
10.0	4.80	0.1	2.08
4.5	3.64	0.22	2.74
3.0	2.83	0.33	3.53
1.75	2.28	0.57	4.39
1.25	1.65	0.80	6.07
1.0	1.44	1.0	6.96

Figure 32. Plot According to Equation (18) of Above Data.

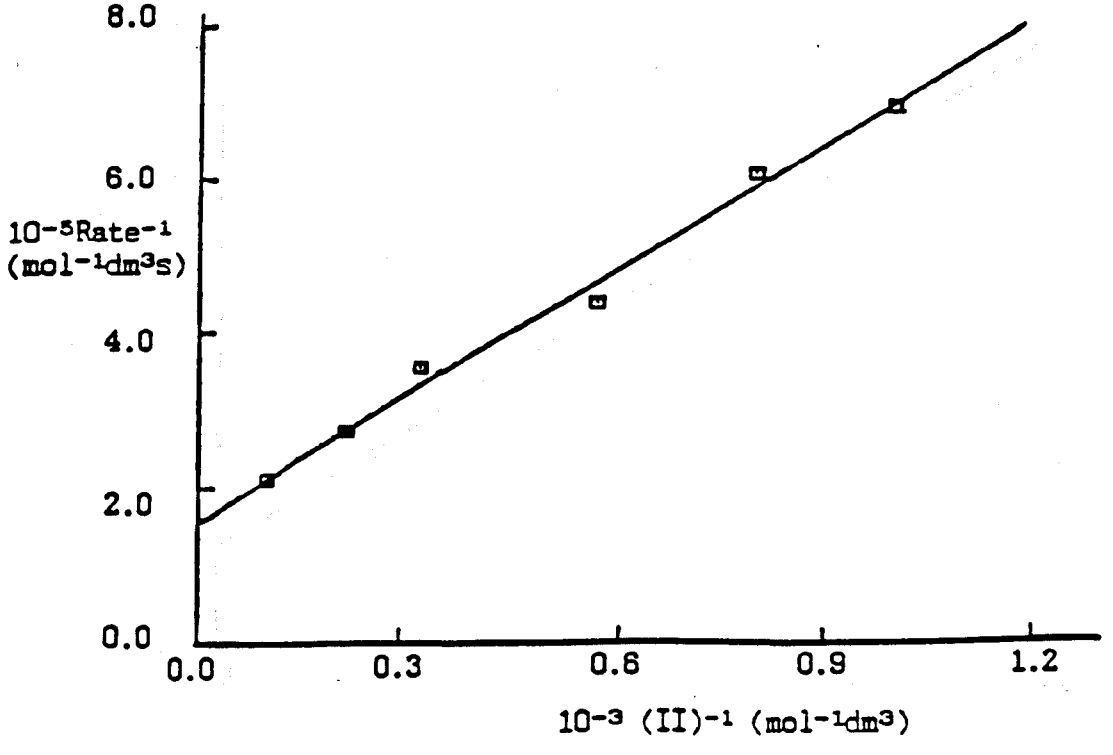


Table 5. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (II) in methanol/water(1:1) at 303 K.

10^{3}(II) (mol dm^{-3})	10^{8}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(II)$^{-1}$ (mol^{-1}dm^{3})	10^{-5}Rate^{-1} (mol^{-1}$dm^{3}s$)
10.0	5.48	0.1	1.82
4.5	3.97	0.22	2.54
3.0	3.17	0.33	3.15
1.75	2.13	0.57	4.67
1.25	1.76	0.80	5.69
1.0	1.64	1.0	6.09

Figure 33. Plot According to Equation (18) of Above Data.

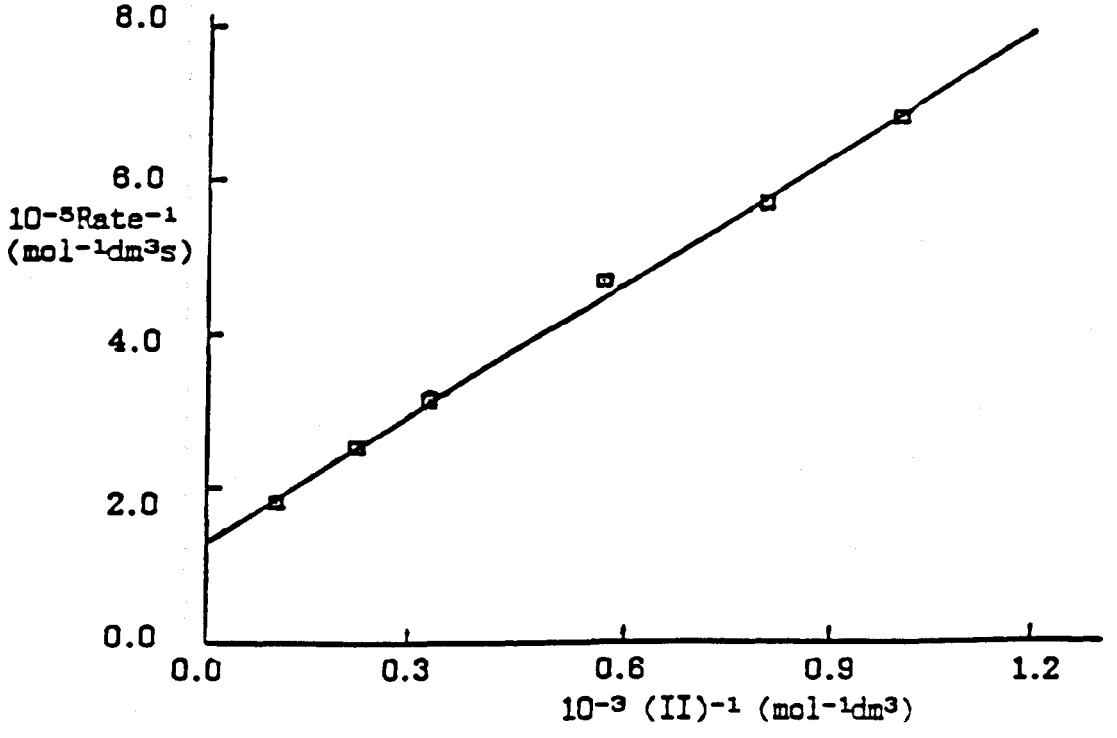


Table 6. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (II) in methanol/water (1:1) at 308 K.

10^{3}(II) (mol dm^{-3})	10^{6}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(II)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-5}Rate^{-1} ($mol^{-1}dm^{3}s$)
10.0	4.45	0.1	2.24
4.5	3.46	0.22	2.89
3.0	2.84	0.33	3.51
1.75	2.05	0.57	4.87
1.25	1.58	0.80	6.35
1.0	1.35	1.0	7.41

Figure 34. Plot According to Equation (18) of Above Data.

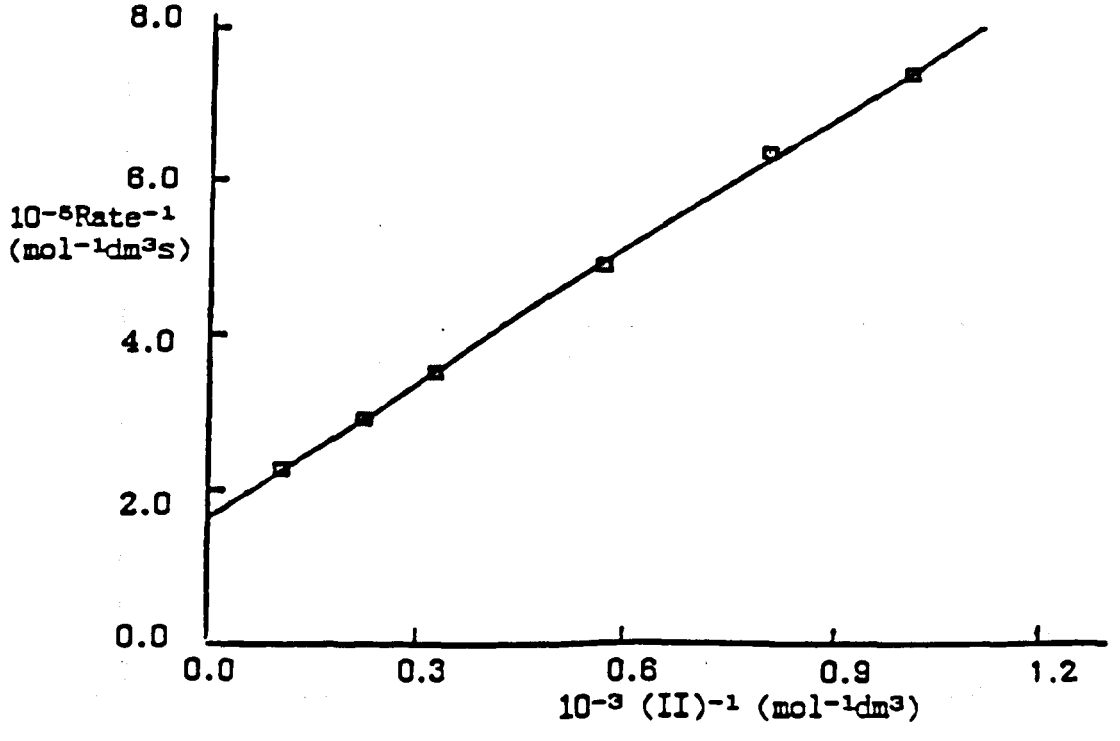


Table 7. Rate Constants for the of Rose Bengal Sensitised Photo-oxidation of compound (II) in methanol/water (1:1).

$10^{-8}k_r$ ($mol^{-1}dm^3s^{-1}$)	T (K)	ln k_r	10^3T^{-1} (K^{-1})
7.85	293	20.48	3.41
8.24	298	20.53	3.36
8.86	303	20.35	3.30
7.99	308	20.50	3.25

Figure 35. Arrhenius Plot According to Above Data.

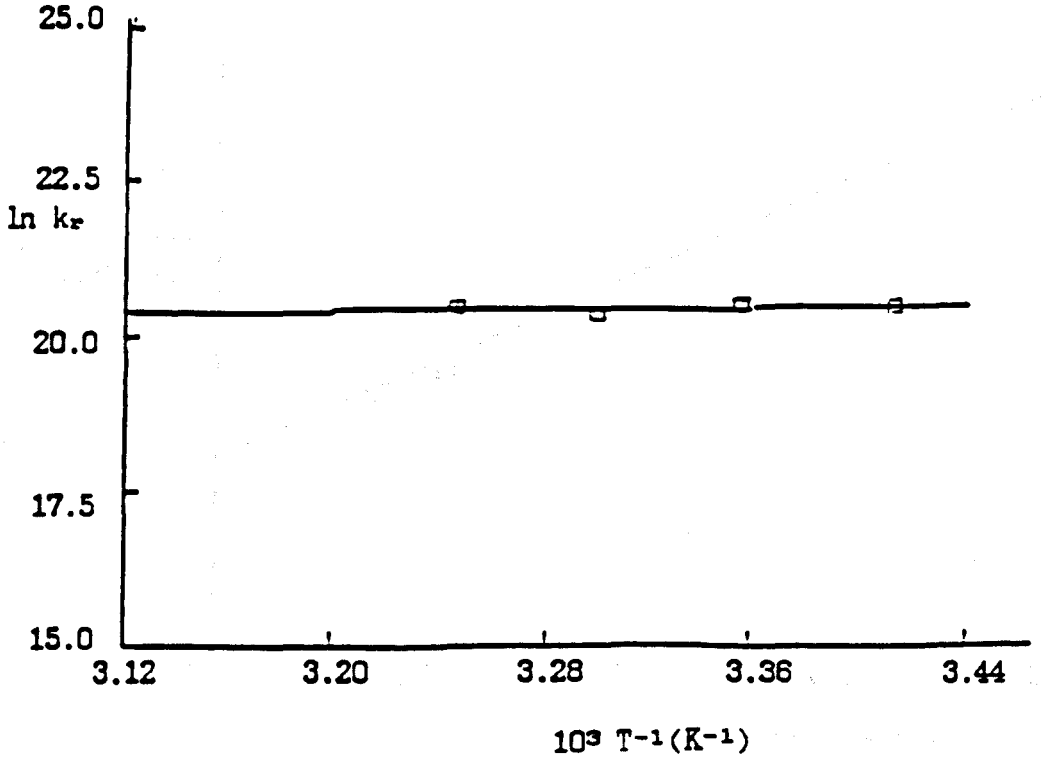


Table 8. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (III) in methanol/water (1:1) at 293 K.

10^{3}(III) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(III)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-7}Rate^{-1} ($mol^{-1}dm^{3}s$)
4.5	1.51	0.22	0.66
3.0	1.39	0.33	0.72
2.0	1.14	0.50	0.88
1.7	0.79	0.59	1.06
1.0	0.79	1.0	1.27

Figure 36. Plot According to Equation (18) of Above Data.

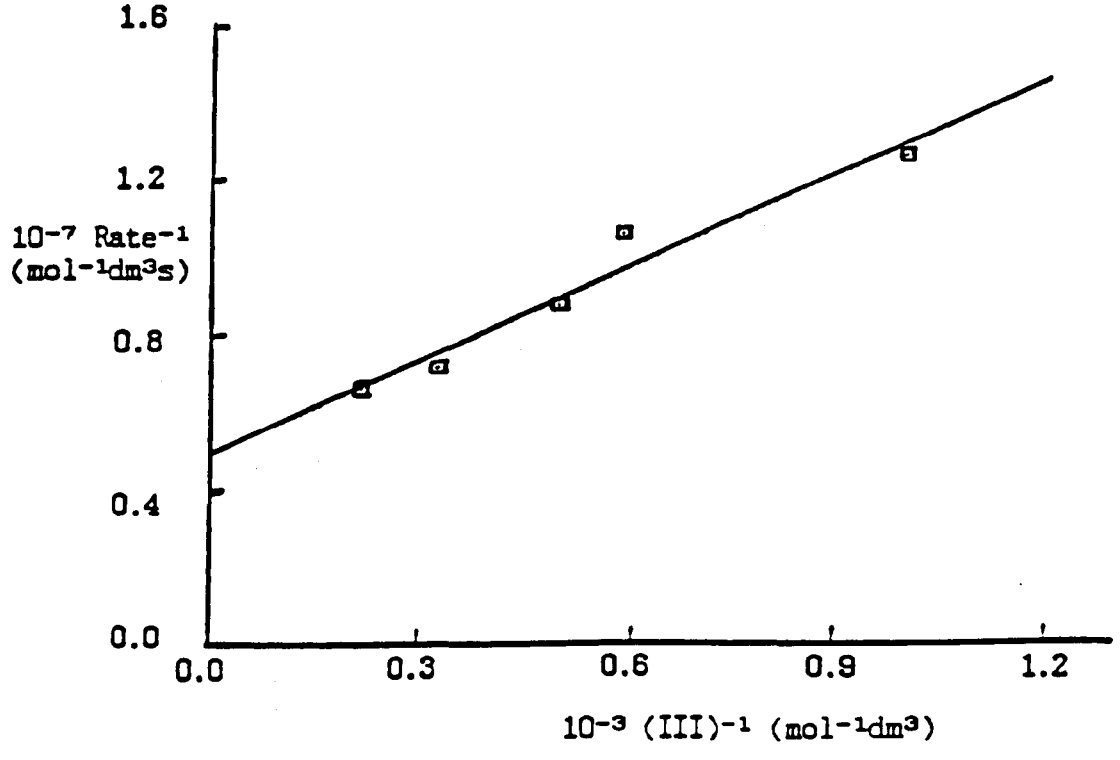


Table 9. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (III) in methanol/water (1:1) at 298 K.

10^{3}(III) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(III)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-7}Rate^{-1} ($mol^{-1}dm^{3}s$)
10.0	1.72	0.1	0.58
4.5	1.47	0.22	0.68
3.0	1.33	0.33	0.75
2.0	1.07	0.50	0.94
1.7	0.88	0.59	1.13
1.0	0.75	1.0	1.33

Figure 37. Plot According to Equation (18) of Above Data.

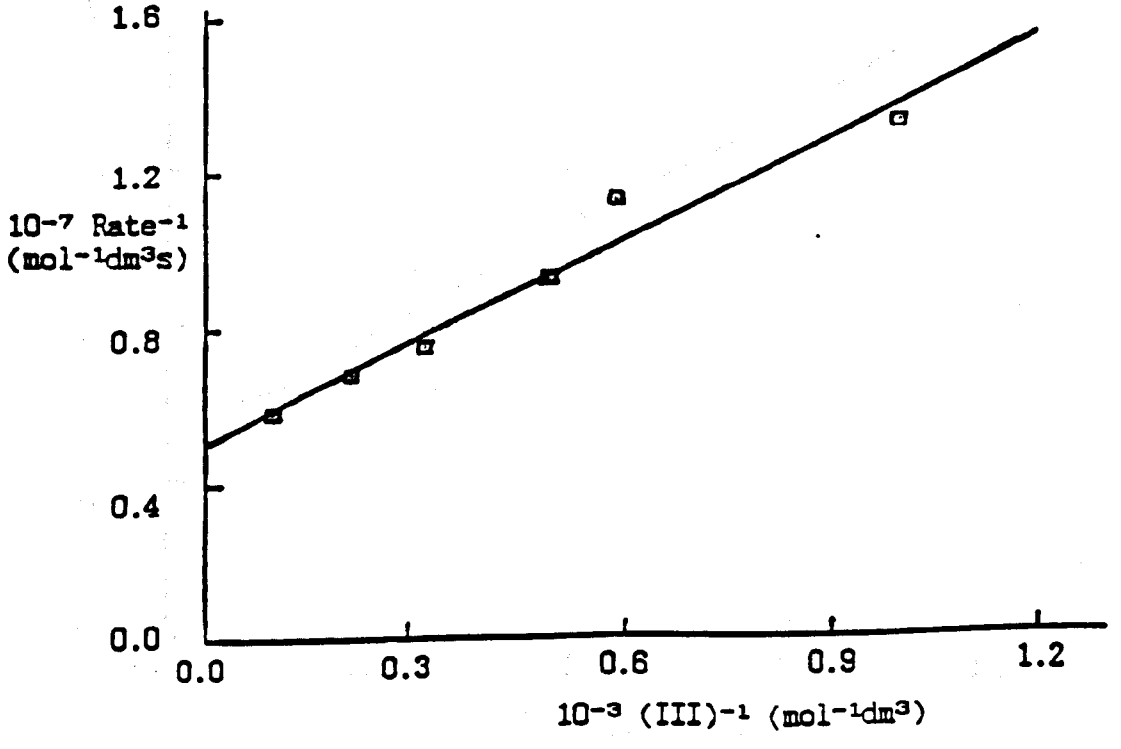


Table 10. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (III) in methanol/water (1:1) at 303 K.

10^{3}(III) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(III)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-8} Rate^{-1} ($mol^{-1}dm^{3}s$)
10.0	1.70	0.1	0.59
4.5	1.46	0.22	0.68
3.0	1.28	0.33	0.78
2.0	1.01	0.50	0.99
1.7	0.94	0.59	1.06
1.0	0.68	1.0	1.46

Figure 38. Plot According to Equation (18) of Above Data.

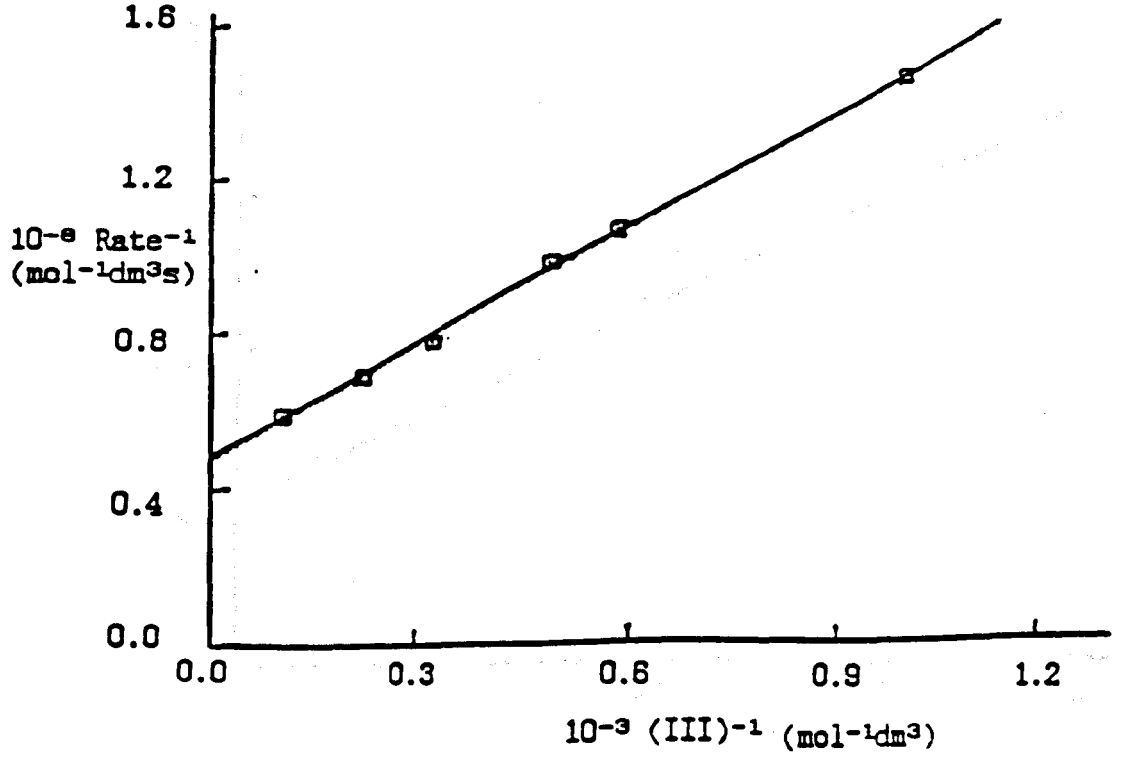


Table 11. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (III) in methanol/water (1:1) at 308 K.

10^{3}(III) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(III)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-7}Rate^{-1} ($mol^{-1}dm^{3}s$)
10.0	1.56	0.1	0.64
4.5	1.35	0.22	0.74
3.0	1.20	0.33	0.84
2.0	0.95	0.50	1.05
1.7	0.84	0.59	1.18
1.0	0.64	1.0	1.57

Figure 39. Plot According to Equation (18) of Above Data.

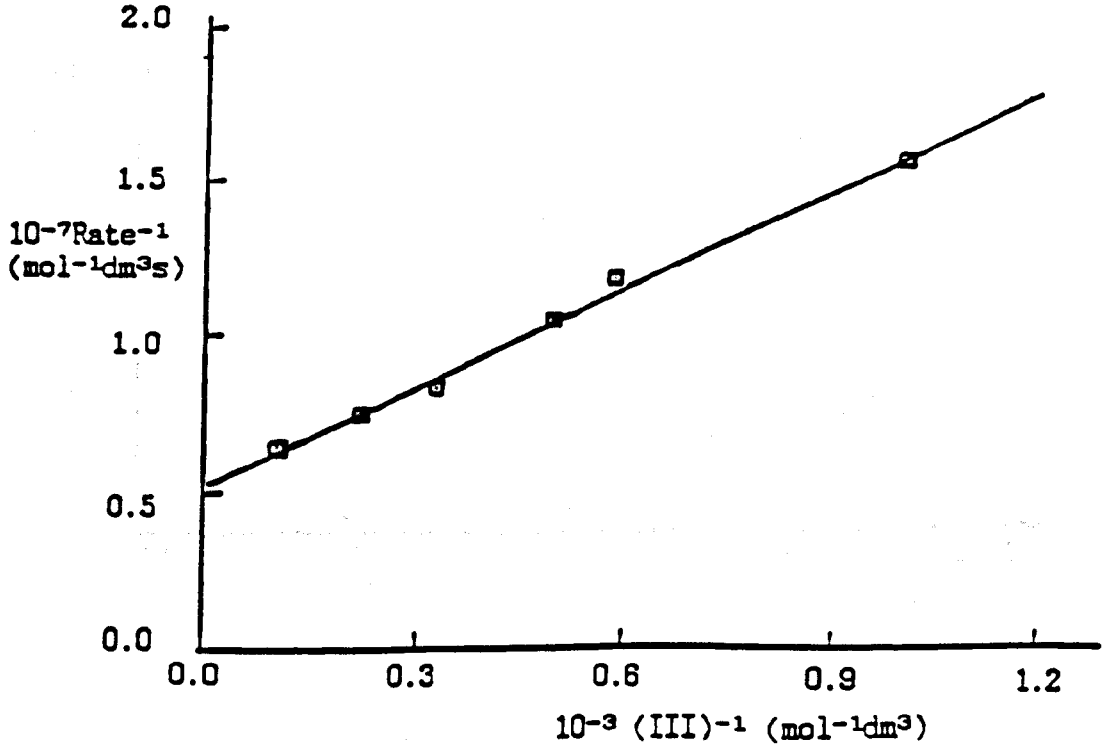


Table 12. Rate Constants for the Rose Bengal Sensitised Photo-oxidation of compound (III) in methanol/water (1:1).

$10^{-8}k_r$ ($mol^{-1}dm^3s^{-1}$)	T (K)	ln k_r	10^3T (K^{-1})
1.73	293	18.97	3.41
1.57	298	18.87	3.36
1.38	303	18.75	3.30
1.23	308	18.63	3.25

Figure 40. Arrhenius Plot According to Above Data.

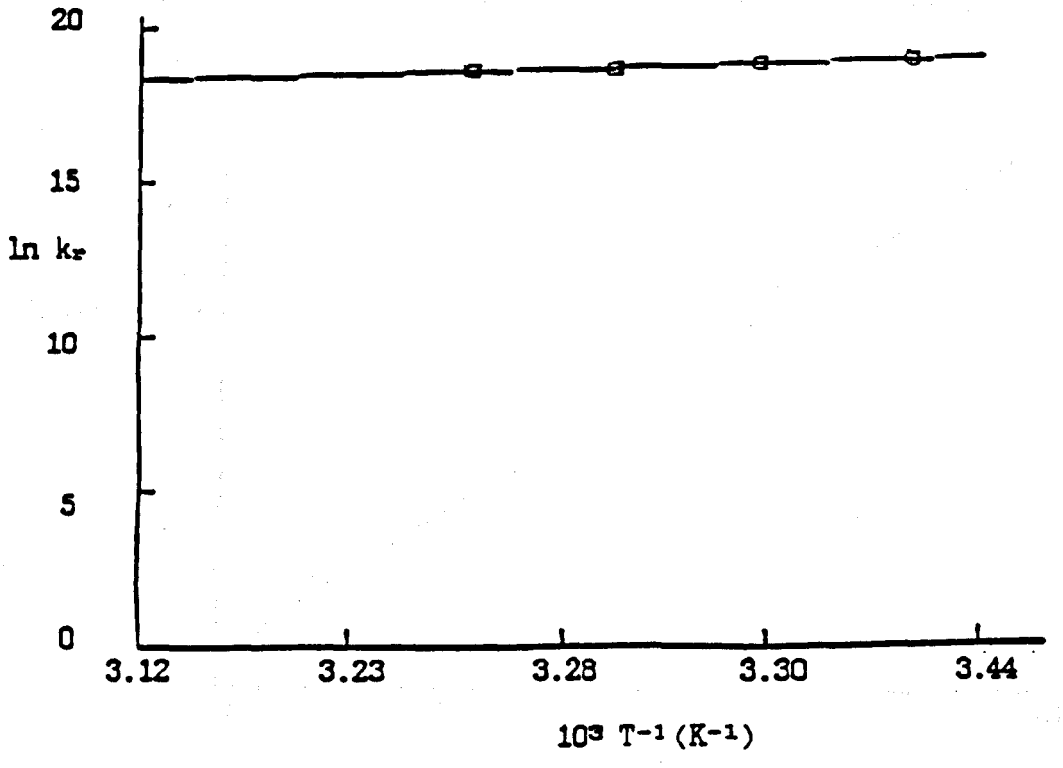


Table 13. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (IV) in methanol/water (1:1) at 293 K.

10^{3}(IV) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(IV)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-7}Rate^{-1} ($mol^{-1}dm^{3}s$)
10.0	0.96	0.10	1.04
4.5	0.61	0.22	1.64
3.0	0.41	0.33	2.44
1.75	0.28	0.57	3.83
1.25	0.18	0.80	5.55

Figure 41. Plot According to Equation (18) of Above Data.

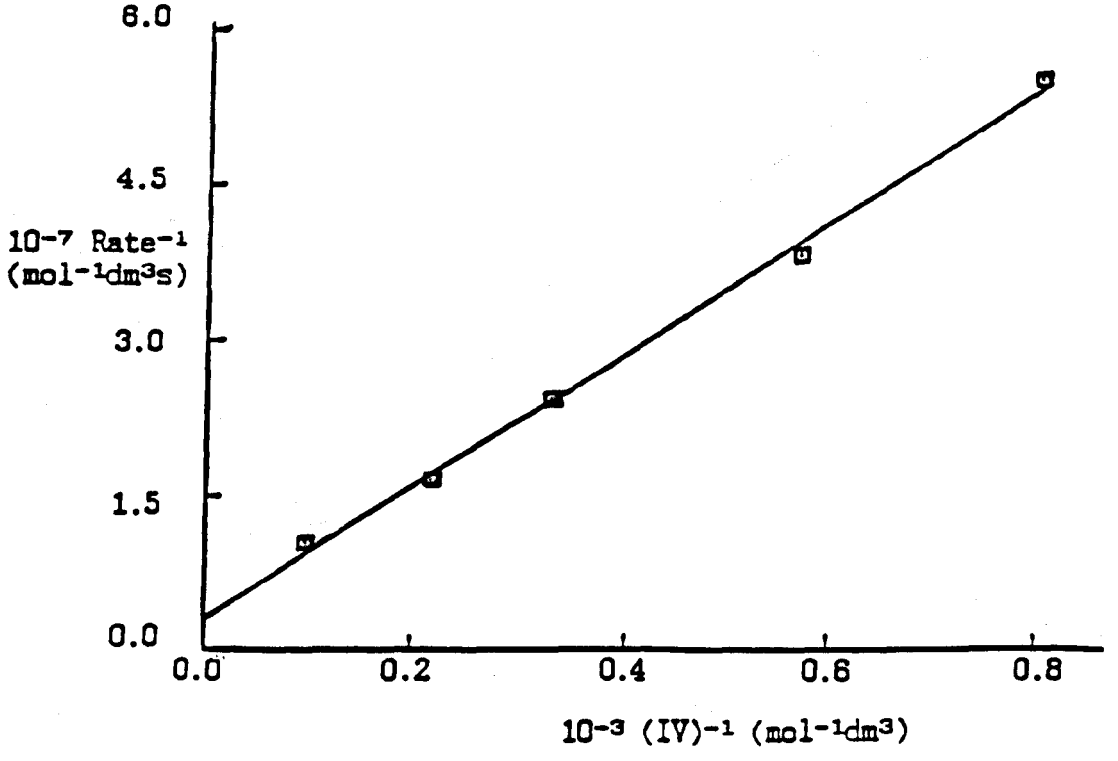


Table 14. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (IV) in methanol/water (1:1) at 298 K.

10^{3}(IV) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(IV)$^{-1}$ (mol$^{-1}dm^{3}$)	10^{-7}Rate^{-1} (mol$^{-1}dm^{3}s$)
10.0	0.87	0.10	1.14
4.5	0.43	0.22	2.31
3.0	0.29	0.33	3.50
1.75	0.17	0.57	5.75
1.25	0.17	0.80	6.00

Figure 42. Plot According to Equation (18) of Above Data.

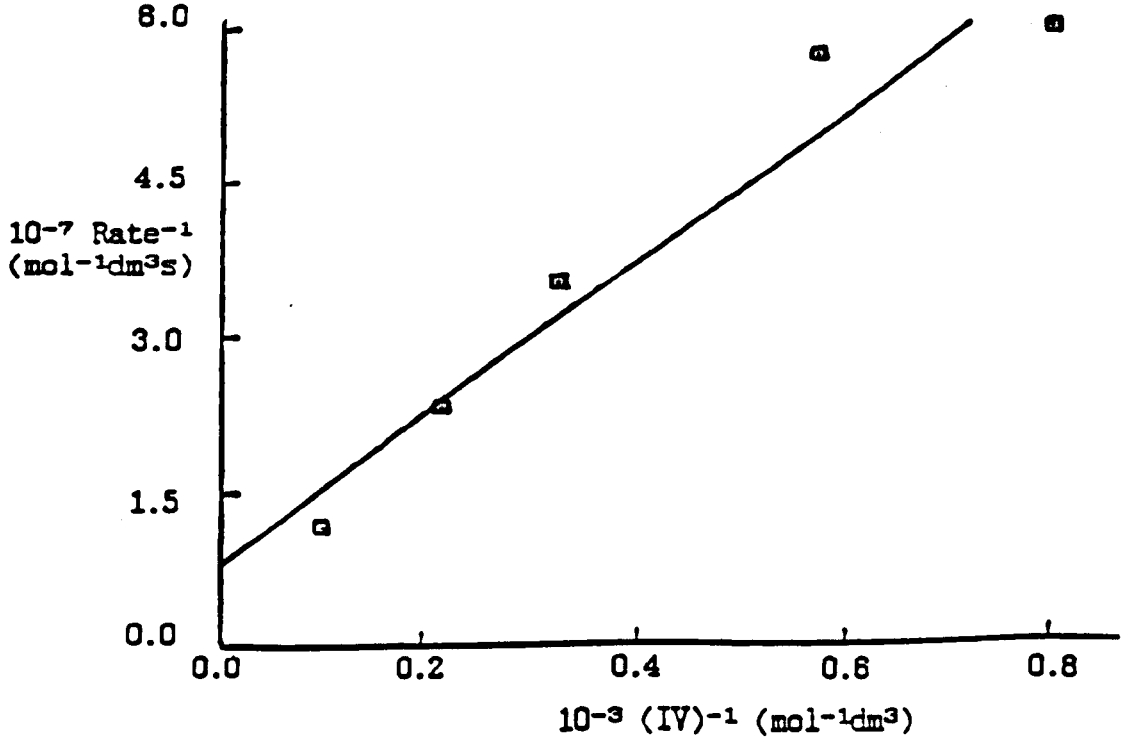


Table 15. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (IV) in methanol/water (1:1) at 303 K.

10^{3}(IV) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(IV)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-7}Rate^{-1} ($mol^{-1}dm^{3}s$)
4.5	0.38	0.22	2.62
3.0	0.31	0.33	3.22
1.75	0.25	0.57	4.03
1.25	0.19	0.80	5.13
1.0	0.13	1.00	7.42

Figure 43. Plot According to Equation (18) of Above Data.

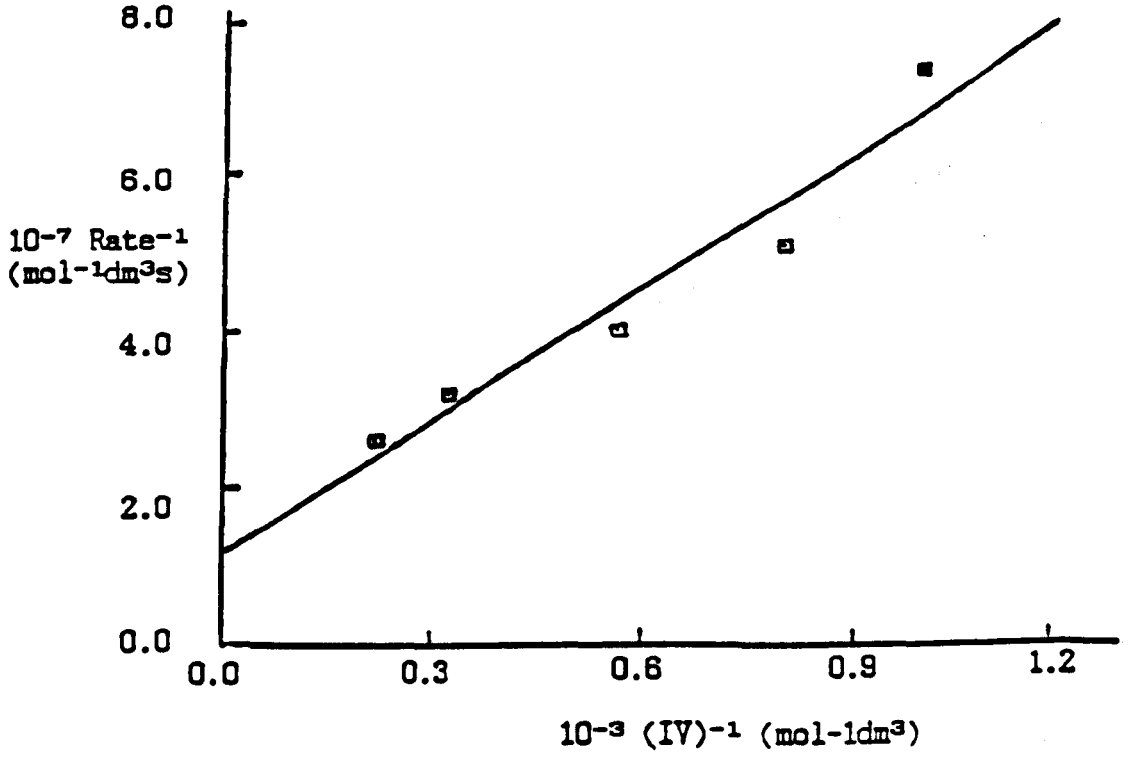


Table 16. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (IV) in methanol/water (1:1) at 308 K.

10^{3}(IV) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(IV)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-7}Rate^{-1} ($mol^{-1}dm^{3}s$)
10.0	0.57	0.10	1.76
4.5	0.42	0.22	2.40
3.0	0.36	0.33	2.76
1.75	0.24	0.57	4.23
1.25	0.20	0.80	4.92

Figure 44. Plot According to Equation (18) of Above Data.

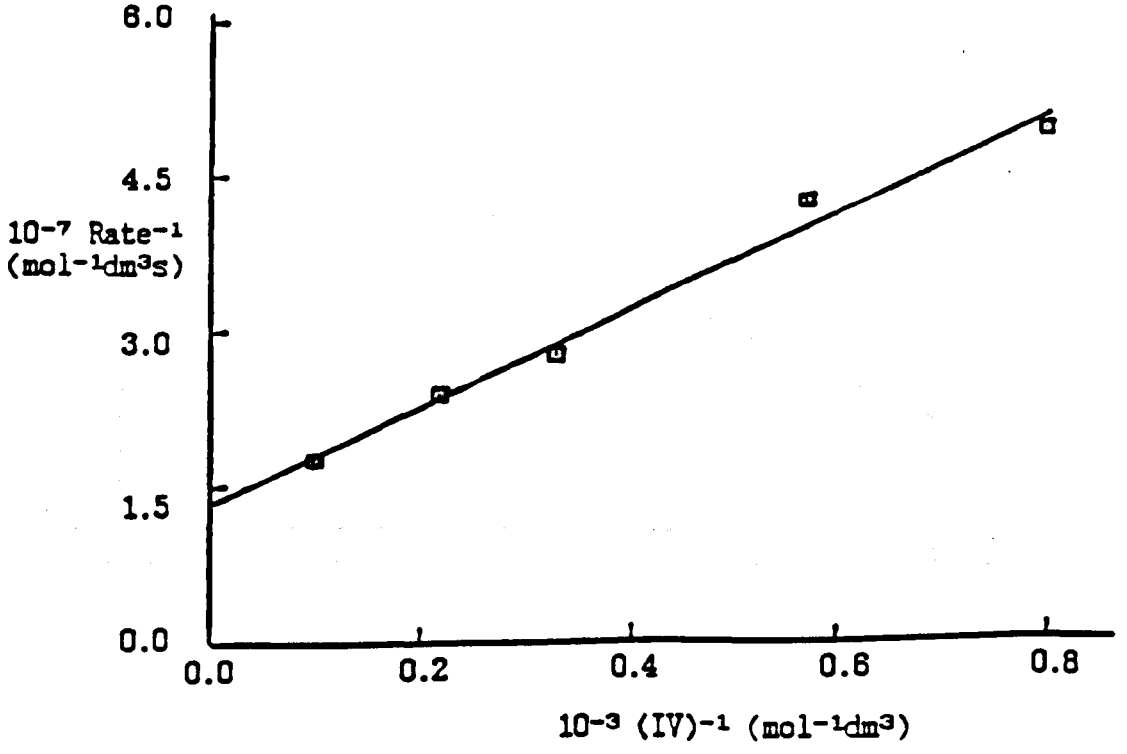


Table 17. Rate Constants for the Rose Bengal Sensitised Photo-oxidation of compound (IV) in methanol/water (1:1).

$10^{-7}k_r$ ($mol^{-1}dm^3s^{-1}$)	T (K)	ln k_r	10^3T (K^{-1})
1.33	293	16.40	3.41
2.09	298	16.86	3.36
4.15	303	17.54	3.30
8.50	308	18.26	3.25

Figure 45. Arrhenius Plot According to Above Data.

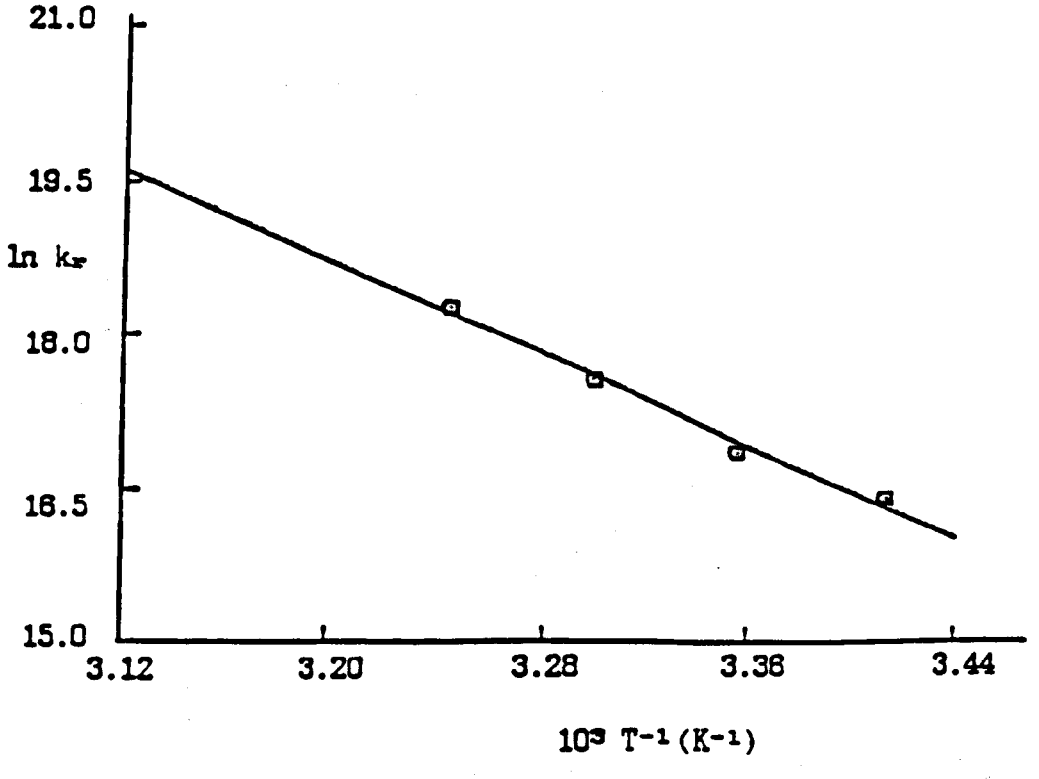


Table 18. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (V) in methanol/water (1:1) at 293 K.

10^{3}(V) (mol dm^{-3})	10^{6}Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(V)^{-1}$ ($mol^{-1}dm^{3}$)	$10^{-6}Rate^{-1}$ ($mol^{-1}dm^{3}s$)
10.0	1.59	0.10	0.63
4.5	0.71	0.22	1.41
3.0	0.48	0.33	2.09
1.75	0.31	0.57	3.28
1.25	0.21	0.80	4.88
1.0	0.17	1.0	6.03

Figure 48. Plot According to Equation (18) of Above Data.

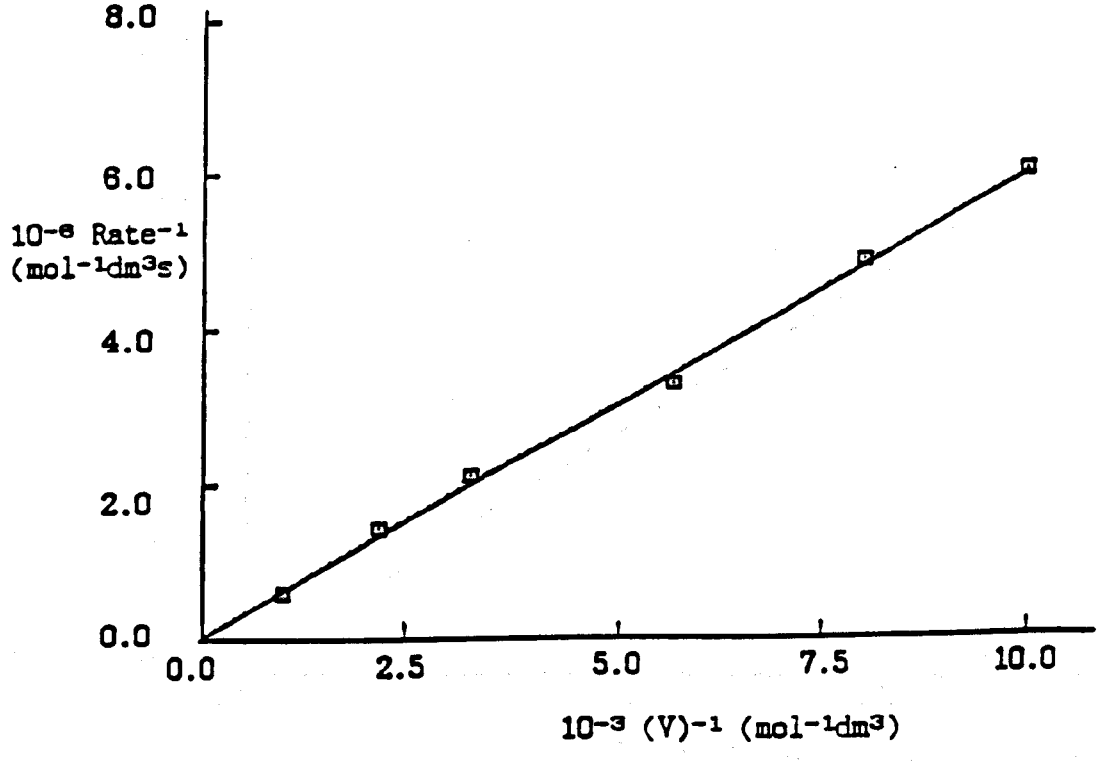


Table 19. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (V) in methanol/water (1:1) at 298 K.

10^{3}(V) (mol dm^{-3})	10^{6}Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(V)^{-1}$ ($mol^{-1}dm^{3}$)	$10^{-6}Rate^{-1}$ ($mol^{-1}dm^{3}s$)
10.0	0.89	0.10	1.13
4.5	0.54	0.22	1.87
3.0	0.34	0.33	2.98
1.75	0.22	0.57	4.63
1.25	0.14	0.80	6.91
1.0	0.12	1.0	8.64

Figure 47. Plot According to Equation (18) of Above Data.

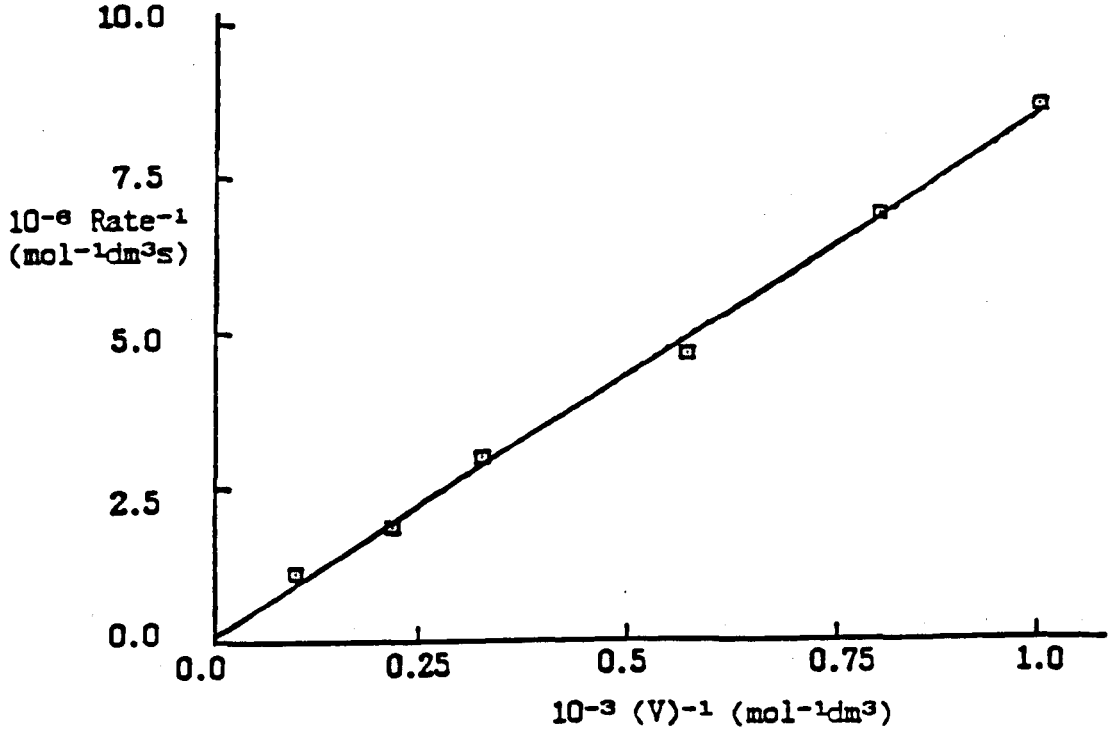


Table 20. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (V) in methanol/water (1:1) at 303 K.

10^{3}(V) (mol dm^{-3})	10^{6}Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(V)^{-1}$ ($mol^{-1}dm^{3}$)	$10^{-6}Rate^{-1}$ ($mol^{-1}dm^{3}s$)
10.0	1.28	0.10	0.78
4.5	0.58	0.22	1.73
3.0	0.39	0.33	2.58
1.75	0.21	0.57	4.78
1.25	0.15	0.80	6.58
1.0	0.13	1.0	7.81

Figure 48. Plot According to Equation (18) of Above Data.

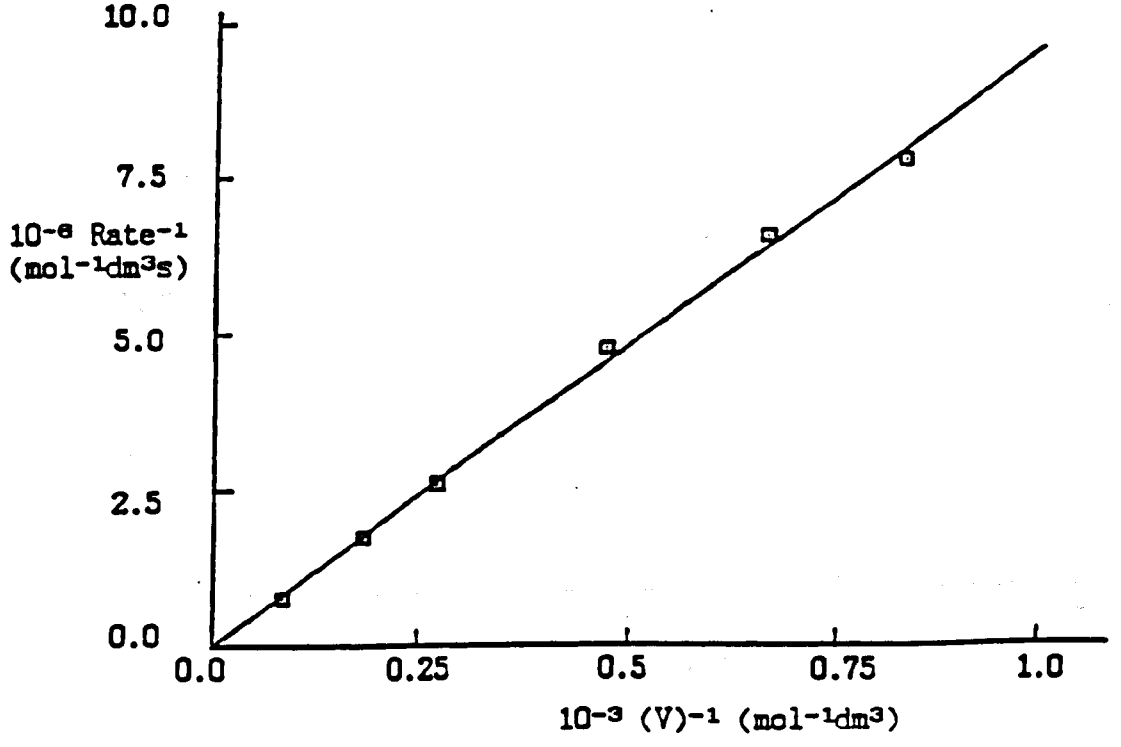


Table 21. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (V) in methanol/water (1:1) at 308 K.

10^{3}(V) (mol dm^{-3})	10^{6}Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(V)^{-1}$ ($mol^{-1}dm^{3}$)	$10^{-6}Rate^{-1}$ ($mol^{-1}dm^{3}s$)
10.0	3.45	0.10	0.29
4.5	1.75	0.22	0.57
3.0	0.97	0.33	1.03
1.75	0.60	0.57	1.67
1.25	0.43	0.80	2.30

Figure 49. Plot According to Equation (18) of Above Data.

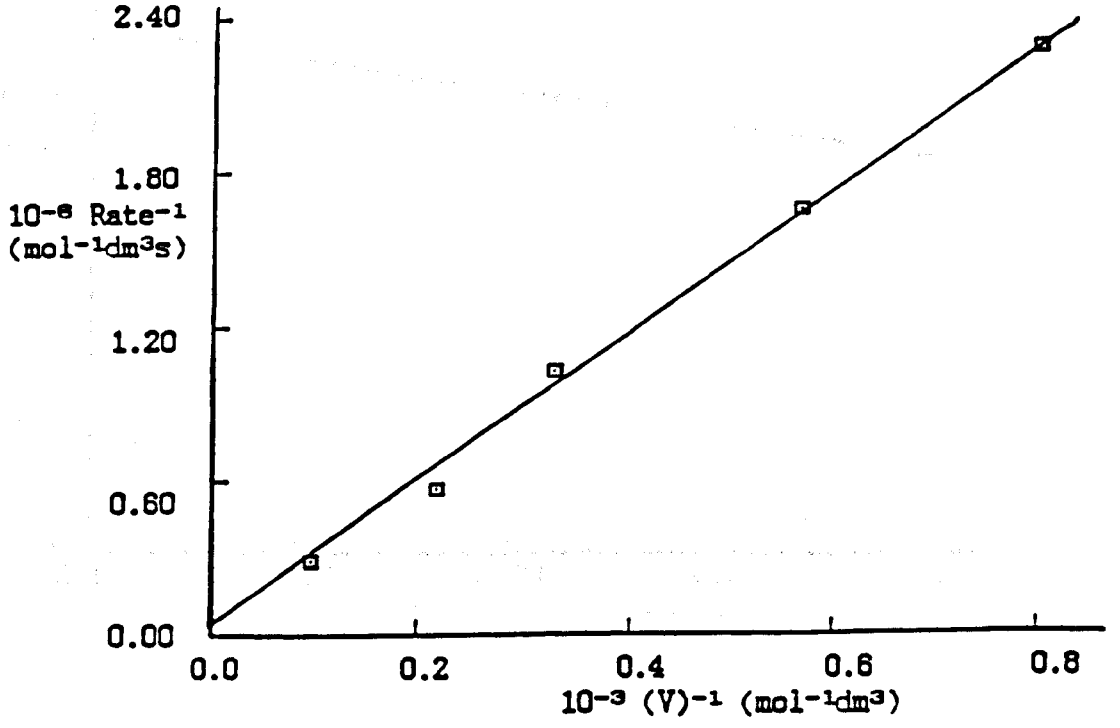


Table 22. Rate Constants for the Rose Bengal Sensitised Photo-oxidation of compound (V) in methanol/water (1:1).

$10^{-5}k_r$ ($mol^{-1}dm^3s^{-1}$)	T (K)	ln k_r	10^3T (K^{-1})
4.52	293	13.02	3.41
5.01	298	13.12	3.36
6.97	303	13.45	3.30
8.63	308	13.67	3.25

Figure 50. Arrhenius Plot According to Above Data.

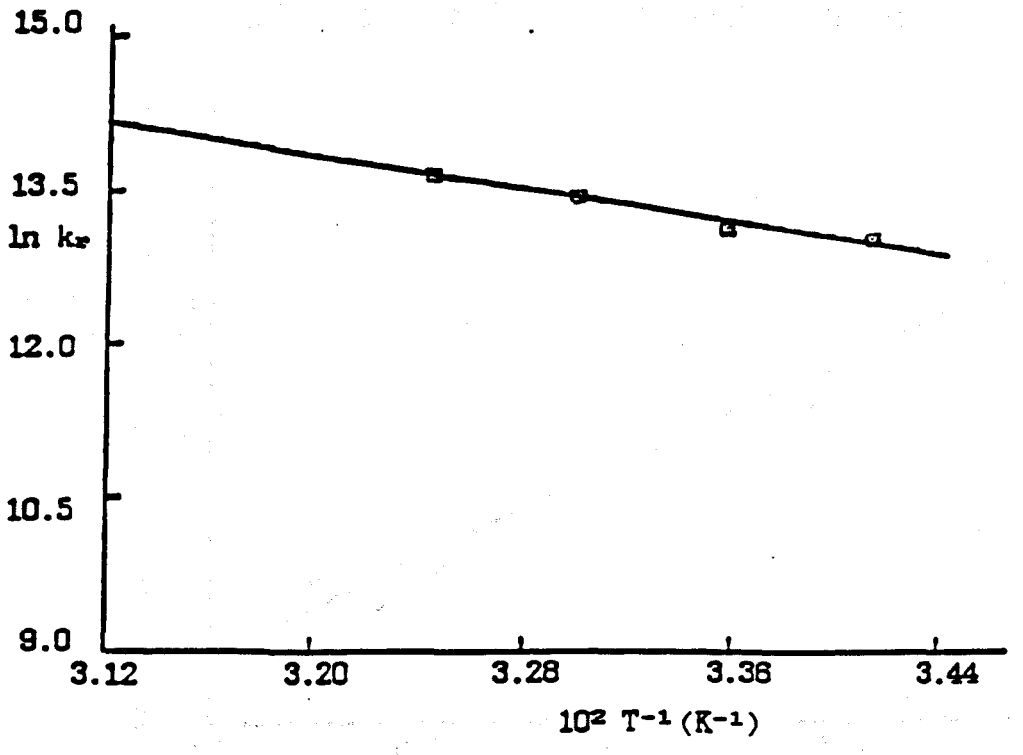


Table 23. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (I) in Methanol at 293 K.

10^{3}(I) (mol dm^{-3})	10^{6}Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(I)^{-1}$ ($mol^{-1}dm^{3}$)	$10^{-7}Rate^{-1}$ ($mol^{-1}dm^{3}s$)
5.0	0.28	0.2	3.62
2.25	0.25	0.44	3.96
1.5	0.16	0.67	6.32
0.88	0.12	1.14	8.01
0.63	0.08	1.60	12.30

Figure 51. Plot According to Equation (18) of Above Data.

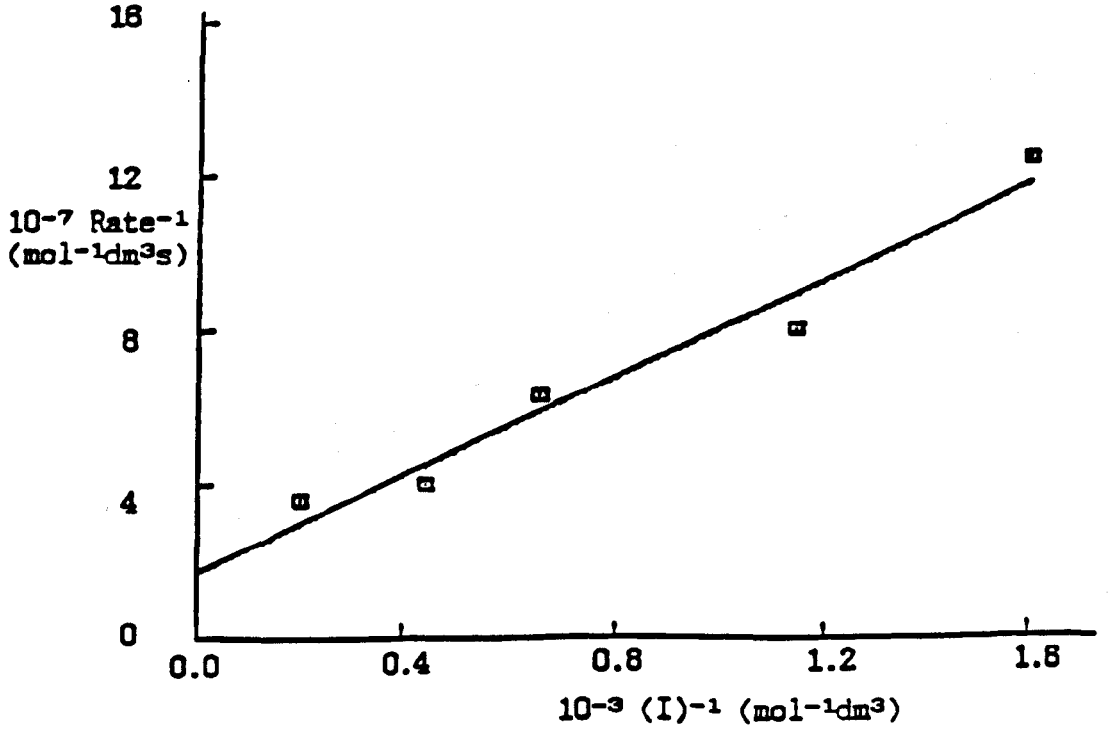


Table 24. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (I) in Methanol at 298 K.

10^{3}(I) (mol dm^{-3})	10^{6}Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(I)^{-1}$ ($mol^{-1}dm^{3}$)	$10^{-7}Rate^{-1}$ ($mol^{-1}dm^{3}s$)
5.0	0.50	0.2	1.99
2.25	0.31	0.444	3.22
1.5	0.22	0.667	4.50
0.875	0.14	1.143	7.16
0.625	0.10	1.60	9.93

Figure 52. Plot According to Equation (18) of Above Data.

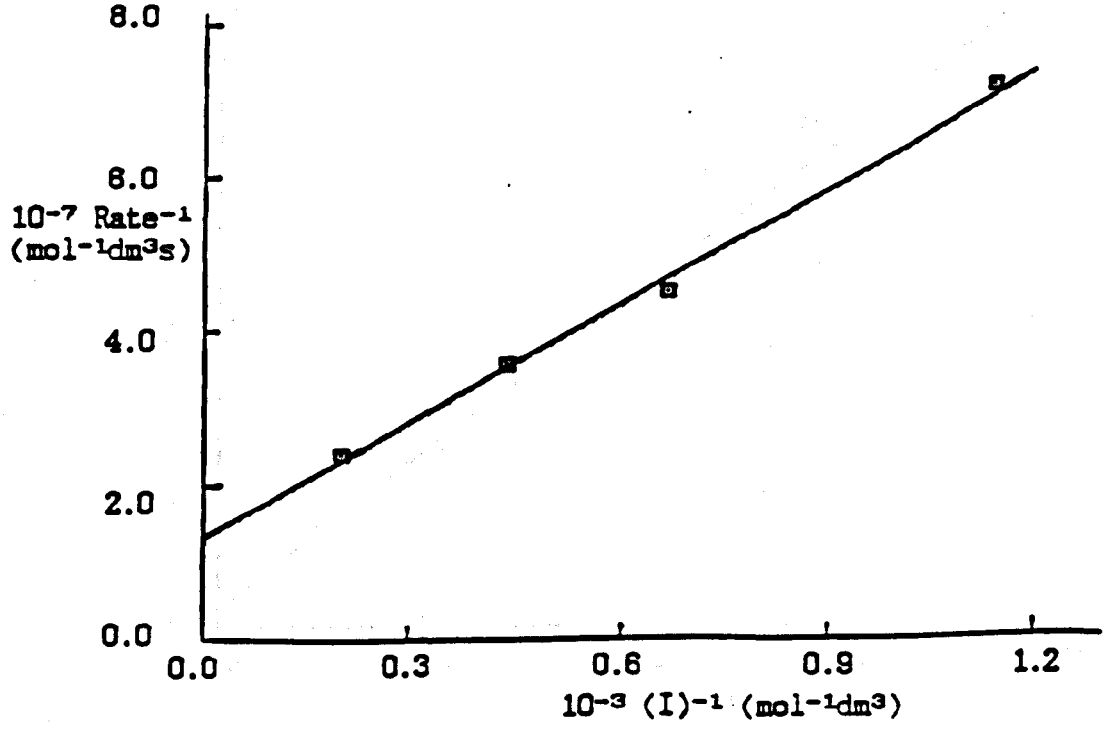


Table 25. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (I) in Methanol at 303 K.

10^{3}(I) (mol dm^{-3})	10^{6}Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(I)^{-1}$ ($mol^{-1}dm^{3}$)	$10^{-7}Rate^{-1}$ ($mol^{-1}dm^{3}s$)
10.0	0.37	0.1	1.56
4.50	0.35	0.22	2.98
3.0	0.31	0.33	4.46
1.75	0.12	0.571	8.19
1.25	0.10	0.80	10.11

Figure 53. Plot According to Equation (18) of Above Data.

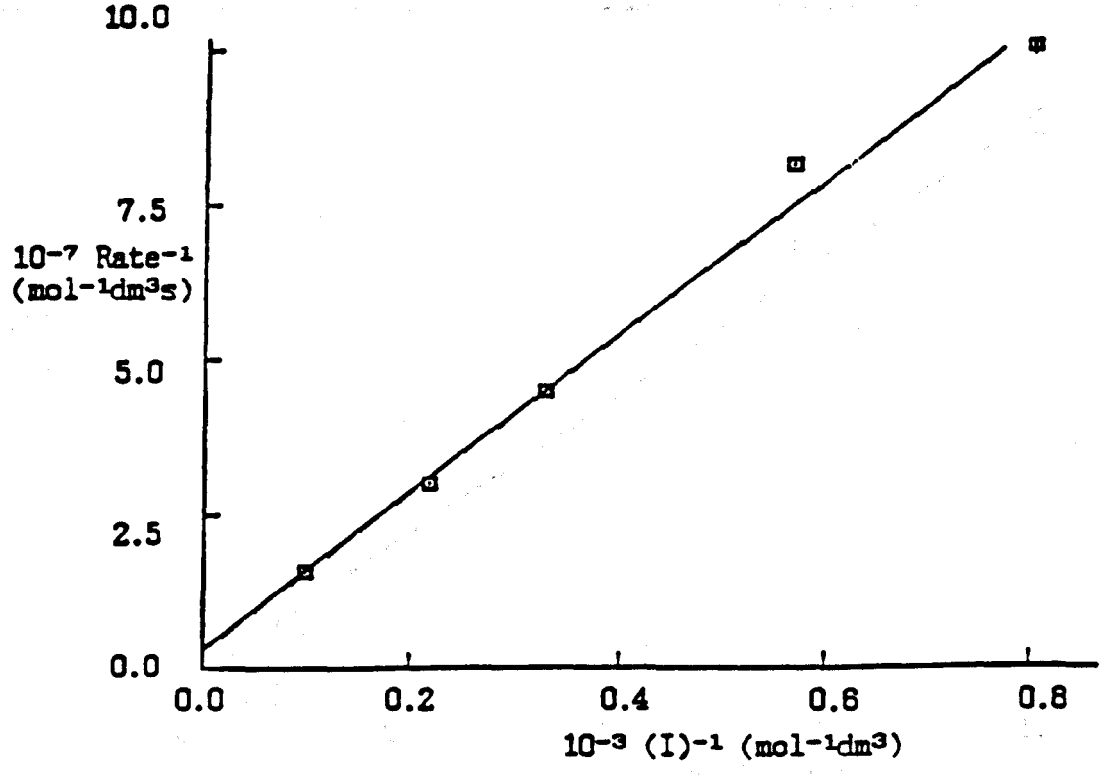


Table 26. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (I) in Methanol at 308 K.

10^{3}(I) (mol dm^{-3})	10^{6}Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(I)^{-1}$ ($mol^{-1}dm^{3}$)	$10^{-7}Rate^{-1}$ ($mol^{-1}dm^{3}s$)
5.0	4.68	0.2	2.14
2.25	1.55	0.44	6.46
1.5	0.93	0.667	10.81
0.875	0.58	1.143	17.0
0.625	0.48	1.60	20.97

Figure 54. Plot According to Equation (18) of Above Data.

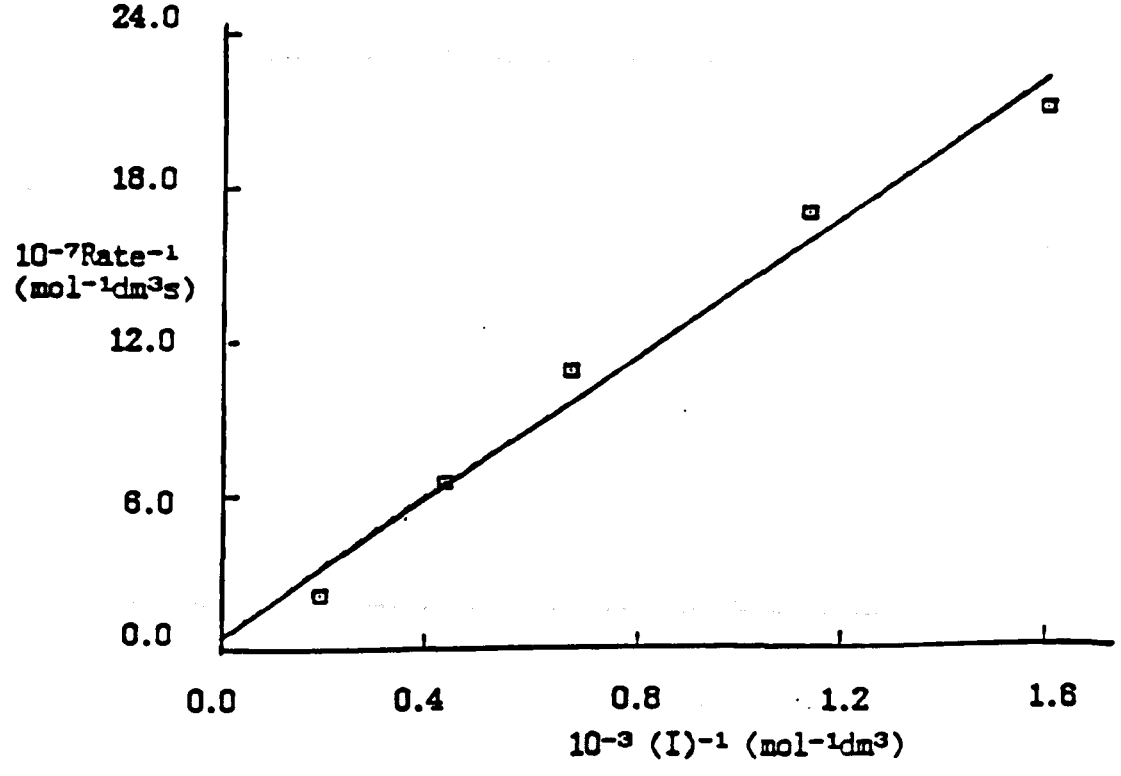


Table 27. Rate Constants for the Rose Bengal Sensitised Photo-oxidation of Compound (I) in Methanol.

$10^{-7}k_r$ ($mol^{-1}dm^3s^{-1}$)	T (K)	ln k_r	10^3T (K^{-1})
5.93	293	17.90	3.41
5.25	298	17.78	3.36
4.52	303	17.63	3.30
5.98	308	17.90	3.25

Figure 55. Arrhenius Plot According to Above Data.

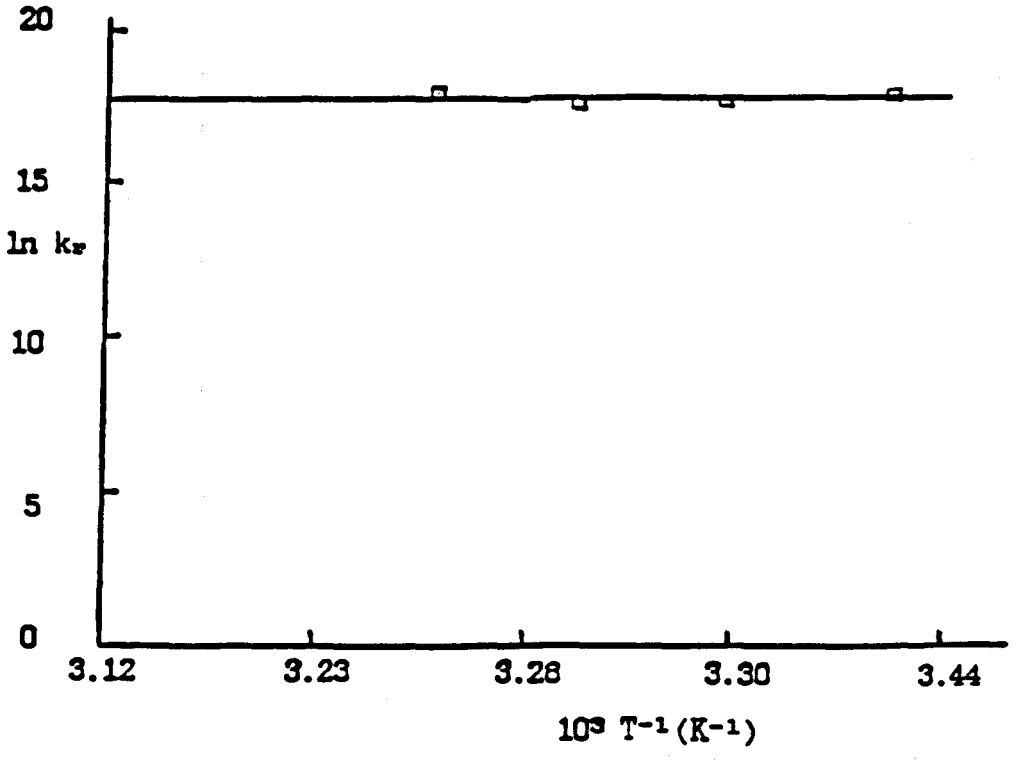


Table 28. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (II) in Methanol at 293 K.

10^{3}(II) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(II)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-6}Rate^{-1} ($mol^{-1}dm^{3}s$)
10.0	1.81	0.1	5.53
4.5	1.59	0.22	6.28
3.0	1.38	0.33	7.27
1.75	0.84	0.57	11.92
1.25	0.60	0.80	16.78

Figure 56. Plot According to Equation (18) of Above Data.

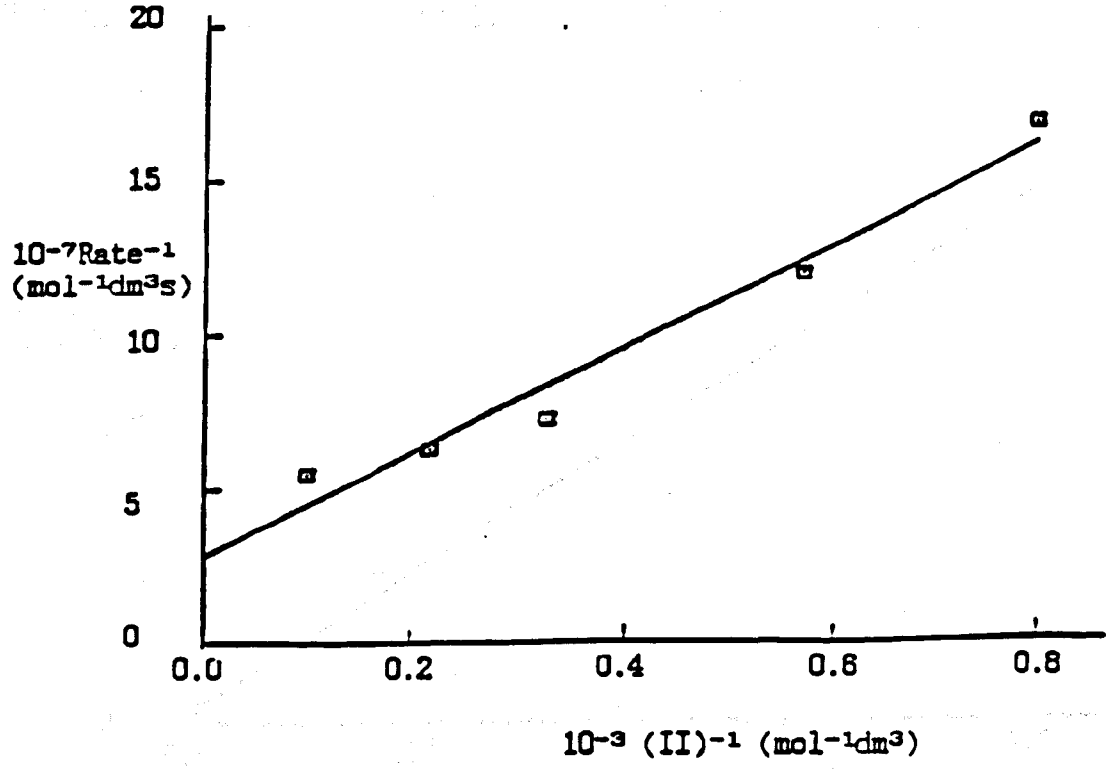


Table 29. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (II) in Methanol at 298 K.

10^{3}(II) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(II)$^{-1}$ (mol$^{-1}dm^{3}$)	10^{-6}Rate^{-1} (mol$^{-1}dm^{3}s$)
10.0	4.90	0.1	2.04
4.5	3.31	0.22	3.02
3.0	2.98	0.33	3.38
1.75	2.31	0.57	4.33
1.25	1.26	0.80	7.96
1.0	0.87	1.0	11.54

Figure 57. Plot According to Equation (18) of Above Data.

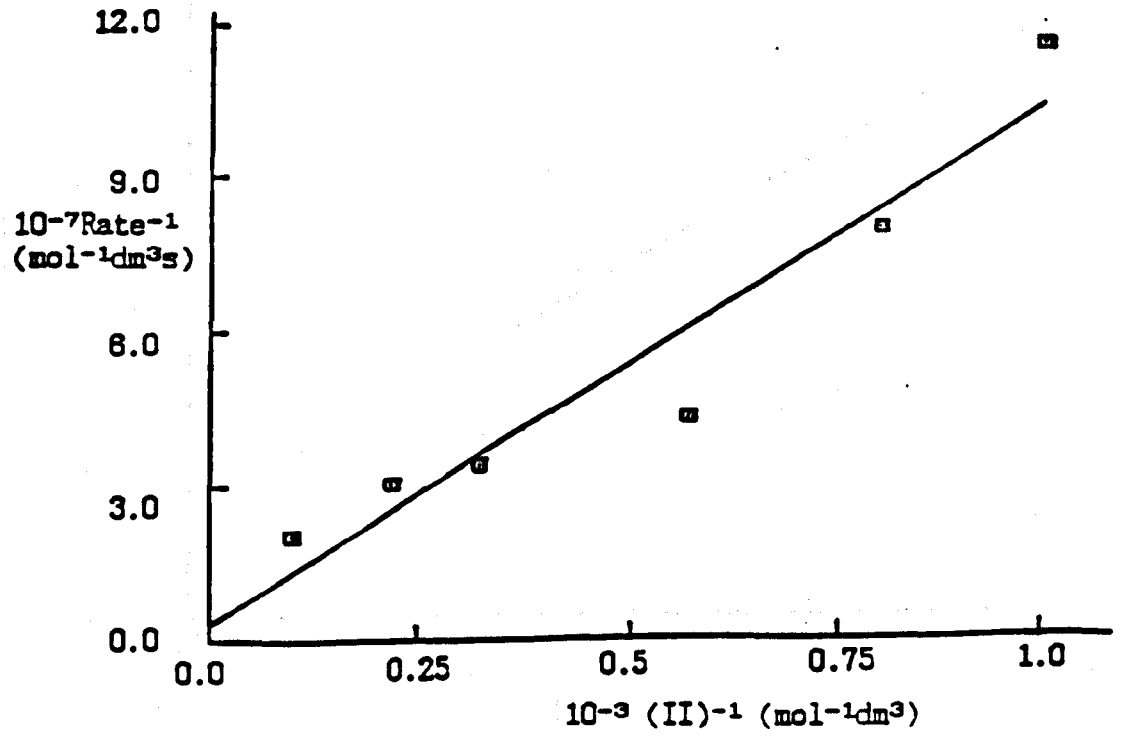


Table 30. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (II) in Methanol at 303 K.

10^{3}(II) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(II)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-6}Rate^{-1} ($mol^{-1}dm^{3}s$)
4.5	2.37	0.22	4.22
3.0	1.53	0.33	6.55
1.75	0.74	0.57	13.47
1.25	0.59	0.80	18.90
1.0	0.44	1.0	22.57

Figure 58. Plot According to Equation (18) of Above Data.

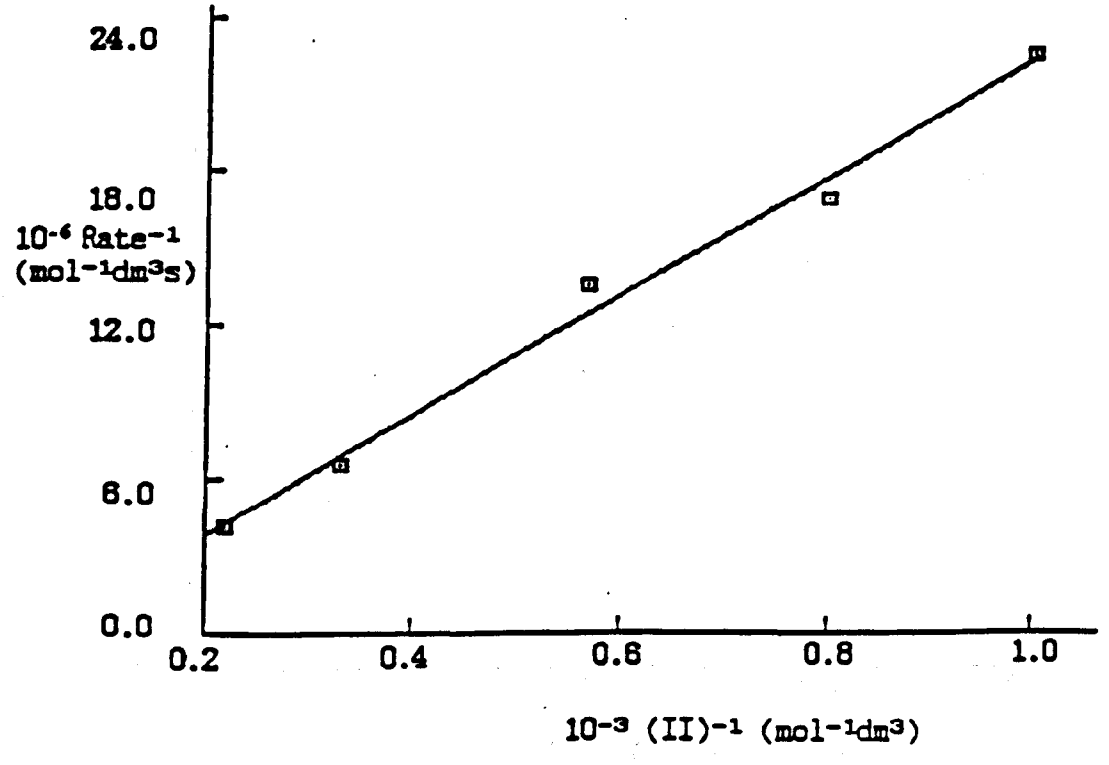


Table 31. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (II) in Methanol at 308 K.

10^{3}(II) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(II)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-6}Rate^{-1} ($mol^{-1}dm^{3}s$)
10.0	1.91	0.1	5.24
4.5	1.79	0.22	5.58
3.0	0.98	0.33	10.23
1.75	0.78	0.57	12.76
1.25	0.60	0.80	16.73

Figure 59. Plot According to Equation (18) of Above Data.

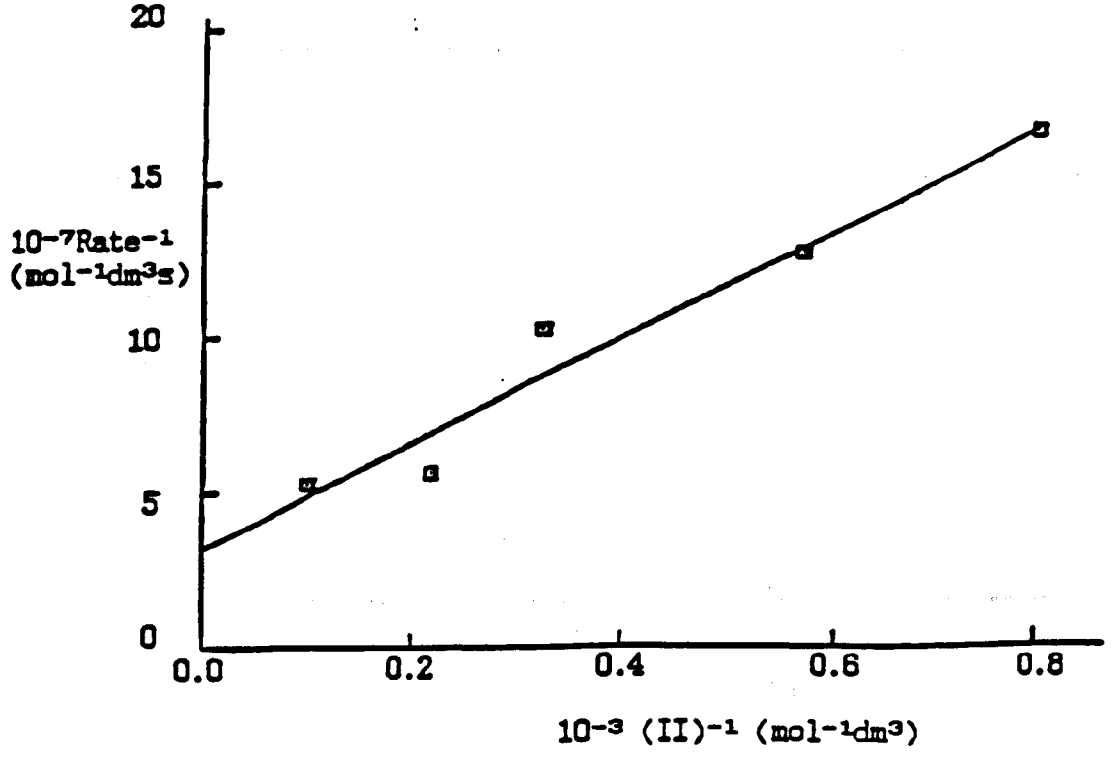


Table 32. Rate Constants for the Rose Bengal Sensitised Photo-oxidation of Compound (II) in Methanol.

$10^{-7}k_r$ ($mol^{-1}dm^3s^{-1}$)	T (K)	ln kr	10^3T (K^{-1})
5.05	293	17.74	3.41
6.35	298	17.97	3.36
6.25	303	17.95	3.30
5.24	308	17.78	3.25

Figure 60. Arrhenius Plot According to Above Data.

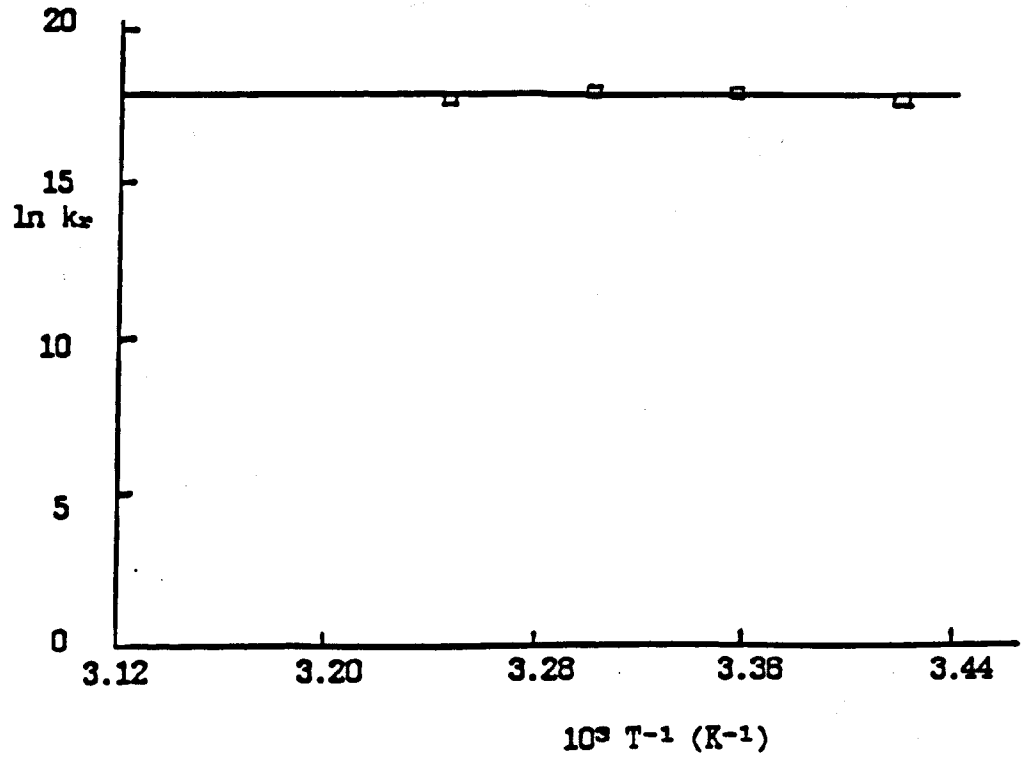


Table 33. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (III) in Methanol at 293 K.

10^{3}(III) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(III)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-6}Rate^{-1} ($mol^{-1}dm^{3}s$)
10.0	5.33	0.10	1.88
4.50	4.33	0.22	2.31
3.00	3.30	0.33	3.03
1.75	2.68	0.57	3.74
1.25	1.90	0.80	5.27
1.00	1.73	1.00	5.78

Figure 61. Plot According to Equation (18) of Above Data.

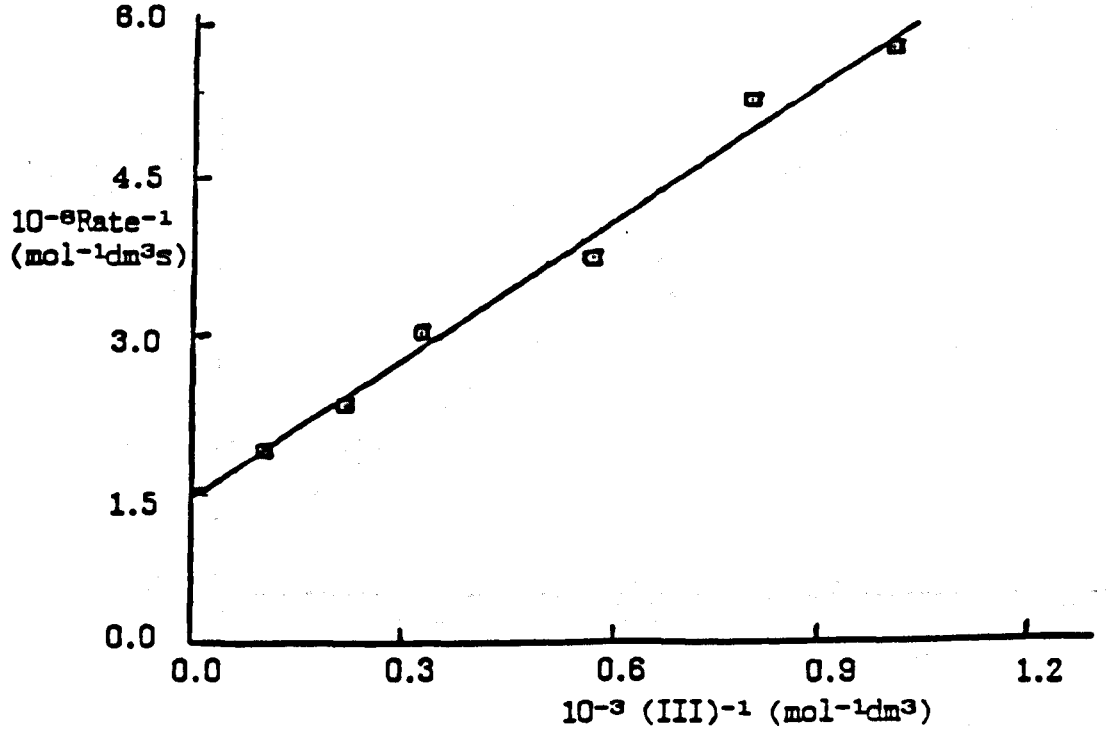


Table 34. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (III) in Methanol at 298 K.

10^{3}(III) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(III)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-6}Rate^{-1} ($mol^{-1}dm^{3}s$)
10.0	5.07	0.10	0.20
4.50	3.22	0.22	0.31
3.00	2.51	0.33	0.40
2.00	1.56	0.50	0.64
1.70	1.26	0.57	0.89

Figure 62. Plot According to Equation (18) of Above Data.

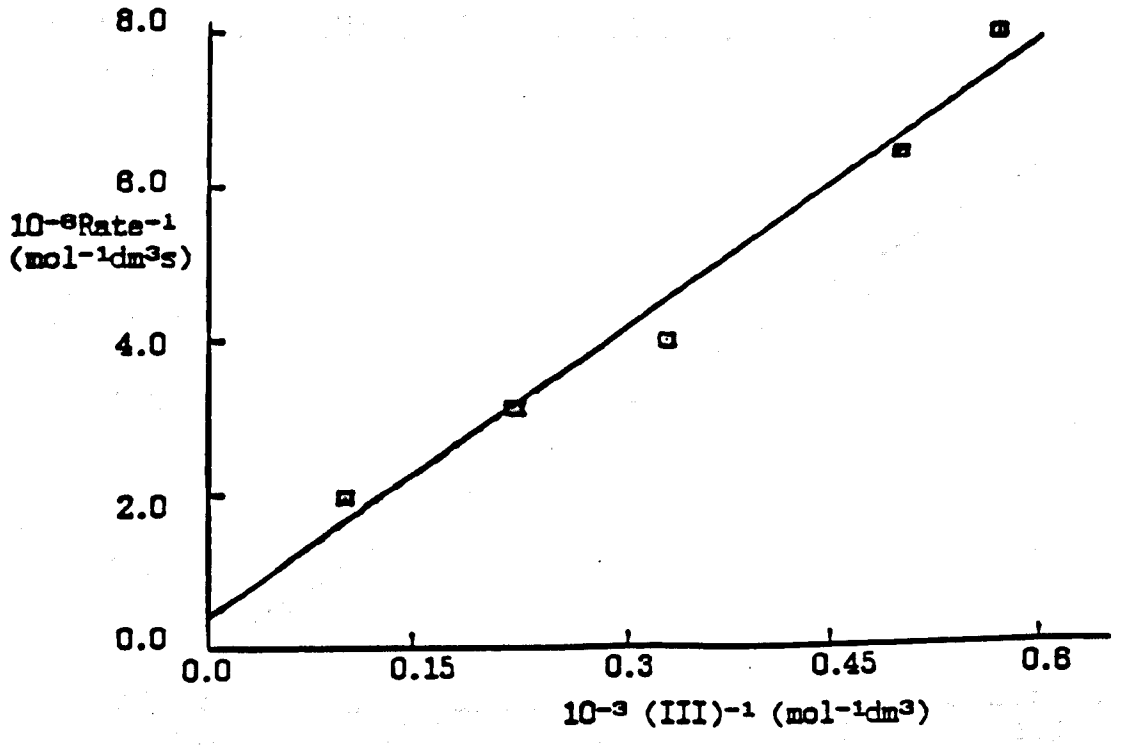


Table 35. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (III) in Methanol at 303 K.

10^{3}(III) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(III)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-8}Rate^{-1} ($mol^{-1}dm^{3}s$)
10.0	5.88	0.10	1.70
4.50	4.58	0.22	2.19
3.00	2.28	0.33	4.39
1.75	1.85	0.57	5.39
1.25	1.48	0.80	6.77
1.00	1.11	1.00	9.01

Figure 63. Plot According to Equation (18) of Above Data.

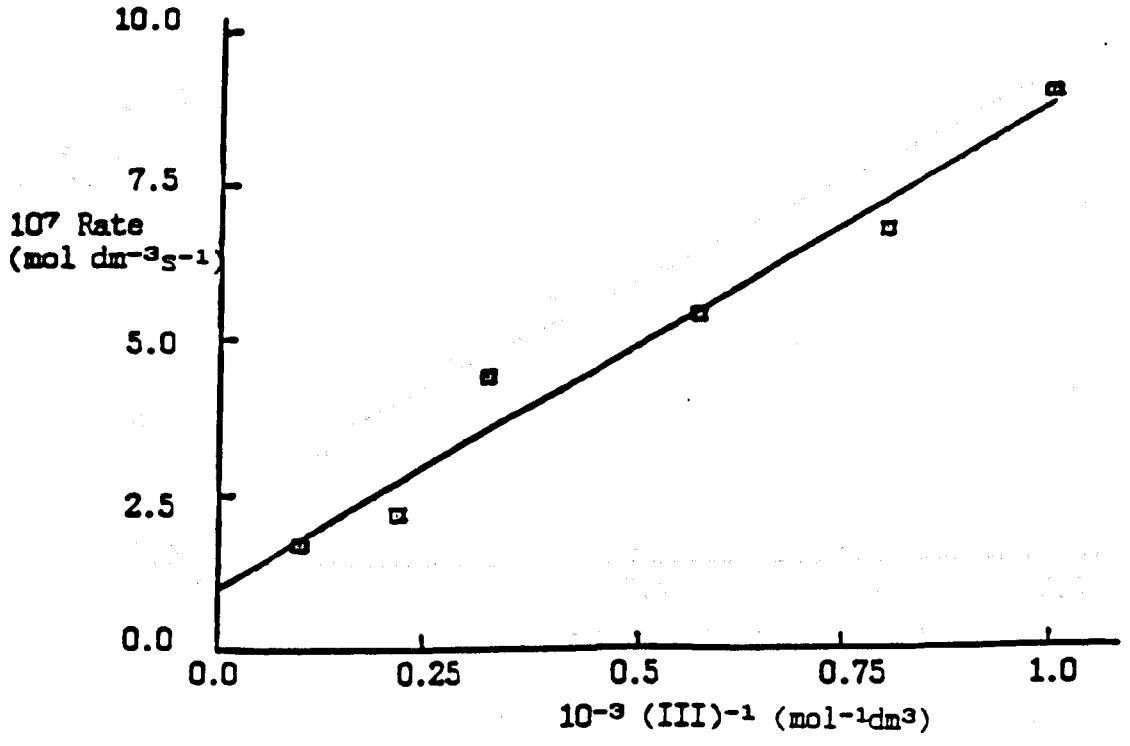


Table 36. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (III) in Methanol at 308 K.

10^{3}(III) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(III)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-6}Rate^{-1} ($mol^{-1}dm^{3}s$)
10.0	3.36	0.10	2.97
4.50	1.90	0.22	5.26
3.00	1.47	0.33	6.82
1.75	1.21	0.57	8.29
1.25	0.76	0.80	13.08

Figure 64. Plot According to Equation (18) of Above Data.

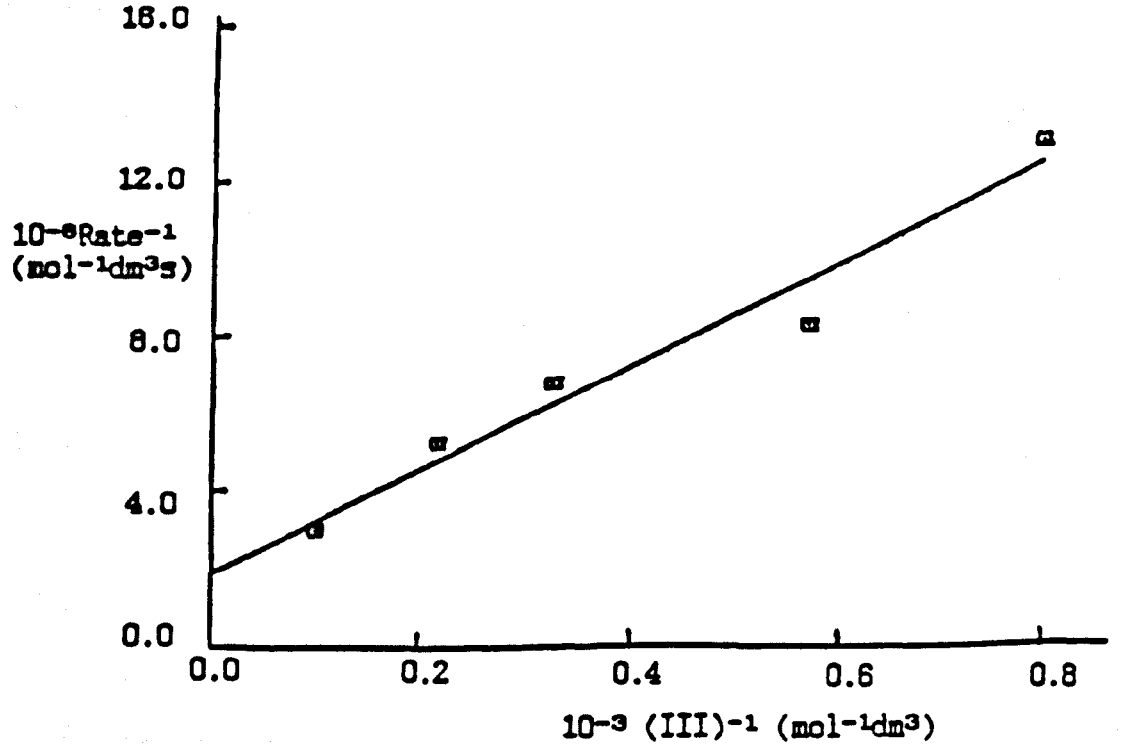


Table 37. Rate Constants for the Rose Bengal Sensitised Photo-oxidation of compound (III) in Methanol.

$10^{-7}k_r$ ($mol^{-1}dm^3s^{-1}$)	T (K)	ln k_r	10^3T (K^{-1})
2.95	293	17.20	3.41
2.99	298	17.21	3.36
2.51	303	17.04	3.30
2.94	308	17.20	3.25

Figure 65. Arrhenius Plot According to Above Data.

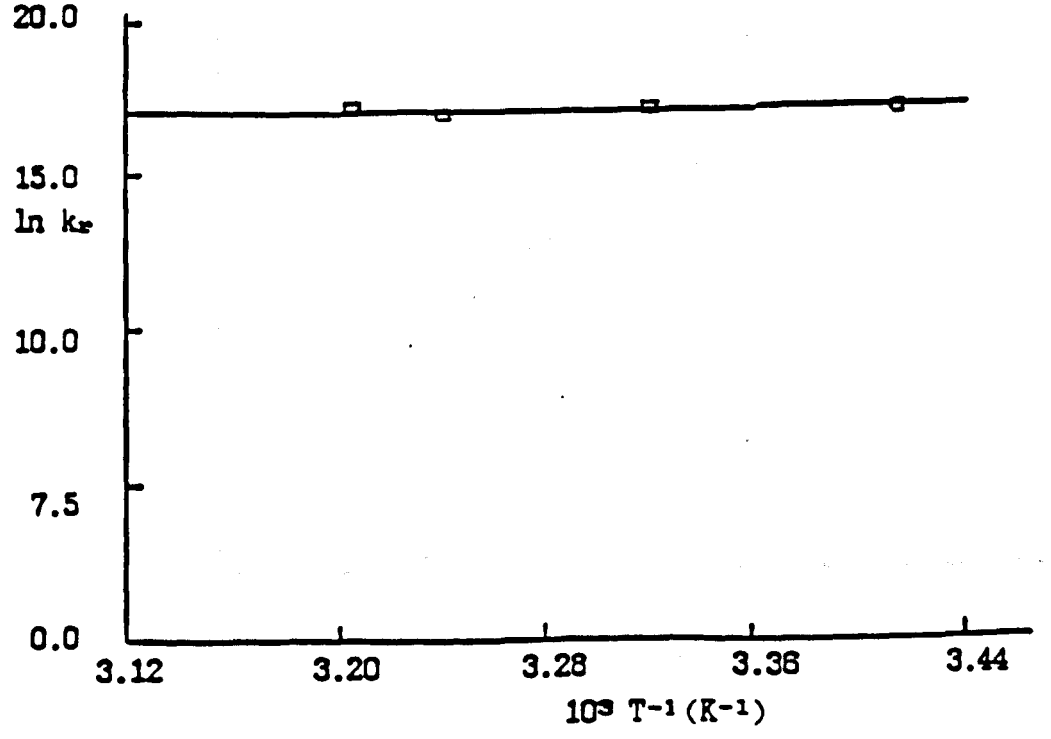


Table 38. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (V) in Methanol at 289 K.

10^{3}(V) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(V)^{-1}$ ($mol^{-1}dm^{3}$)	$10^{-8}Rate^{-1}$ ($mol^{-1}dm^{3}s$)
10	0.70	0.10	14.37
4.5	0.50	0.22	20.12
3.0	0.36	0.33	27.59
1.75	0.29	0.57	35.07

Figure 66. Plot According to Equation (18) of Above Data.

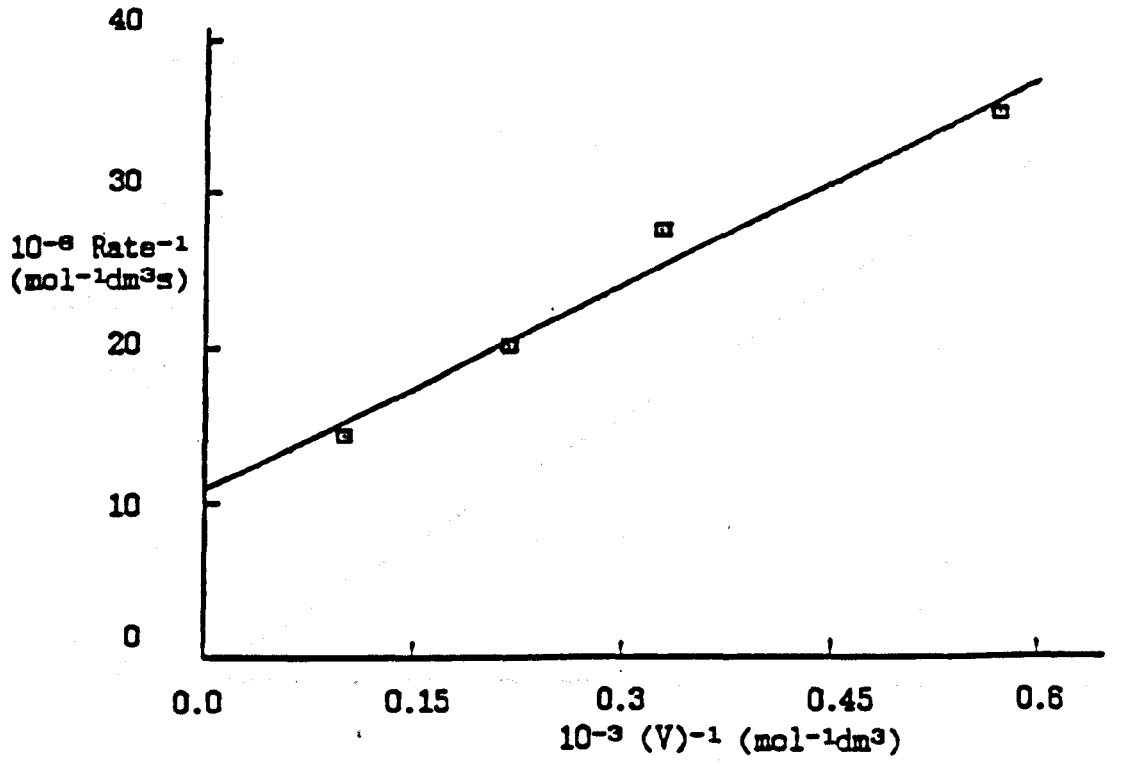


Table 39. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (V) in Methanol at 294 K.

10^{3}(V) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(V)^{-1}$ ($mol^{-1}dm^{3}$)	$10^{-6}Rate^{-1}$ ($mol^{-1}dm^{3}s$)
10	2.33	0.10	9.28
4.5	0.66	0.22	18.26
3.0	0.32	0.33	30.87
1.75	0.21	0.57	48.70

Figure 67. Plot According to Equation (18) of Above Data.

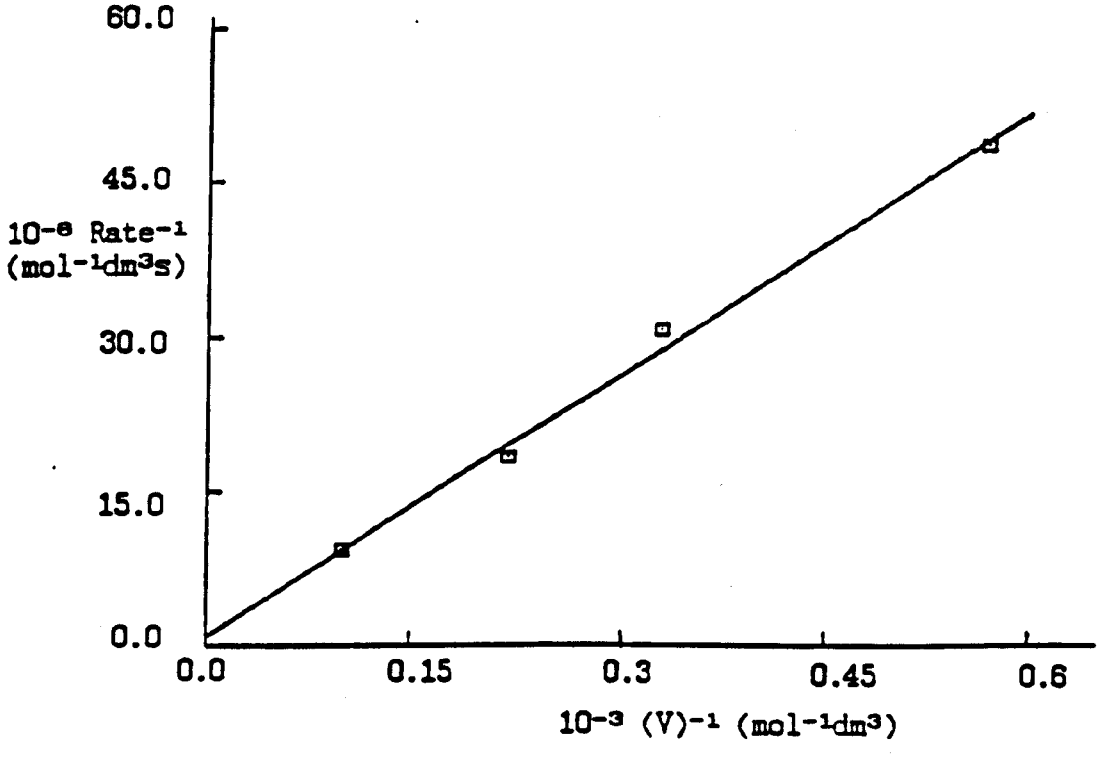


Table 40. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (V) in Methanol at 298 K.

10^{3}(V) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(V)^{-1}$ ($mol^{-1}dm^{3}$)	$10^{-6}Rate^{-1}$ ($mol^{-1}dm^{3}s$)
10	4.35	0.1	2.30
4.5	2.12	0.22	4.71
3.0	1.37	0.33	7.31
1.75	0.84	0.57	11.95
1.25	0.58	0.80	17.26

Figure 68. Plot according to Equation (18) of the Above Data.

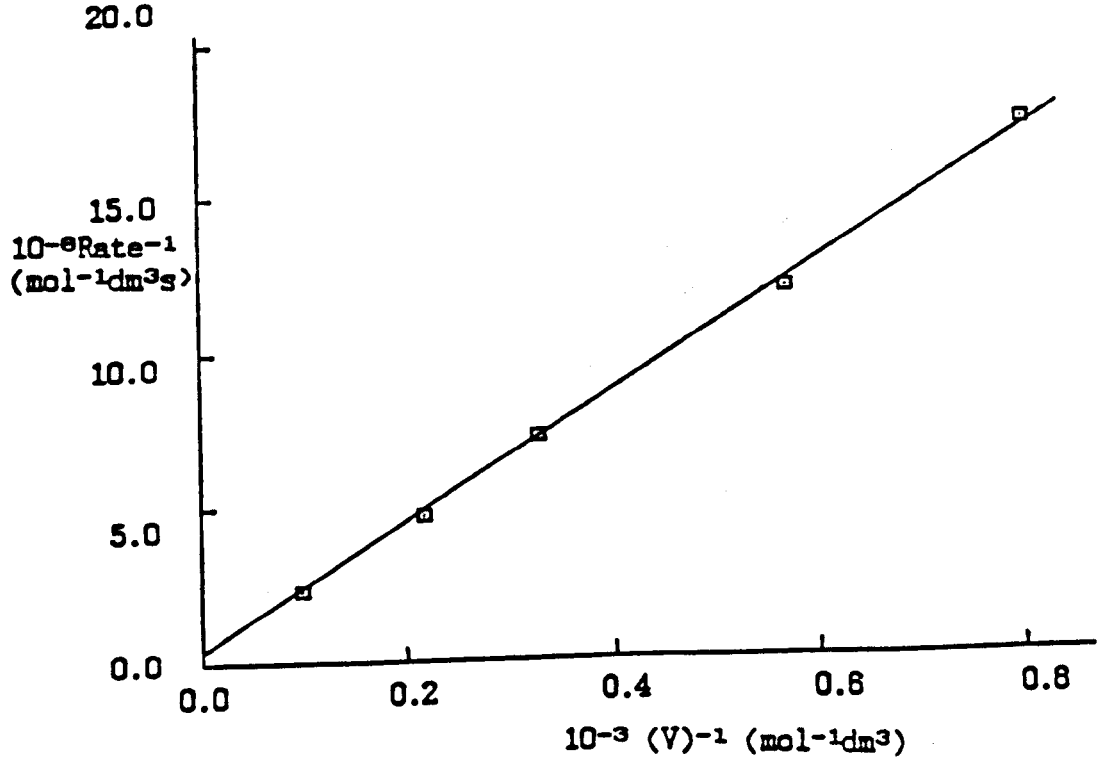


Table 41. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (V) in Methanol at 303 K.

10^{3}(V) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(V)^{-1}$ ($mol^{-1}dm^{3}$)	$10^{-6}Rate^{-1}$ ($mol^{-1}dm^{3}s$)
10	9.56	0.10	1.05
4.5	4.76	0.22	2.10
3.0	2.54	0.33	3.93
1.75	1.92	0.57	5.21

Figure 69. Plot According to Equation (18) of Above Data.

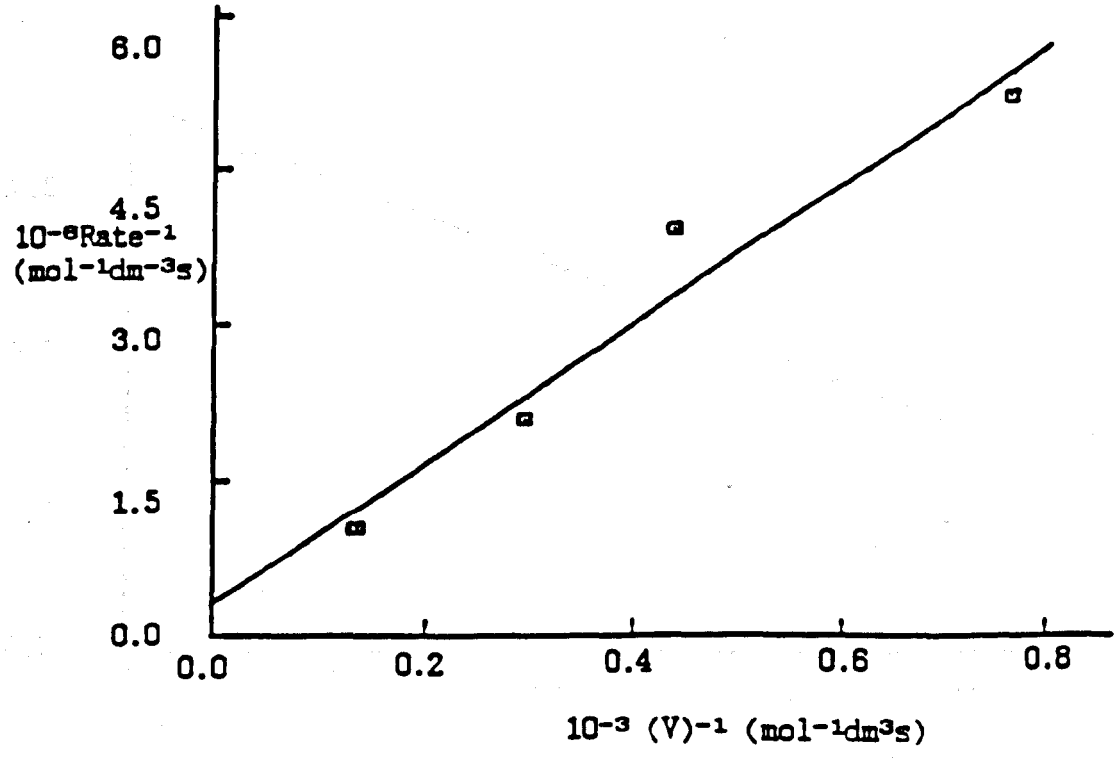


Table 42. Rate Constants for the Rose Bengal Sensitised Photo-oxidation of compound (V) in Methanol.

$10^{-8}k_r$ ($mol^{-1}dm^3s^{-1}$)	T (K)	ln k_r	10^3T (K^{-1})
2.25	284	14.63	3.46
4.96	298	15.42	3.40
15.04	298	16.53	3.36
72.10	303	18.09	3.25

Figure 70. Arrhenius Plot According to Above Data.

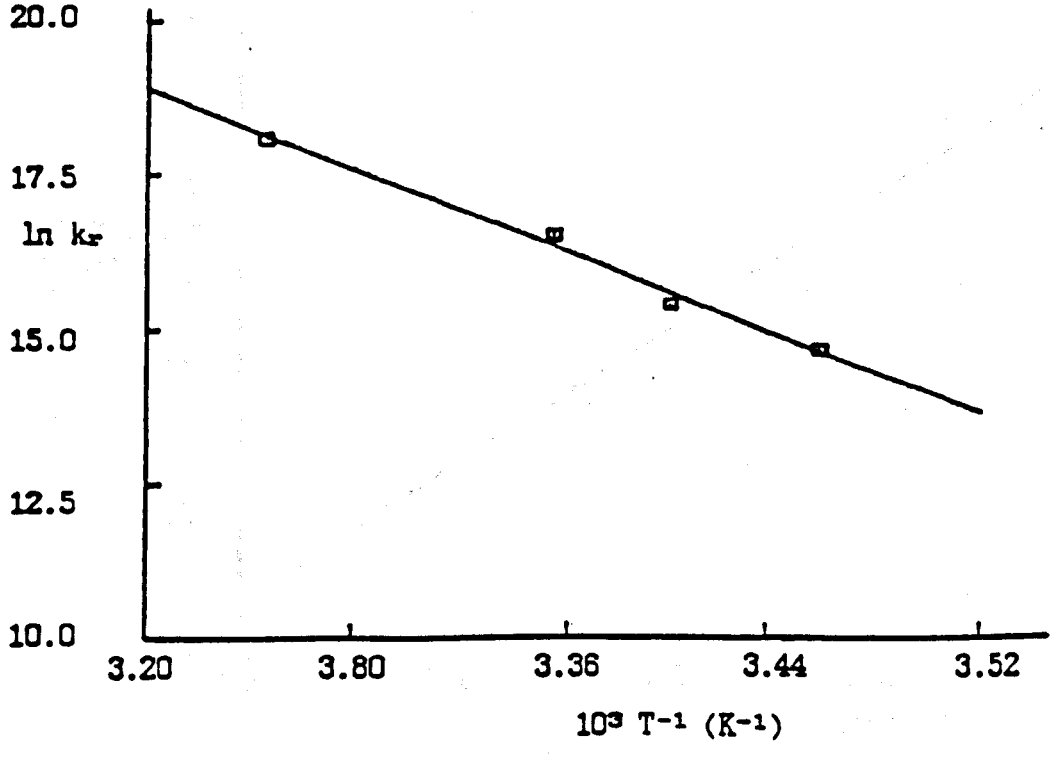


Table 43. Rate of Rose Bengal Sensitised Photo-oxidation of ADE in Methanol at 293 K.

10^{3}(ADE) (mol dm^{-3})	10^{6}Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(ADE)^{-1}$ ($mol^{-1}dm^{3}$)	$10^{-7}Rate^{-1}$ ($mol^{-1}dm^{3}s$)
20.0	0.87	0.05	1.45
9.00	0.43	0.11	2.66
6.00	0.29	0.17	3.05
3.50	0.17	0.29	5.58
2.50	0.17	0.40	7.29

Figure 71. Plot According to Equation (18) of Above Data.

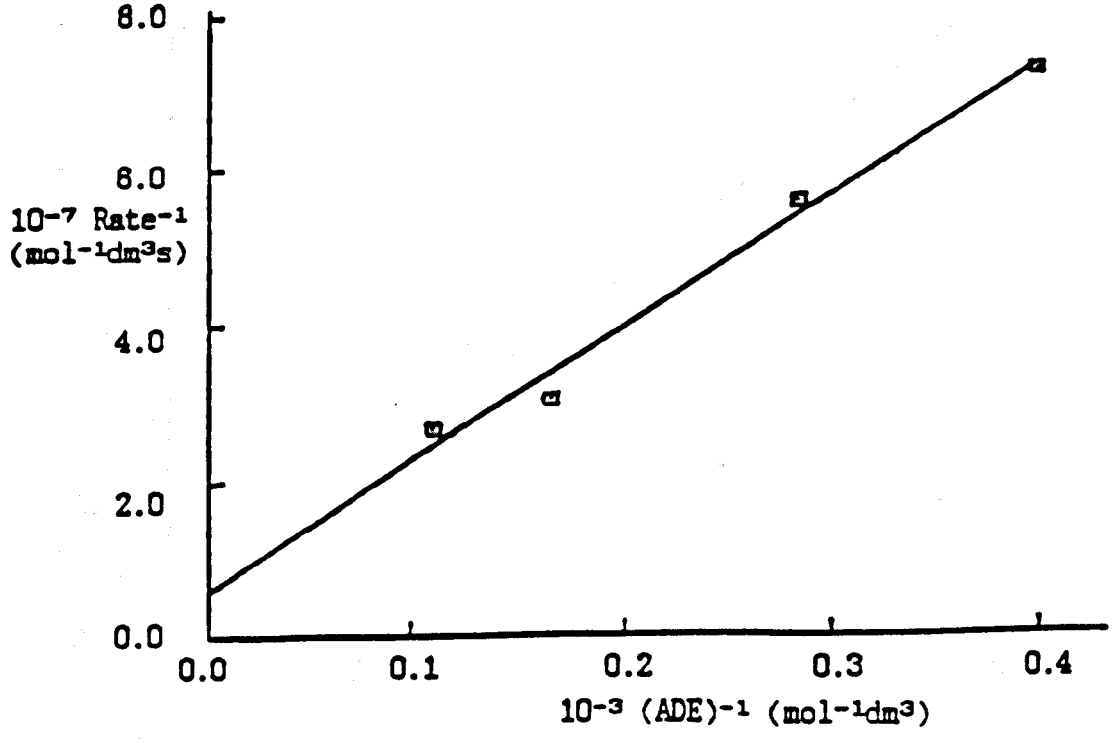


Table 44. Rate of Rose Bengal Sensitised Photo-oxidation of ADE in Methanol at 298 K.

10^{3}(ADE) (mol dm^{-3})	10^{6}Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(ADE)^{-1}$ ($mol^{-1}dm^{3}$)	$10^{-7}Rate^{-1}$ ($mol^{-1}dm^{3}s$)
20.0	0.66	0.05	6.08
9.00	0.49	0.11	12.16
6.00	0.26	0.17	18.02
3.50	0.22	0.29	30.91

Figure 72. Plot According to Equation (18) of Above Data.

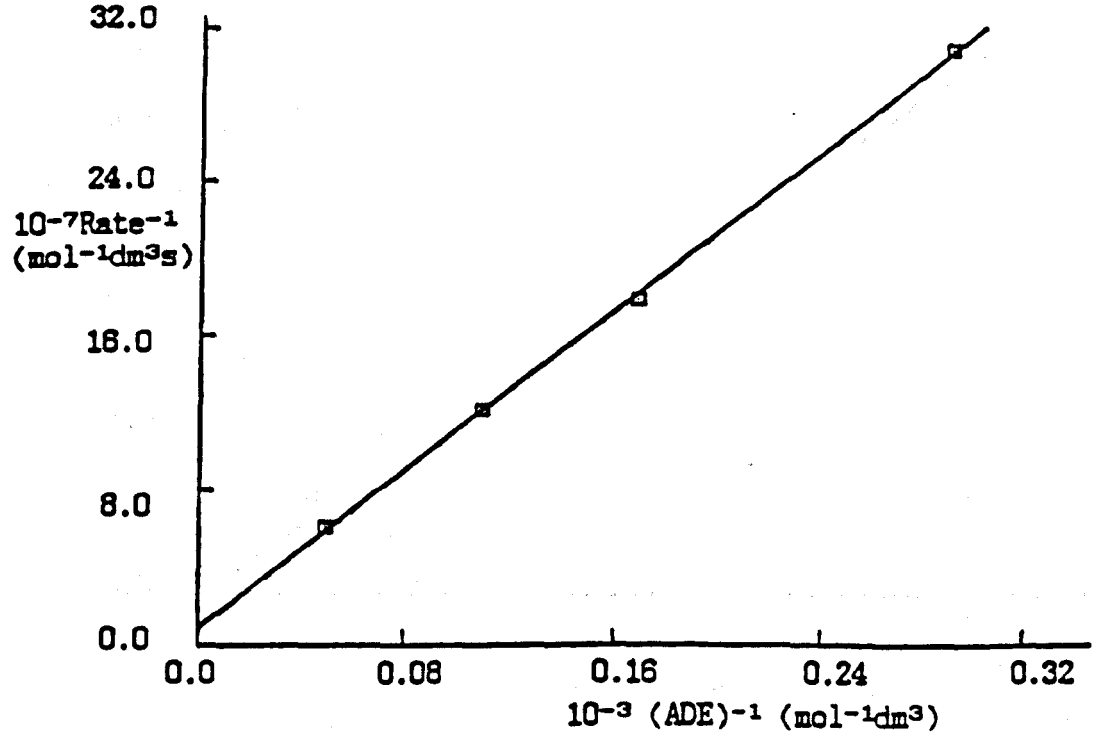


Table 45. Rate of Rose Bengal Sensitised Photo-oxidation of ADE in Methanol at 303 K.

10^{3}(ADE) (mol dm^{-3})	10^{6}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(ADE)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-7}Rate^{-1} ($mol^{-1}dm^{3}s$)
20.0	10.26	0.05	0.97
9.00	7.35	0.11	1.36
6.00	4.14	0.17	2.42
3.50	2.46	0.29	4.06
2.50	1.75	0.40	5.72

Figure 73. Plot According to Equation (18) of Above Data.

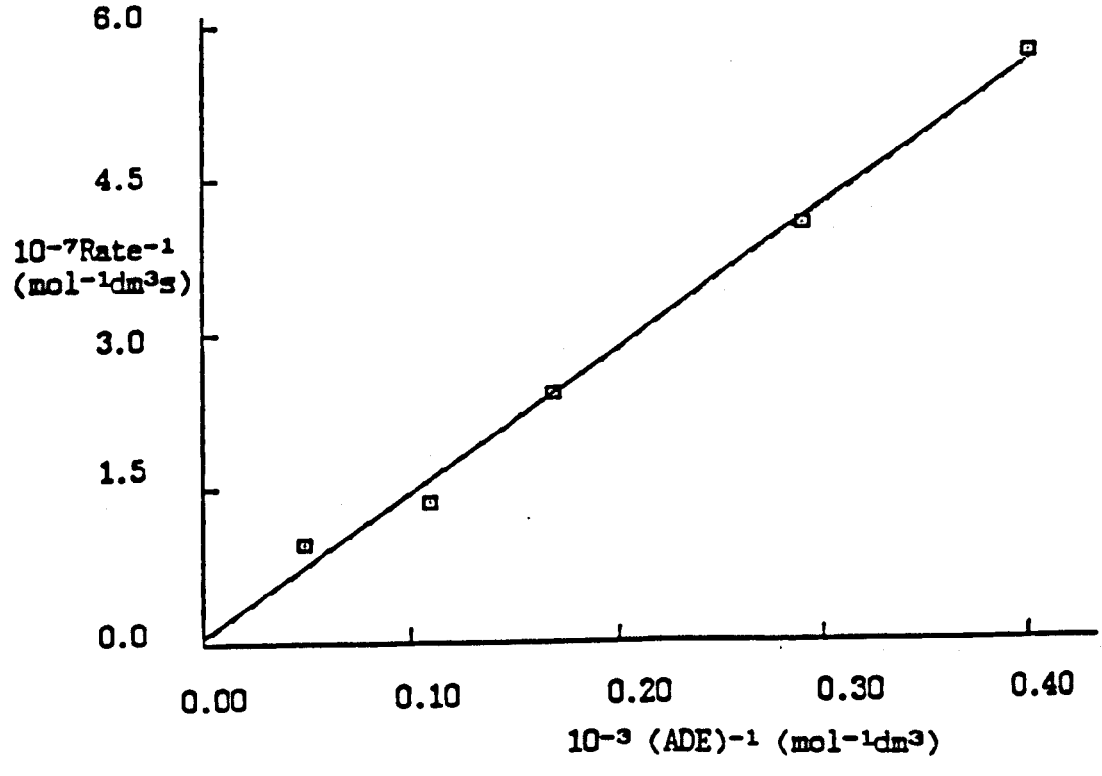


Table 46. Rate of Rose Bengal Sensitised Photo-oxidation of ADE in Methanol at 308 K.

10^{3}(ADE) (mol dm^{-3})	10^{6}Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(ADE)^{-1}$ ($mol^{-1}dm^{3}$)	$10^{-7}Rate^{-1}$ ($mol^{-1}dm^{3}s$)
20.0	1.09	0.05	9.18
9.00	0.47	0.11	21.44
6.00	0.35	0.17	28.80
3.50	0.20	0.29	50.71

Figure 74. Plot According to Equation (18) of Above Data.

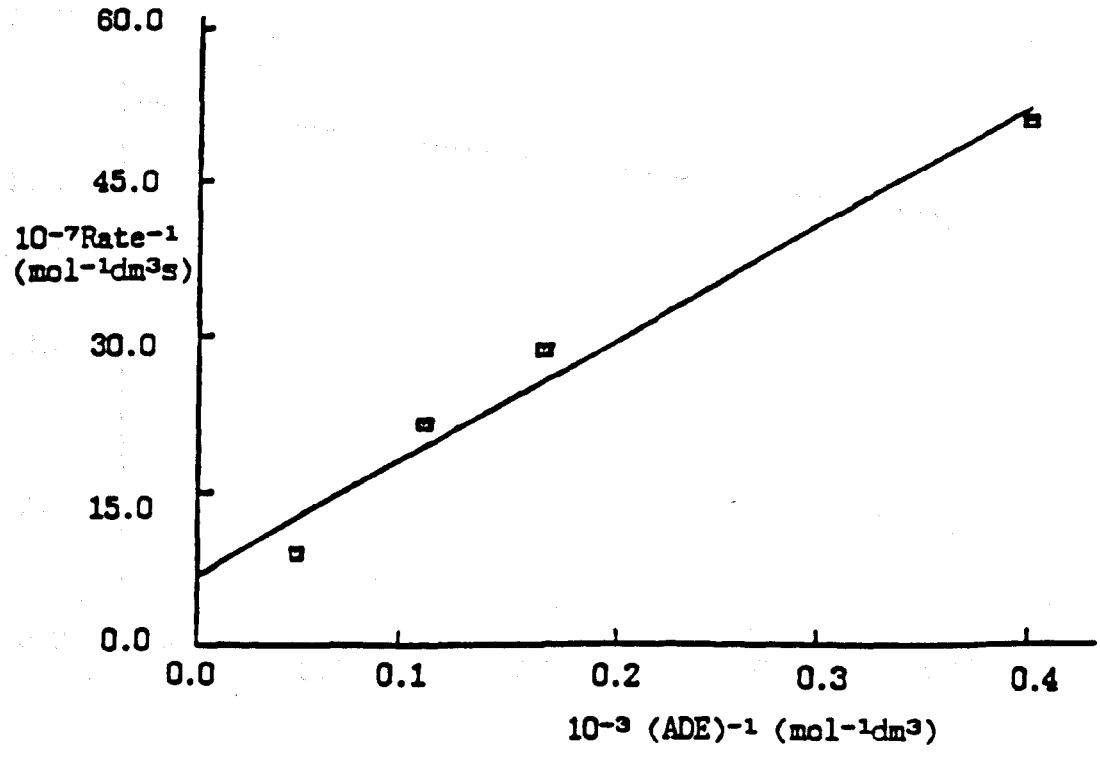


Table 47. Rate Constants for the Rose Bengal Sensitised Photo-oxidation oxidation of ADE in Methanol.

$10^{-8}k_r$ ($mol^{-1}dm^3s^{-1}$)	T (K)	ln k_r	10^3T (K^{-1})
2.25	293	14.63	3.46
4.96	298	15.42	3.40
15.04	303	16.53	3.36
72.10	308	18.10	3.25

Figure 75. Arrhenius Plot According to Above Data.

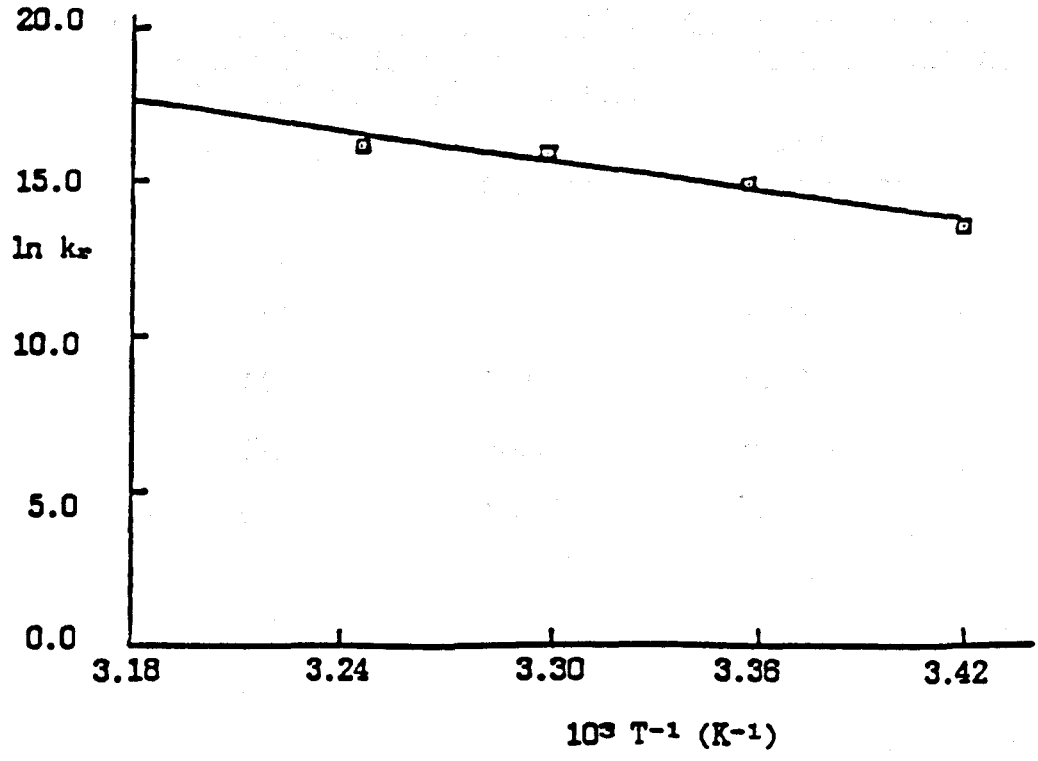


Table 48. Energy, E^*, and Entropy, ΔS^*, of Activation for the Rose Bengal Sensitised Photo-oxidation of Compounds (II)-(V) in Methanol/Water (1:1).

Compound	E^* kJ mol^{-1}	ΔS^* J K^{-1}mol^{-1}
(II)	≈ 0	- 74.8
(III)	≈ 0	- 87.2
(IV)	93.4	209.4
(V)	0.05	-133.6

Table 49. Energy, E^*, and Entropy, ΔS^*, of Activation for the Rose Bengal Sensitised Photo-oxidation of Compounds (I), (II), (III), (IV) and ADE in Methanol.

Compound	E^* kJ mol^{-1}	ΔS^* J K^{-1}mol^{-1}
(I)	≈ 0	- 97.9
(II)	≈ 0	- 96.5
(III)	≈ 0	-102.7
(V)	0.03	- 2.2
ADE	139.0	345.7

Table 50. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (III) at pH = 4.

10^{3}(III) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(III)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-7}Rate^{-1} ($mol^{-1}dm^{3}s$)
10	8.37	0.1	0.12
4.5	6.49	0.22	0.15
3.0	4.40	0.33	0.23
1.75	3.50	0.571	0.29
1.25	2.75	0.80	0.36
1.0	2.41	1.0	0.41

Figure 78. Plot According to Equation (18) of Above Data.

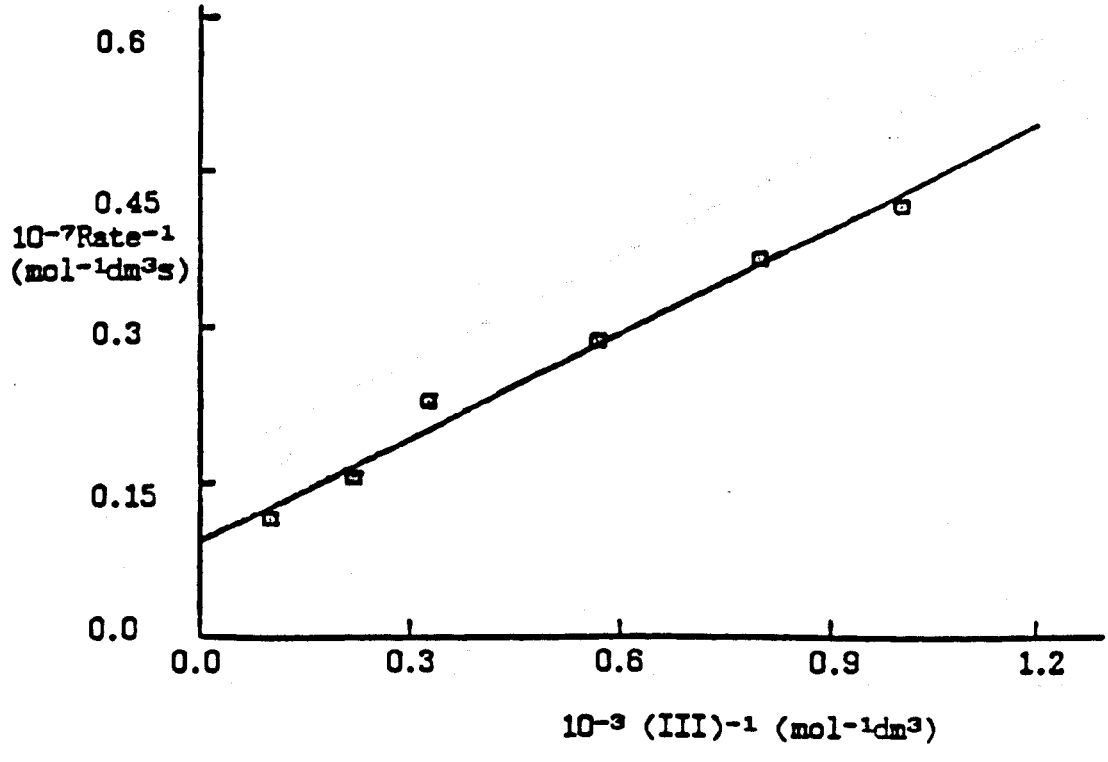


Table 51. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (III) at pH = 7.

10^{3}(III) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(III)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-7}Rate^{-1} ($mol^{-1}dm^{3}s$)
10	10.15	0.1	0.10
4.5	6.96	0.22	0.14
3.0	5.36	0.33	0.19
1.75	4.32	0.571	0.23
1.25	3.69	0.80	0.27
1.0	3.29	1.0	0.30

Figure 77. Plot According to Equation (18) of Above Data.

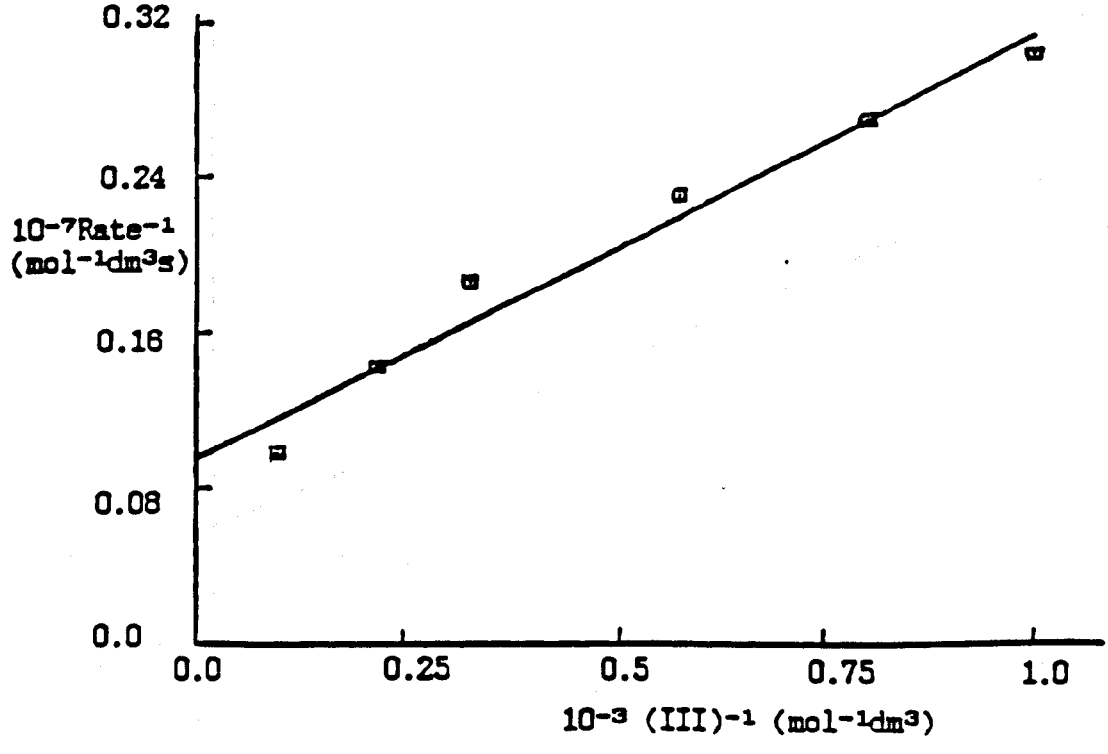


Table 52. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (III) at pH = 9.

10^{3}(III) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(III)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-7}Rate^{-1} ($mol^{-1}dm^{3}s$)
10	14.09	0.1	0.07
4.5	10.76	0.22	0.09
3.0	8.55	0.33	0.12
1.75	6.62	0.571	0.15
1.25	5.81	0.8	0.18
1.00	4.86	1.0	0.21

Figure 78. Plot According to Equation (18) of Above Data.

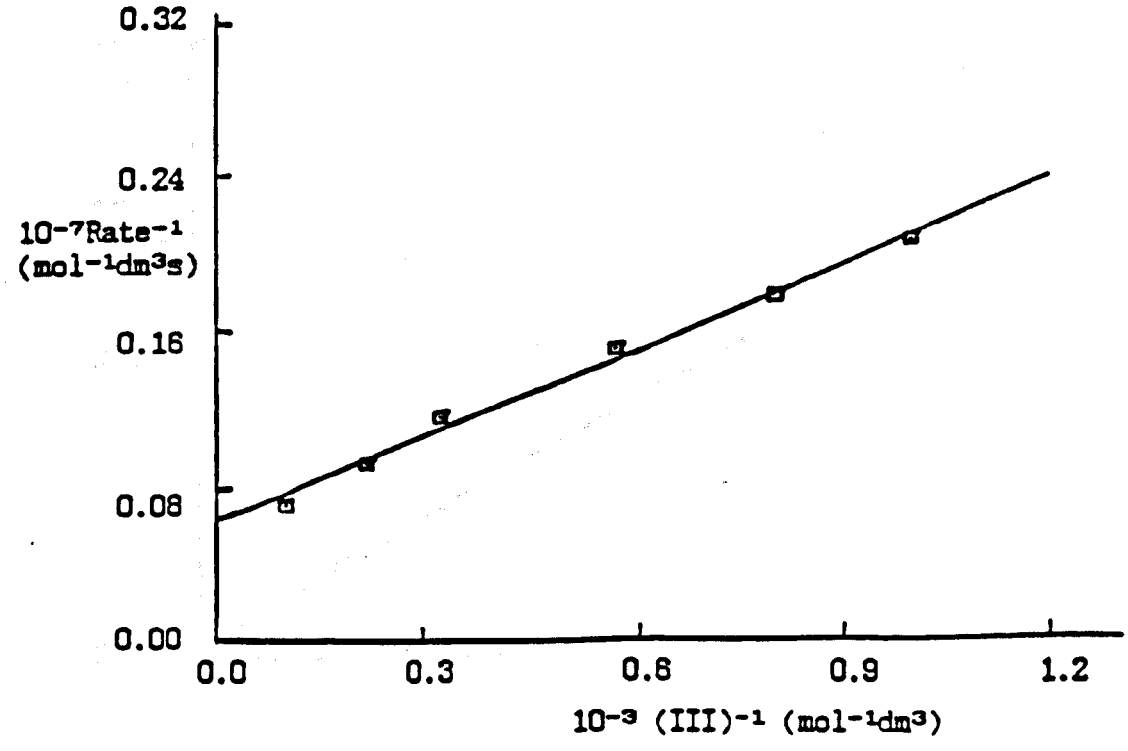


Table 53. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (IV) at pH = 4.

10^{3}(IV) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(IV)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-7}Rate^{-1} ($mol^{-1}dm^{3}s$)
10	3.85	0.1	0.26
4.5	2.07	0.22	0.48
3.0	1.47	0.33	0.68
2.0	0.95	0.50	1.05
1.7	0.88	0.571	1.13

Figure 79. Plot According to Equation (18) of Above Data.

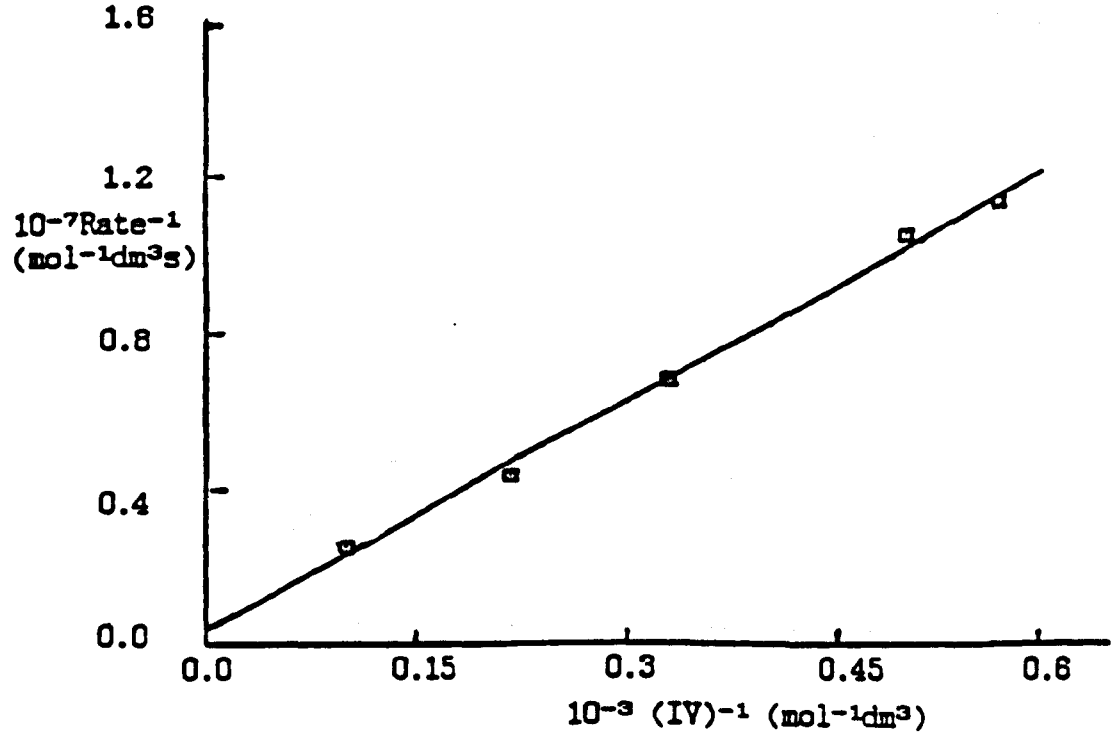


Table 54. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (IV) at pH = 7.

10^{3}(IV) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(IV)^{-1}$ ($mol^{-1}dm^{3}$)	$10^{-7}Rate^{-1}$ ($mol^{-1}dm^{3}s$)
10	5.07	0.1	0.20
4.5	3.22	0.22	0.31
3.0	2.51	0.33	0.40
2.0	1.58	0.50	0.64
1.7	1.26	0.571	0.80

Figure 80. Plot According to Equation (18) of Above Data.

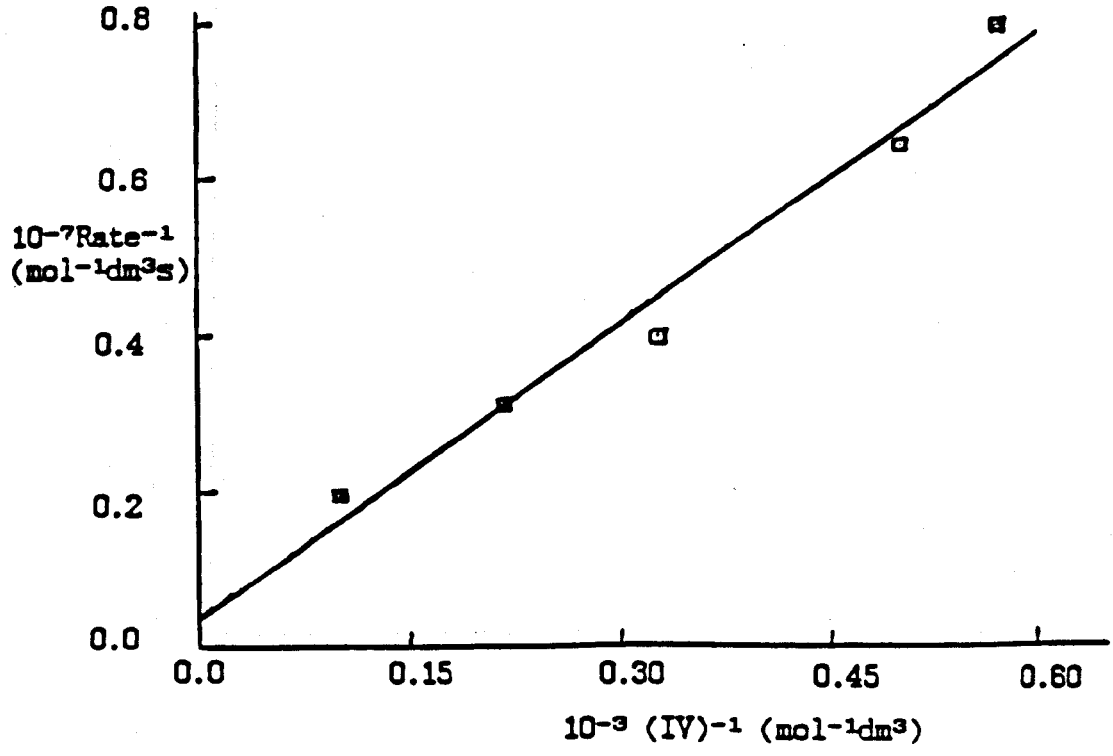


Table 55. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (IV) at pH = 9.

10^{3}(IV) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(IV)^{-1}$ ($mol^{-1}dm^{3}$)	$10^{-7}Rate^{-1}$ ($mol^{-1}dm^{3}s$)
10	6.74	0.1	0.15
4.5	2.87	0.22	0.37
3.0	1.76	0.33	0.57
2.0	1.27	0.50	0.78
1.7	1.06	0.571	0.94

Figure 81. Plot According to Equation (18) of Above Data.

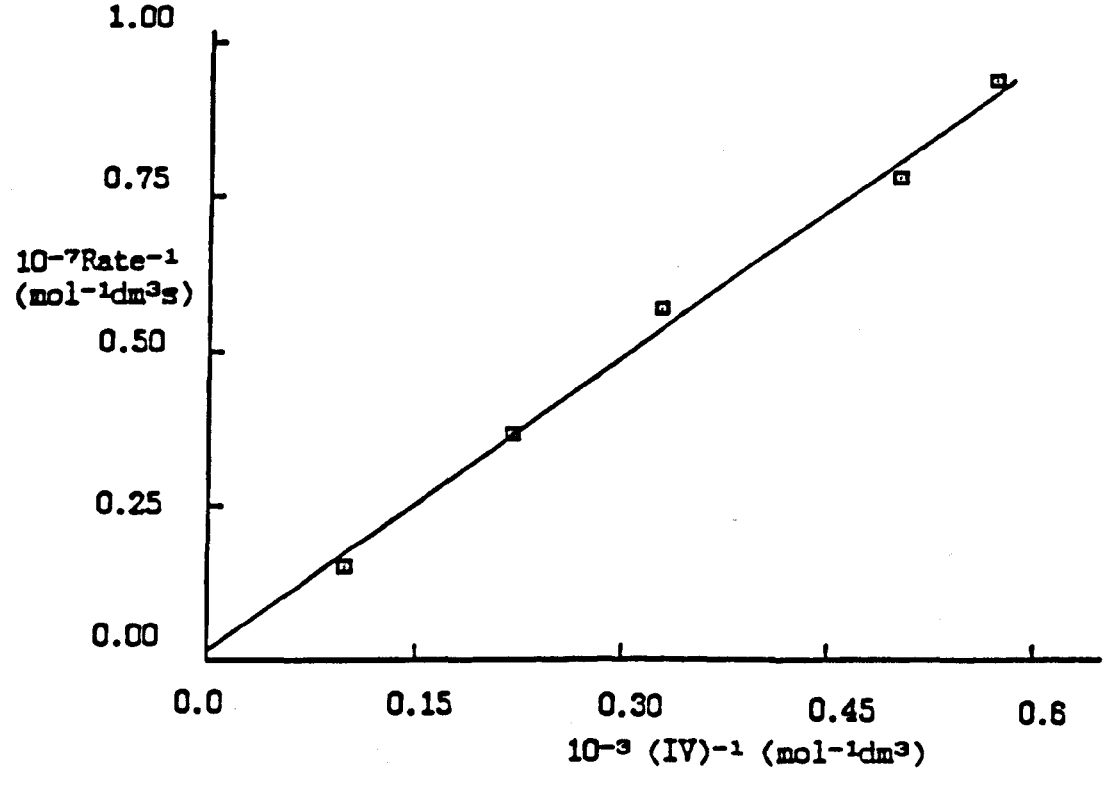


Table 56. Effect of pH on Rate Constants, k_r, for Rose Bengal Sensitised Photo-oxidation of Compounds (III) and (IV). Temperature = 298 K.

pH	$10^{-7}k_r$ (III) $mol^{-1}\ dm^3$	$10^{-7}\ k_r$ (IV) $mol^{-1}\ dm^3$
4.0	7.95	1.29
7.0	11.37	0.44
9.0	21.71	0.37

Table 57. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (III) in (1:1) $CD_3OD:D_2O$.

10^3(III) (mol dm^{-3})	10^6Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(III)$^{-1}$ ($mol^{-1}dm^3$)	10^{-6}Rate^{-1} ($mol^{-1}dm^3s$)
10	1.47	0.1	0.68
2.0	1.38	0.5	0.72
1.25	1.32	0.8	0.76
0.8	1.27	1.25	0.79
0.6	1.13	1.66	0.89
0.5	1.02	2.0	0.98

Figure 82. Plot According to Equation (18) of Above Data.

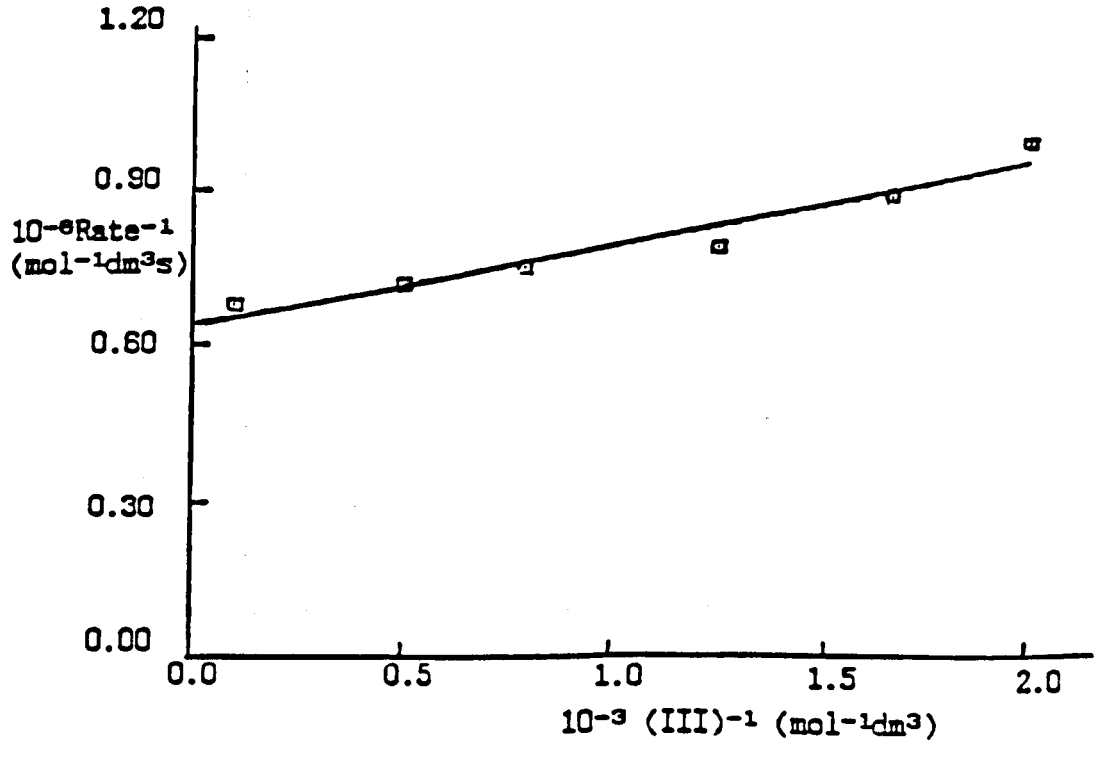


Table 58. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (IV) in (1:1) $CD_3OD:D_2O$.

$10^3(IV)^{-1}$ (mol dm^{-3})	10^7Rate (mol $dm^{-3}s^{-1}$)	$10^{-3}(IV)^{-1}$ ($mol^{-1}dm^3$)	$10^{-7}Rate^{-1}$ ($mol^{-1}dm^3s$)
10	3.84	0.1	0.26
4.5	1.78	0.22	0.56
3.0	1.56	0.33	0.66
2.0	1.08	0.50	0.93
1.7	0.92	0.588	1.09

Figure 83. Plot According to Equation (18) of Above Data.

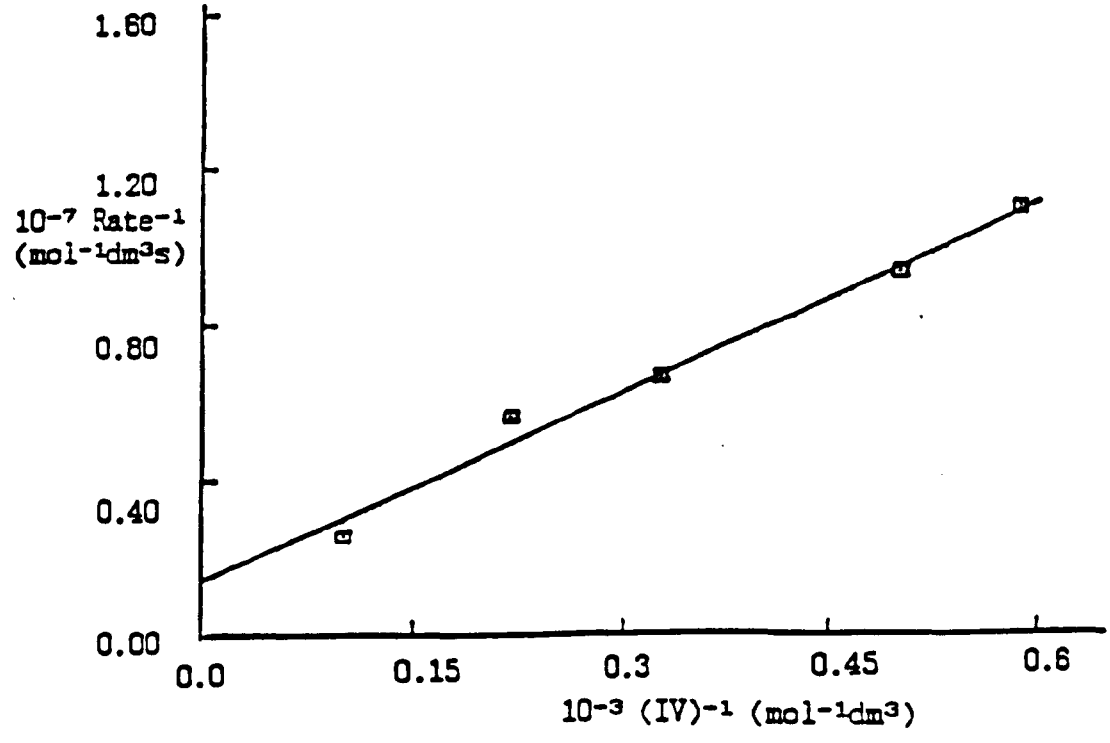


Table 59. Effect of Deuteration on the Rate Constants for the Photo-oxidation of Compounds (III) and (IV). Temperature = 298 K.

Compound	Deuterated[a] $10^{-7}k_r$ (mol^{-1} dm^3)	Non-deuterated[b] $10^{-7}k_r$ (mol^{-1} dm^3)	Isotope Effect
(III)	7.95	1.29	7.0
(IV)	11.37	0.44	8.6

where:

[a] - Solvent: (1:1) deuteromethanol:deuterium oxide

[b] - Solvent: (1:1) methanol:water

NB.

Rate constants for the deuterated solvent systems were derived from Figures 82 and 83 whereas, data for the non-deuterated solvent was derived from Figures 32 and 42.

Table 60. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (III) in Methanol/Water (1:1) at 298K in the presence of Sodium Azide. $[NaN_3] = 1 \times 10^{-4}M$.

10^{3}(III) (mol dm^{-3})	10^{7}Rate (mol $dm^{-3}s^{-1}$)	10^{-3}(III)$^{-1}$ ($mol^{-1}dm^{3}$)	10^{-6}Rate^{-1} ($mol^{-1}dm^{3}s$)
10.0	2.78	0.1	0.36
3.0	2.17	0.33	0.46
1.75	1.72	0.57	0.58
1.25	1.44	0.80	0.69
1.0	1.22	1.0	0.82

Figure 84. Plot According to Equation (18) of Above Data.

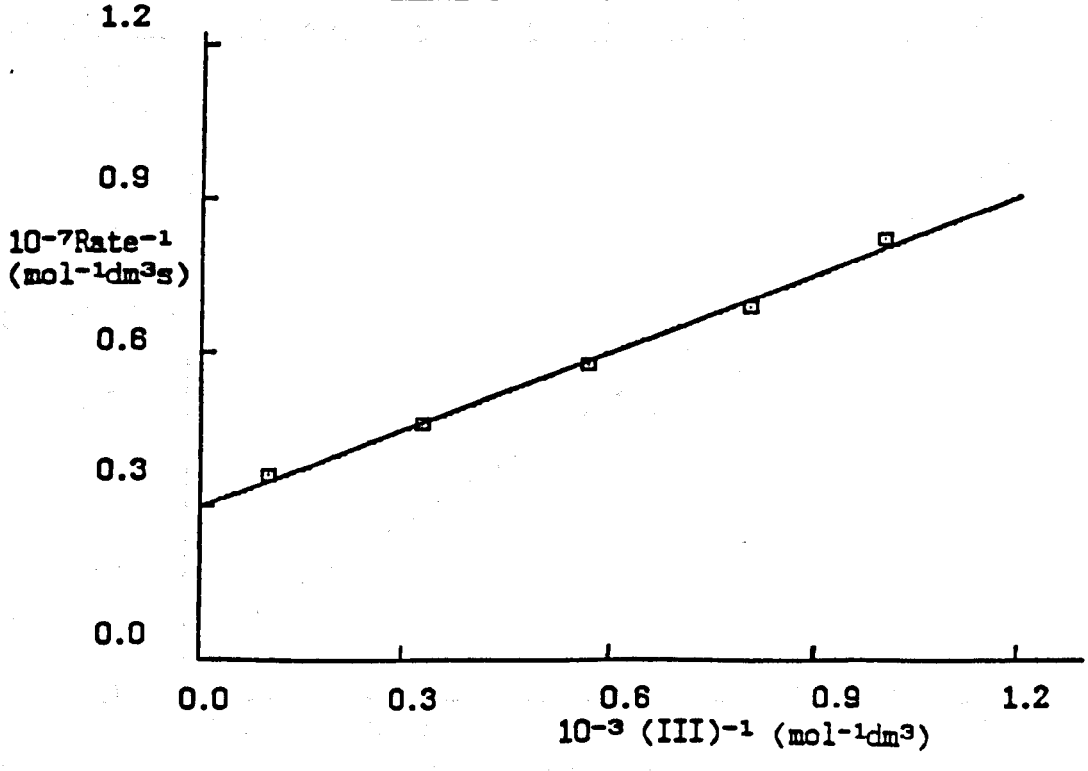


Table 61. Rate of Rose Bengal Sensitised Photo-oxidation of Compound (IV) in Methanol/Water (1:1) at 298K in the presence of Sodium Azide, [NaN$_3$] = 1×10^{-4} M.

10^{3}(IV) (mol dm^{-3})	10^{7}Rate (mol dm^{-3}s^{-1})	10^{-3}(IV)$^{-1}$ (mol^{-1}dm^{3})	10^{-7}Rate^{-1} (mol^{-1}dm^{3}s)
10.0	3.03	0.1	0.33
3.0	1.54	0.33	0.65
1.75	1.01	0.57	0.99
1.25	0.63	0.80	1.60
1.0	0.59	1.0	1.69

Figure 85. Plot According to Equation (18) of Above Data.

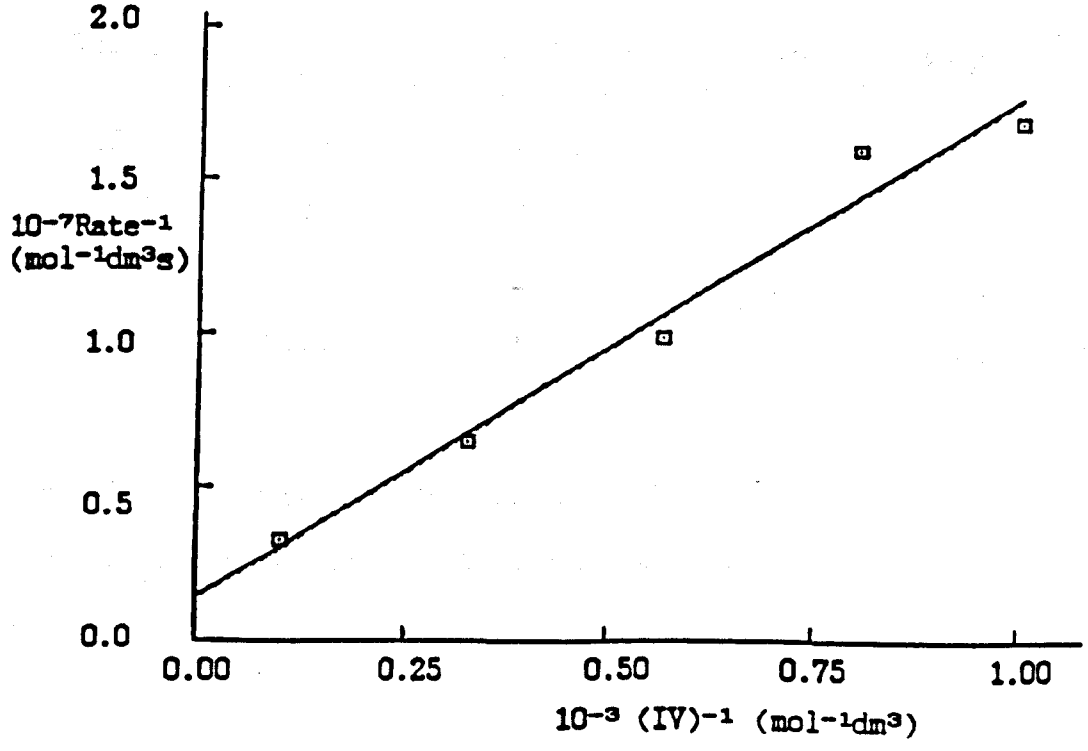


Table 62. Effect of Sodium Azide on the Rate Constants for the Photo-oxidation of Compounds (III) and (IV) in Methanol/Water, (1:1). Temperature = 298 K.

Compound	Quenched [a] $10^{-8}k_r$ (mol^{-1} dm^3)	Non-quenched [b] $10^{-8}k_r$ (mol^{-1} dm^3)	Quencher Effect
(III)	0.98	1.57	1.6
(IV)	0.06	0.21	3.6

[a] $[NaN_3]$ = $1x10^{-4}M$, k_r values derived from Figures 84 and 85.

[b] k_r values taken from Tables 12 and 17.

Table 63. Rate Constants for the Overall Interaction, k_{ov}, Chemical Reaction, k_r, and Physical Quenching, k_q, in the Rose Bengal Sensitised Photo-oxidation of Compounds (I), (II), (III), (V) in Methanol. Temperture = 298K.

Compound	$10^{-8}k_{ov}$ (mol^{-1} dm^3s^{-1})	$10^{-7}k_r$ [a] ($mol^{-1}dm^3s^{-1}$)	$10^{-8}k_q$ [b] (mol^{-1} dm^3s^{-1})	kq / kr
(I)	9.55	5.25	9.03	17.19
(II)	2.13	6.35	1.49	5.00
(III)	0.65	2.99	0.35	1.17
(V)	0.15	4.96	0.10	2.06

[a] Values taken from Tables 27, 32, 37 & 42.

[b] Values derived from equation $k_{ov} = k_r + k_q$

Table 64. Change in Absorbance of RNO with Irradiation Time in the Surface-Separated-Reactor.

Irradiation Time (hrs)	Absorbance at 440nm.	Change in Absorbance
0	1.16	0.00
1	1.06	0.10
2	0.92	0.24
3	0.81	0.35
4	0.67	0.49

Figure 86. Plot of Change in RNO Absorbance with Irradiation Time in the Surface-Separated-Reactor.

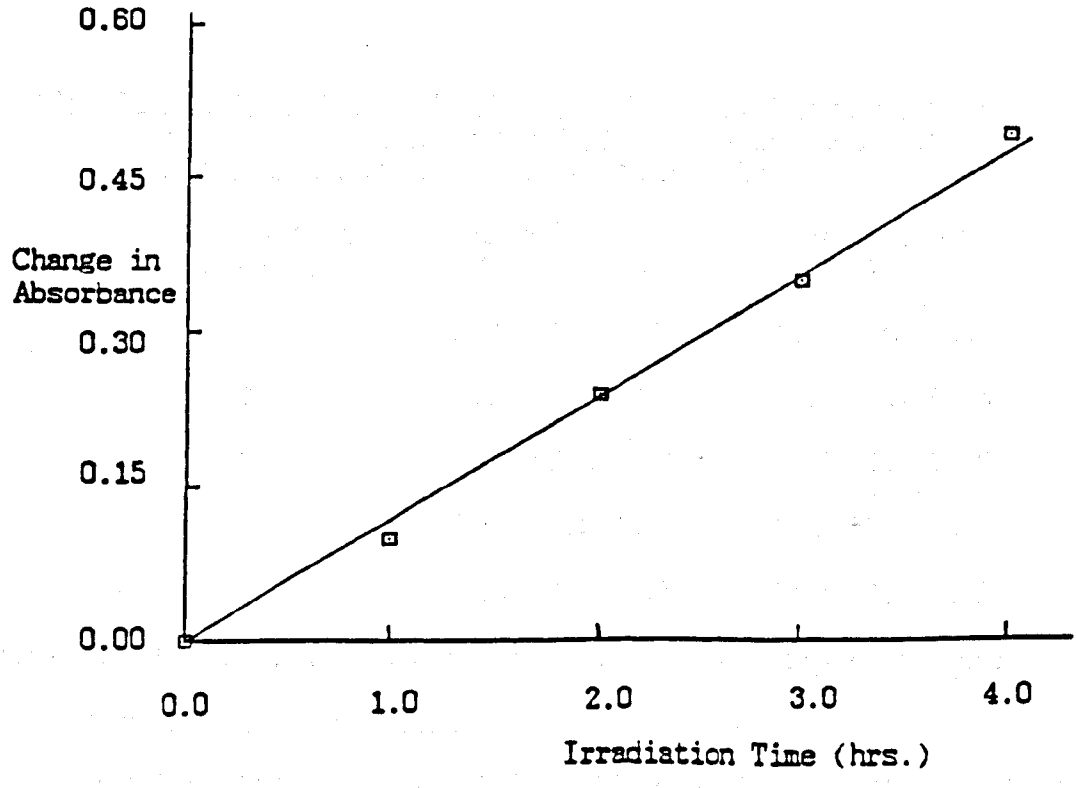


Table 65 The % of Compound (I) Remaining in Solution After Reaction With Exogeneously Generated Singlet Oxygen. Solvent - Benzene. Temperature - 280 K.

Irradiation time (hrs)	Rose Bengal+ C	Q	U	Chlorophyll+ C	Q	U
0	100	100	100	100	100	100
1	87.8	87.3	81.0	96.3	91.8	88.0
2	78.3	67.3	74.3	92.5	82.4	75.6
3	62.6	55.8	49.2	88.6	73.3	64.0
4	62.9	42.8	31.0	85.2	66.0	51.9

where: C = Control, Q = Quenched reaction (Quencher: β-carotene)

U = Unquenched reaction

+ = Sensitiser used for exogeneous generation of singlet oxygen

Table 66. The % of Compound (III) Remaining in Solution After Reaction With Exogeneously Generated Singlet Oxygen. Solvent - Benzene. Temperature - 280 K.

Irradiation time (hrs)	Rose Bengal+ C	Q	U	Chlorophyll+ C	Q	U
0	100	100	100	100	100	100
1	85.5	87.5	82.0	90.3	84.2	84.4
2	79.1	68.1	63.4	67.8	71.3	59.6
3	57.3	53.2	44.6	58.2	55.3	42.0
4	39.0	37.0	23.3	48.5	40.6	29.2

where: C = Control, Q = Quenched reaction (Quencher: β-carotene)

U = Unquenched reaction

+ = Sensitiser used for exogeneous generation of singlet oxygen

Figure 87. Rose Bengal Sensitised Photo-oxidation of Compound (I) in Solution.

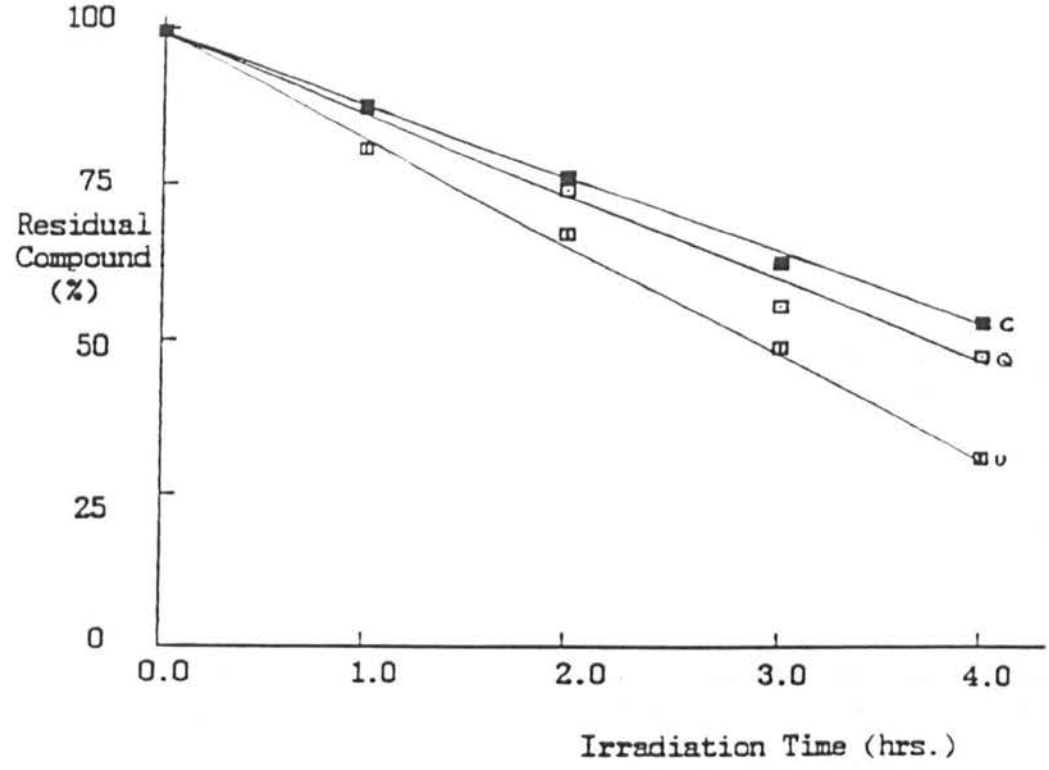


Figure 88. Chlorophyll sensitised Photo-oxidation of Compound (I) in Solution.

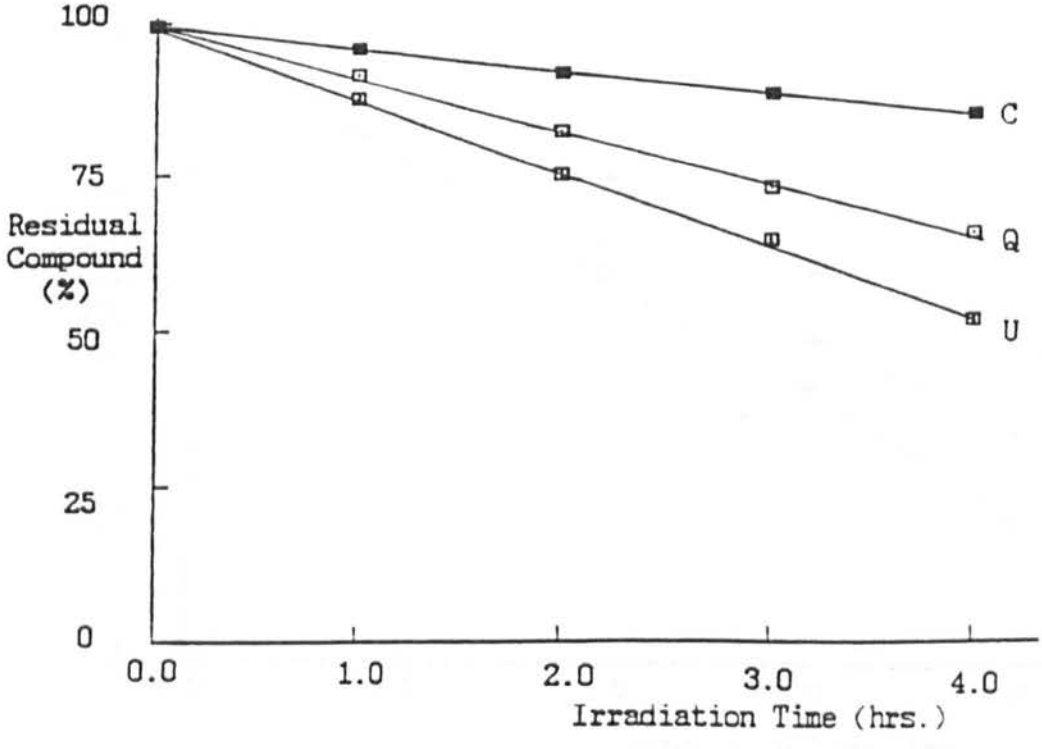


Figure 89. Rose Bengal Sensitised Photo-oxidation of Compound (III) in Solution.

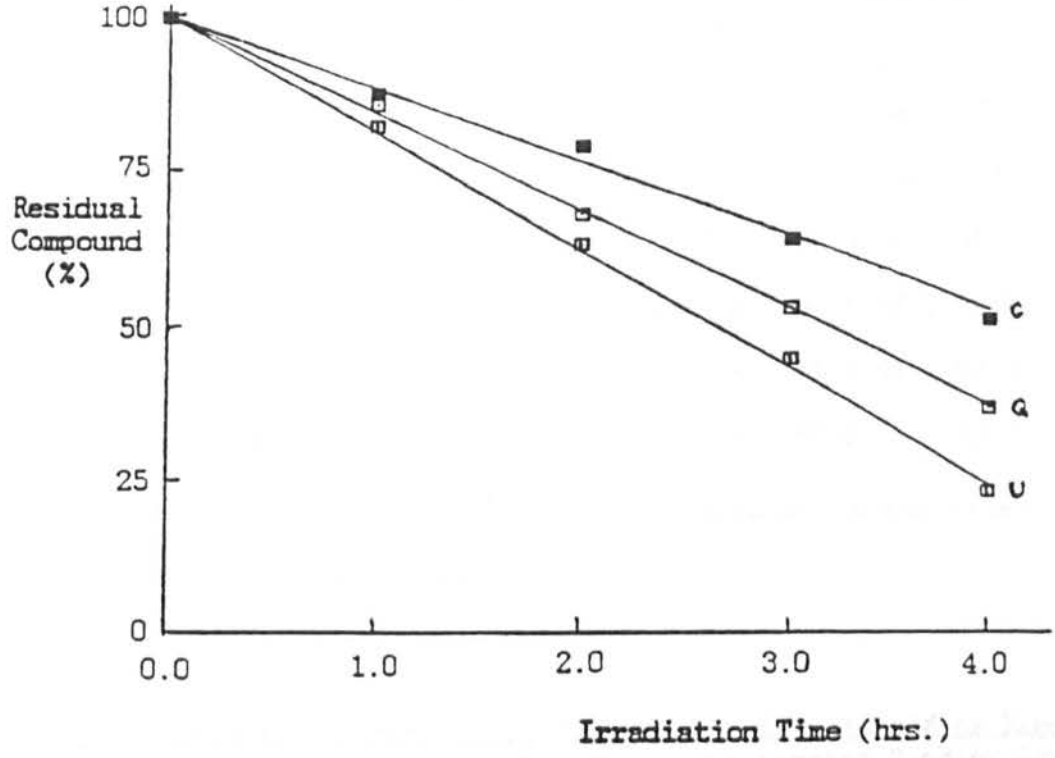


Figure 90. Chlorophyll sensitised Photo-oxidation of Compound (III) in Solution.

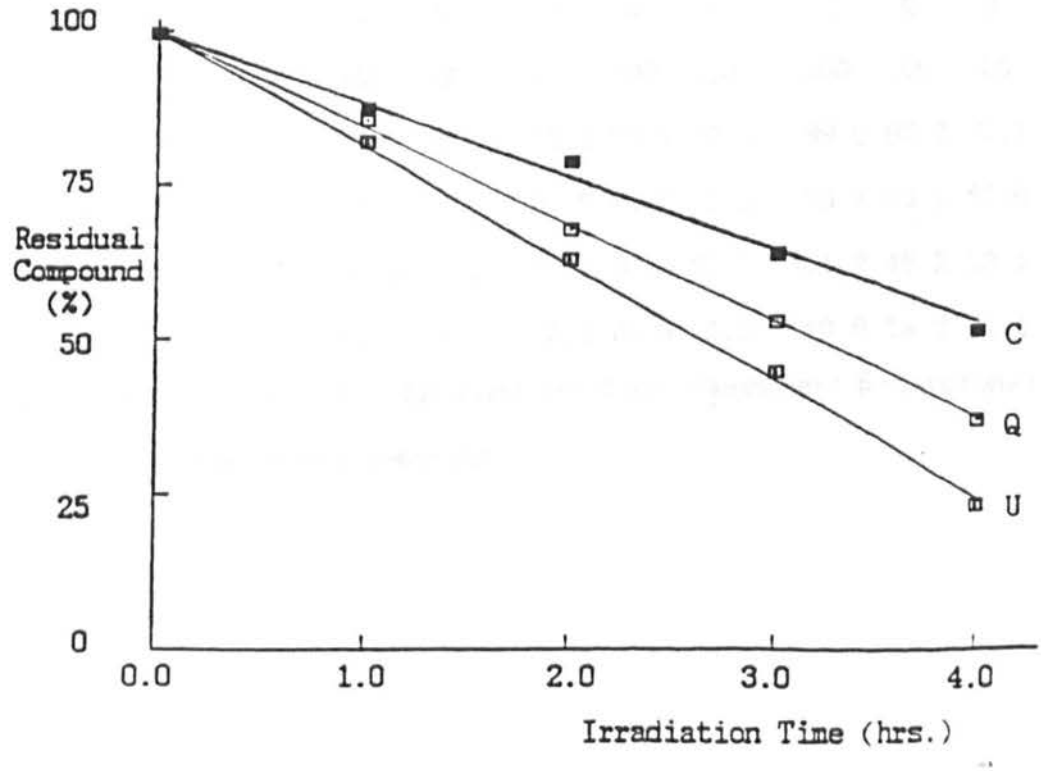


Table 67 The % of Compound (I) Remaining in Solution After Reaction With Soil Sensitised, Exogeneously Generated Singlet Oxygen. Solvent - Benzene. Temperature - 280 K.

Irradiation time (Hrs)	pH 4.2			pH 5.5			pH 7.5		
	C	Q	U	C	Q	U	C	Q	U
0	100	100	100	100	100	100	100	100	100
1	91.0	82.1	82.4	93.2	89.0	87.0	93.6	94.4	88.5
2	80.5	70.5	63.7	88.3	82.4	74.2	90.4	88.1	74.2
3	70.3	55.1	50.5	83.0	68.8	61.9	84.3	81.1	62.3
4	62.4	34.6	28.3	76.7	57.0	48.9	80.8	73.0	52.2

where: C = Control, Q = Quenched reaction (Quencher: β-carotene)

U = Unquenched reaction

Table 68. The % of Compound (III) Remaining in Solution After Reaction With Soil Sensitised, Exogeneously Generated Singlet Oxygen. Solvent - Benzene. Temperature - 280 K.

Irradiation time (Hrs)	pH 4.2			pH 5.5			pH 7.5		
	C	Q	U	C	Q	U	C	Q	U
0	100	100	100	100	100	100	100	100	100
1	94.1	91.1	82.6	92.1	79.7	73.2	89.0	80.3	77.1
2	83.3	81.9	67.0	87.9	61.2	53.2	70.7	59.3	53.8
3	75.3	68.0	51.9	82.4	38.3	27.7	61.2	48.2	30.4
4	69.0	61.8	37.6	75.8	20.6	5.8	48.8	19.9	14.2

where: C = Control, Q = Quenched reaction (Quencher: β-carotene)

U = Unquenched reaction

Figure 91. The Photo-oxidation of Compound (I) using a Soil Sensitiser of pH 4.2.

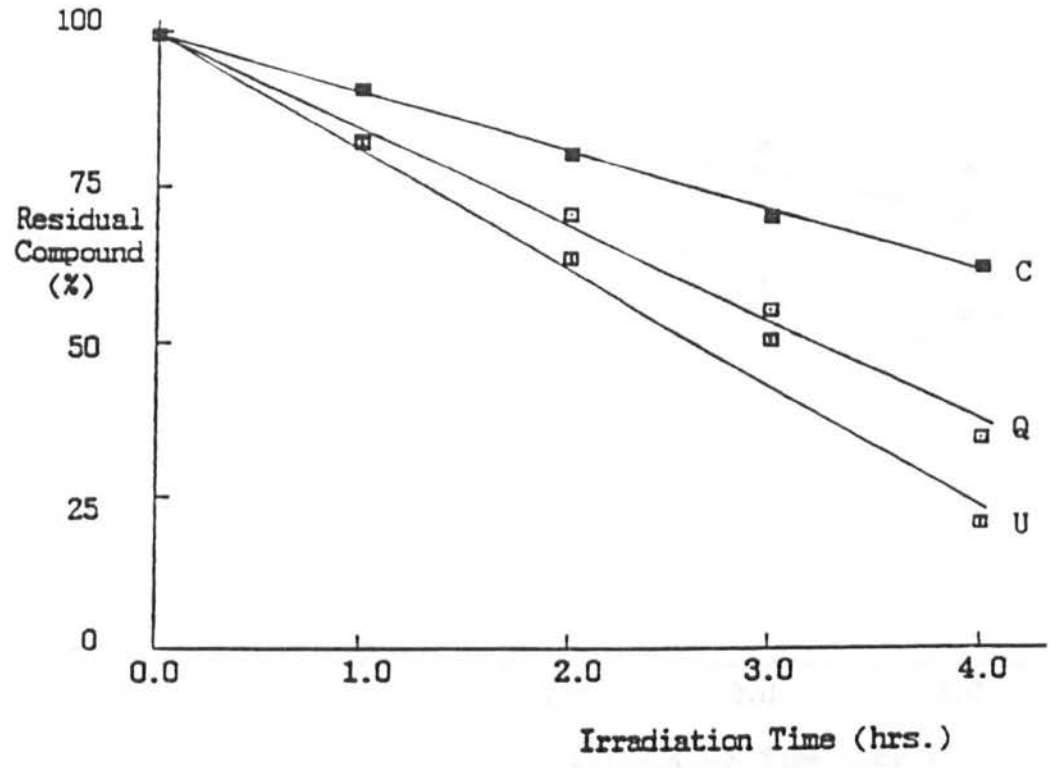


Figure 92. The Photo-oxidation of Compound (I) using a Soil Sensitiser of pH 5.5.

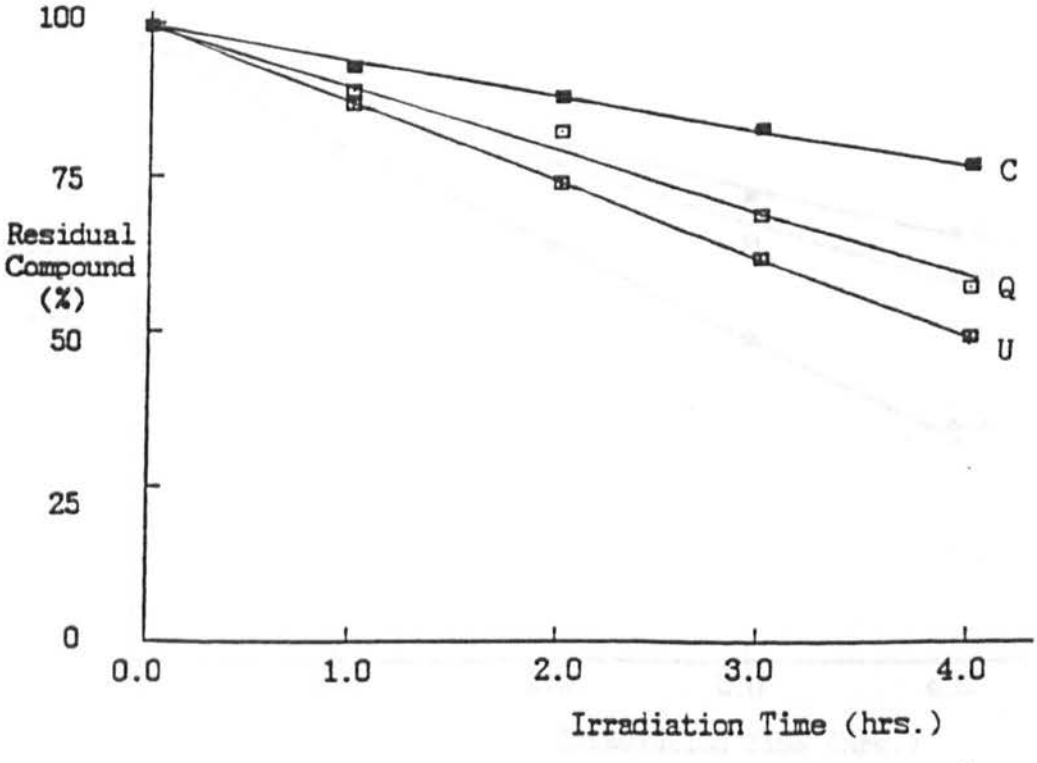


Figure 93. The Photo-oxidation of Compound (I) using a Soil Sensitiser of pH 7.5.

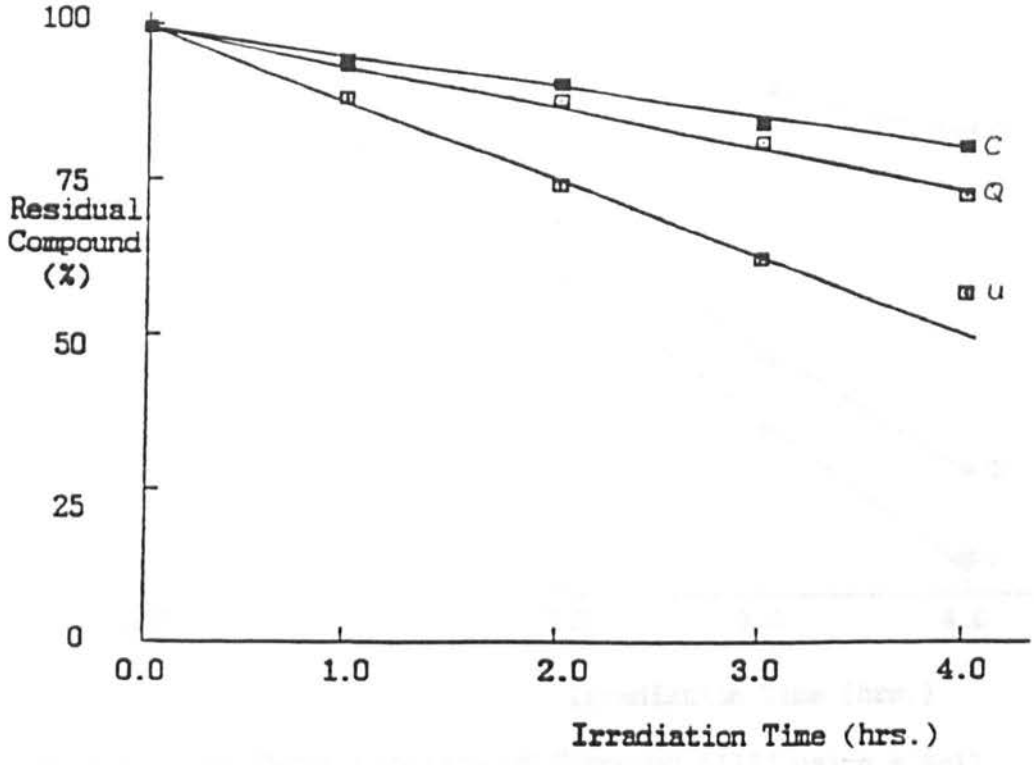


Figure 94. The Photo-oxidation of Compound (III) using a Soil Sensitiser of pH 4.2.

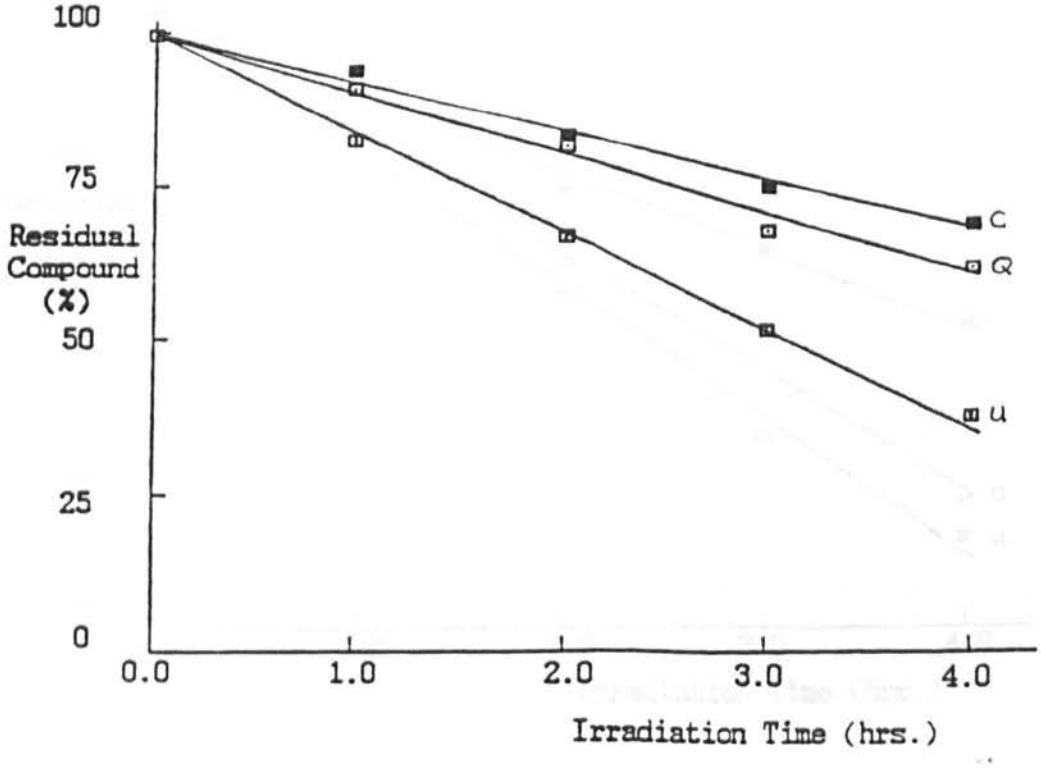


Figure 95. The Photo-oxidation of Compound (III) using a Soil Sensitiser of pH 5.5.

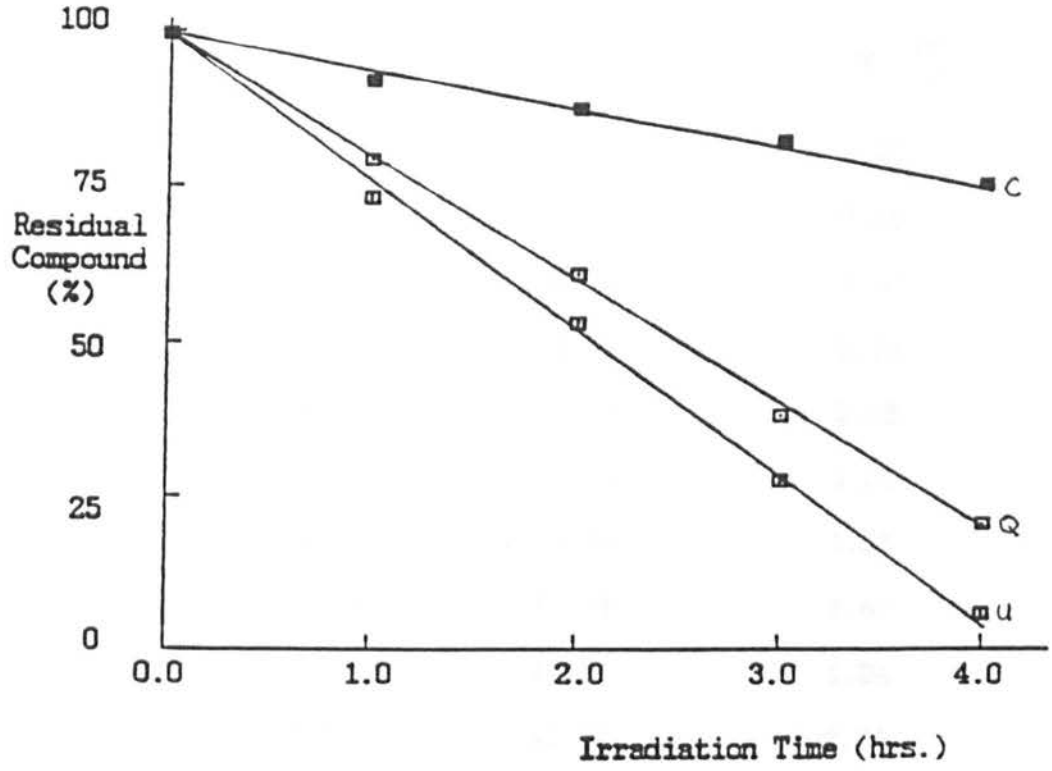


Figure 96. The Photo-oxidation of Compound (III) using a Soil Sensitiser of pH 7.5.

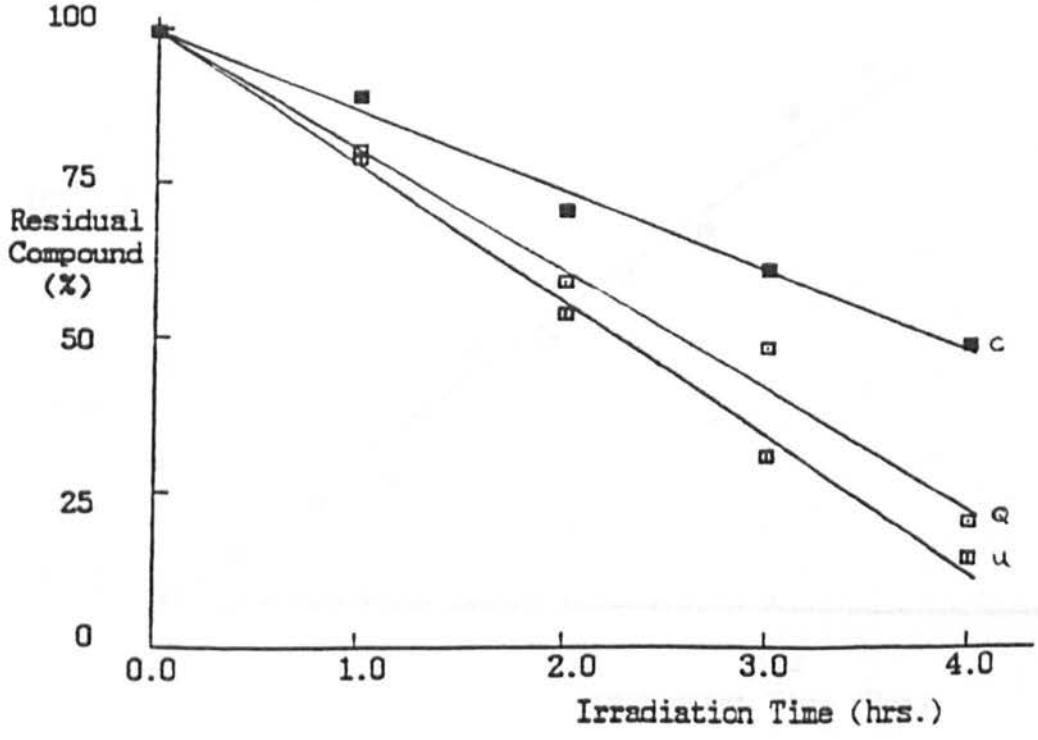


Table 69 Data for the Reaction of Exogeneously Generated Singlet Oxygen with Compound (I). Solvent - Benzene. Sensitiser Rose Bengal.

Irradiation time (Hrs)	Relative % conc. of (I)	log $\frac{[I]_o}{[I]}$
0.0	100.0	0.00
0.75	85.19	0.18
1.5	68.52	0.39
2.25	54.32	0.49
3.0	38.89	0.98
3.75	36.11	1.03
4.5	28.40	1.28
5.25	23.46	1.48
6.0	14.81	1.94
6.75	11.73	2.11

Figure 97. Plot of Data Given Above.

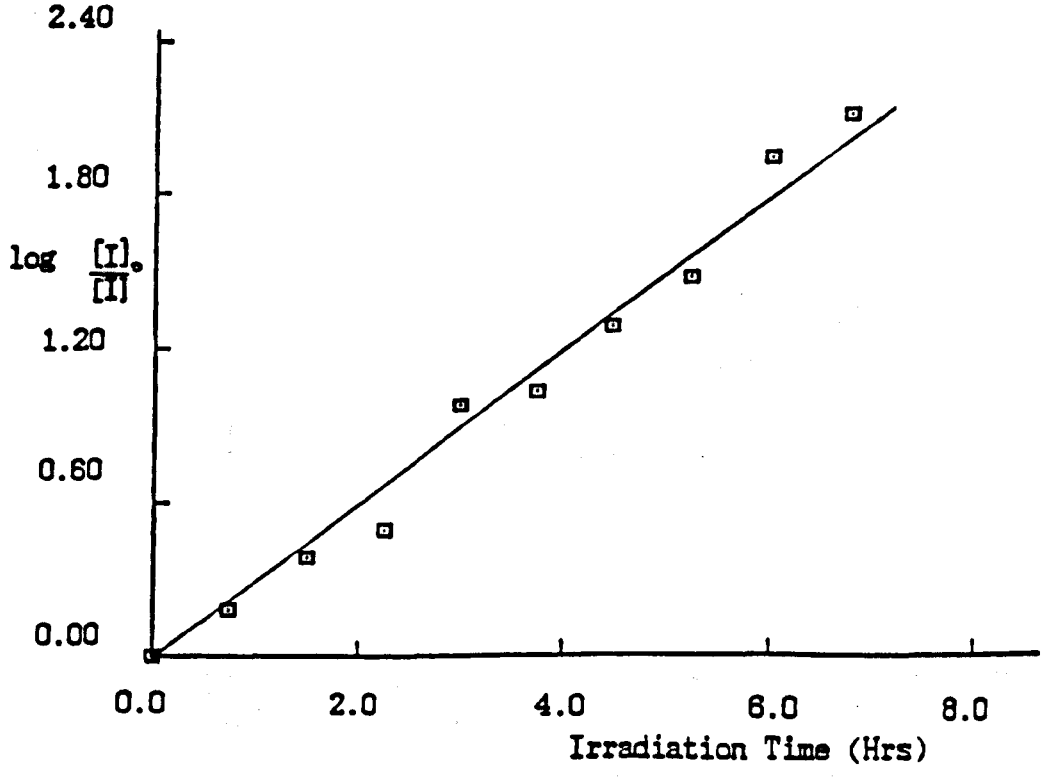


Table 70. Relative concentrations of Compound (I) after reaction with exogeneously generated singlet oxygen. Sensitiser - Rose Bengal. Solvent - Benzene. Temperature - 280 K.

[Quencher [a]]	Relative Concentrations		
(10^{-3}mol dm^{-3})	X[b]	Y[c]	Z[d]
0	1.00	1.00	1.00
1	1.14	1.22	1.42
2	1.15	1.41	1.67
3	1.24	1.81	2.14
4	1.38	1.96	2.57

[a] β-carotene

[b] Initial concentration of compound (I) = 1.0×10^{-3} mol dm^{-3}

[c] Initial concentration of compound (I) = 2.0×10^{-3} mol dm^{-3}

[b] Initial concentration of compound (I) = 3.0×10^{-3} mol dm^{-3}

Figure 98 - Plot of above data according to Equation (29).

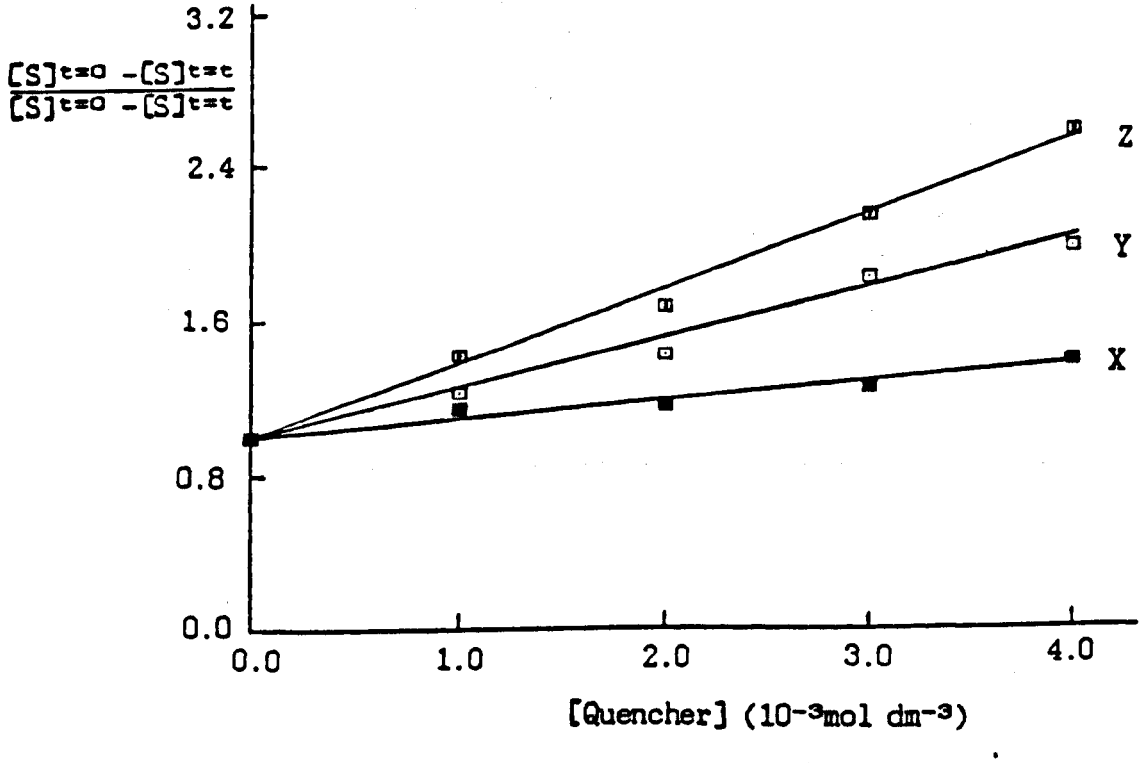


Table 71. Relative concentrations of 2,5-Dimethylfuran (DMF) and compound (I) after reaction with exogeneously generated singlet oxygen. Sensitiser - Rose Bengal. Solvent - Benzene. Temperature - 280 K.

Irradiation Time (Hrs.)	DMF (%)	I (%)
0	100.0	100.0
1	88.2	91.7
2	85.4	79.7
3	55.7	67.4
4	41.7	59.3
5	25.6	46.5

Figure 99 Plot of above data

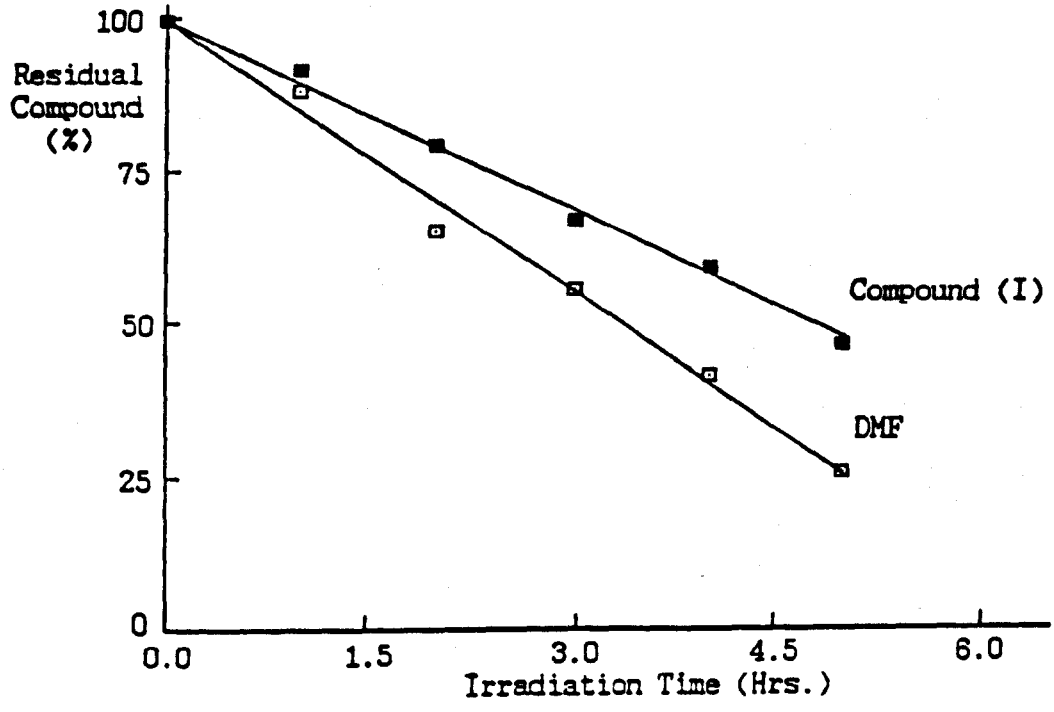


Table 72. Rate constants for the reaction of Compound (I) with exogeneosly - & homogeneously generated singlet oxygen.

$^1O_2$ Generation Method	10^{-8} k_r ($M \cdot dm^{-3}$)
Exogeneous a	1.5 ± 0.3
Exogeneous b	1.0 ± 0.2
Homogeneous c	0.5

where :-

a - average of the three results calculated using the Stern-Volmer Method (I) (re.3.4.5.)

b - result calculated using a reference singlet oxygen trap, Method (II) (re.3.4.6.)

c - average of the results of the data in Table 27.

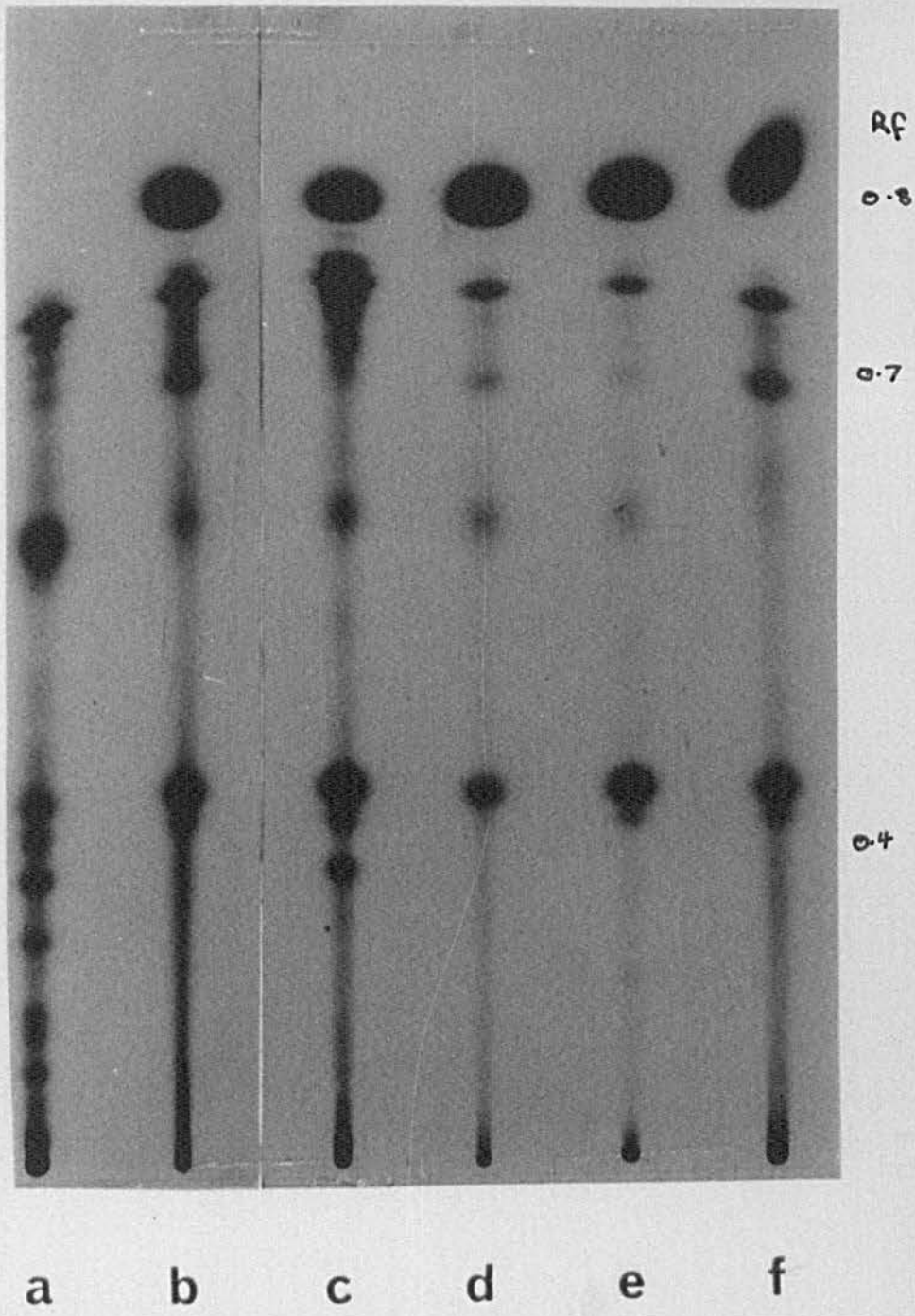


Figure 100 (A) Autoradiogram resulting from the photo-oxidation of 2-14C (I) in benzene using different modes of singlet oxygen generation

(a) & (b) Homogeneously generated singlet oxygen - sample (b) contained β-carotene

(c) & (d) Heterogeneously generated singlet oxygen - sample (d) contained β-carotene

(e) & (f) Exogeneously generated singlet oxygen - sample (f) contained β-carotene

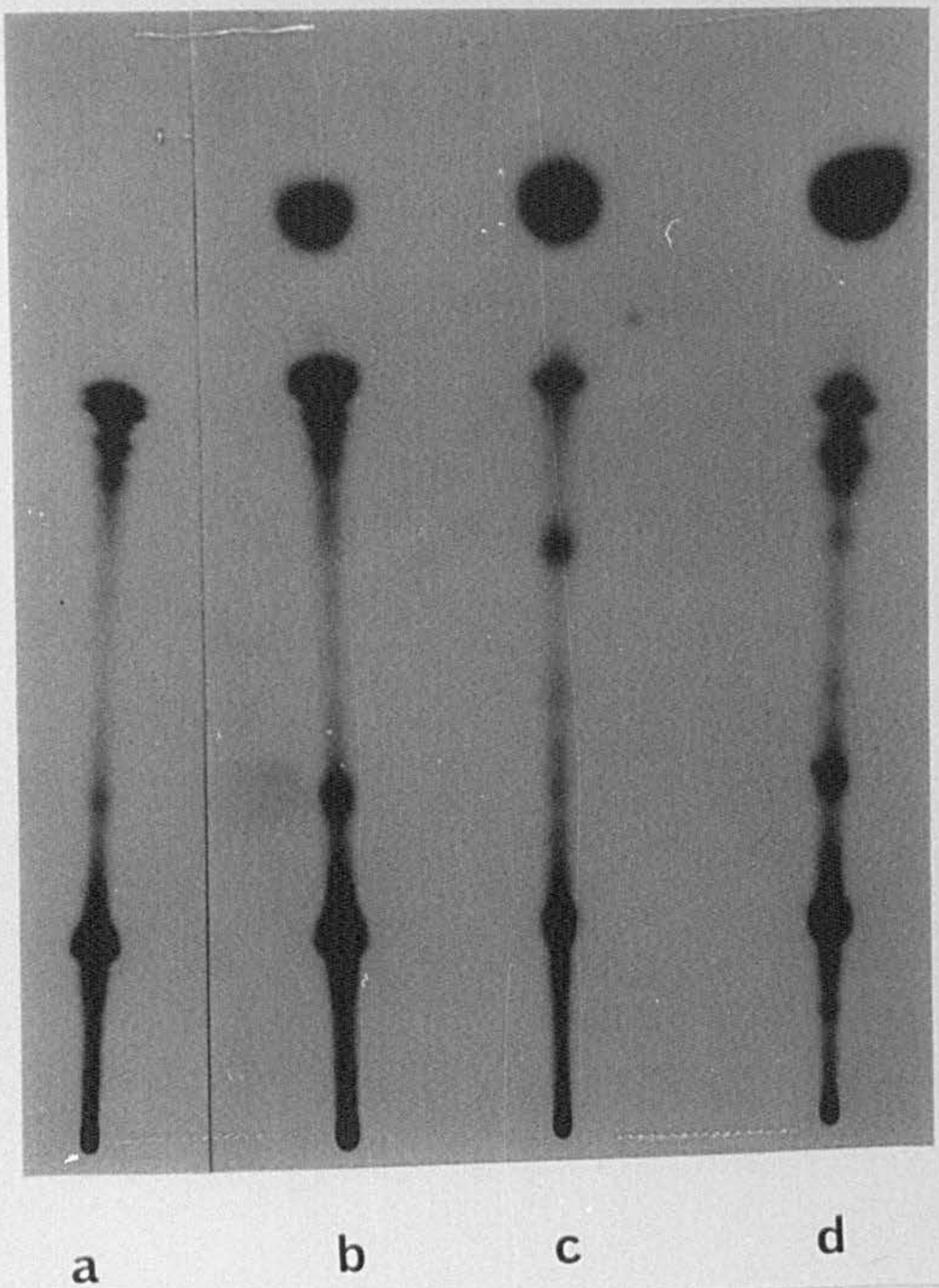


Figure 100 (B) Autoradiogram resulting from the photo-oxidation of 2-14C (I) in benzene using Rose Bengal and a soil sensitiser for singlet generation.

(a) & (b) Rose Bengal, radiation > 420nm, sample (b) contained ß-carotene

(c) & (d) Soil sensitiser, radiation from Hg discharge tube, sample (d) contained ß-carotene

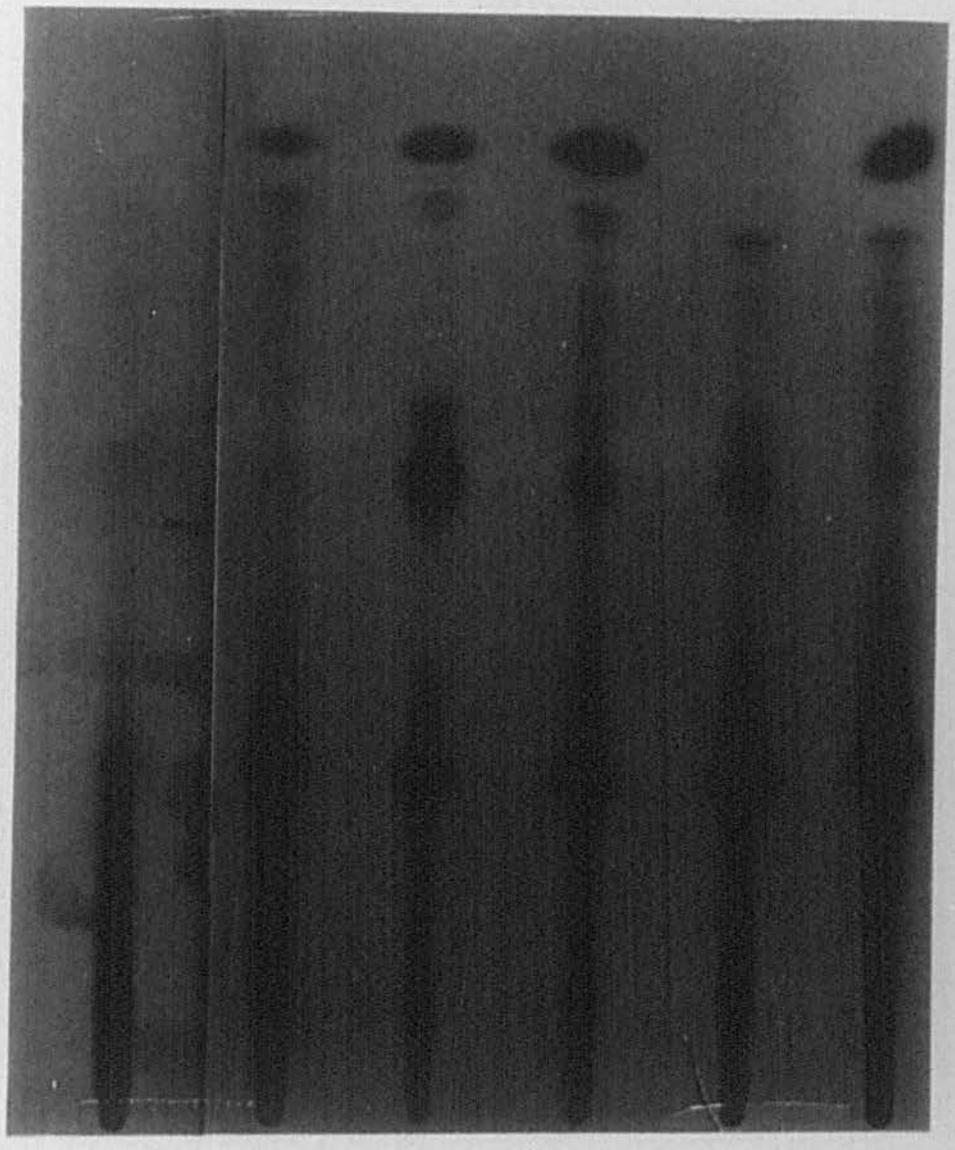
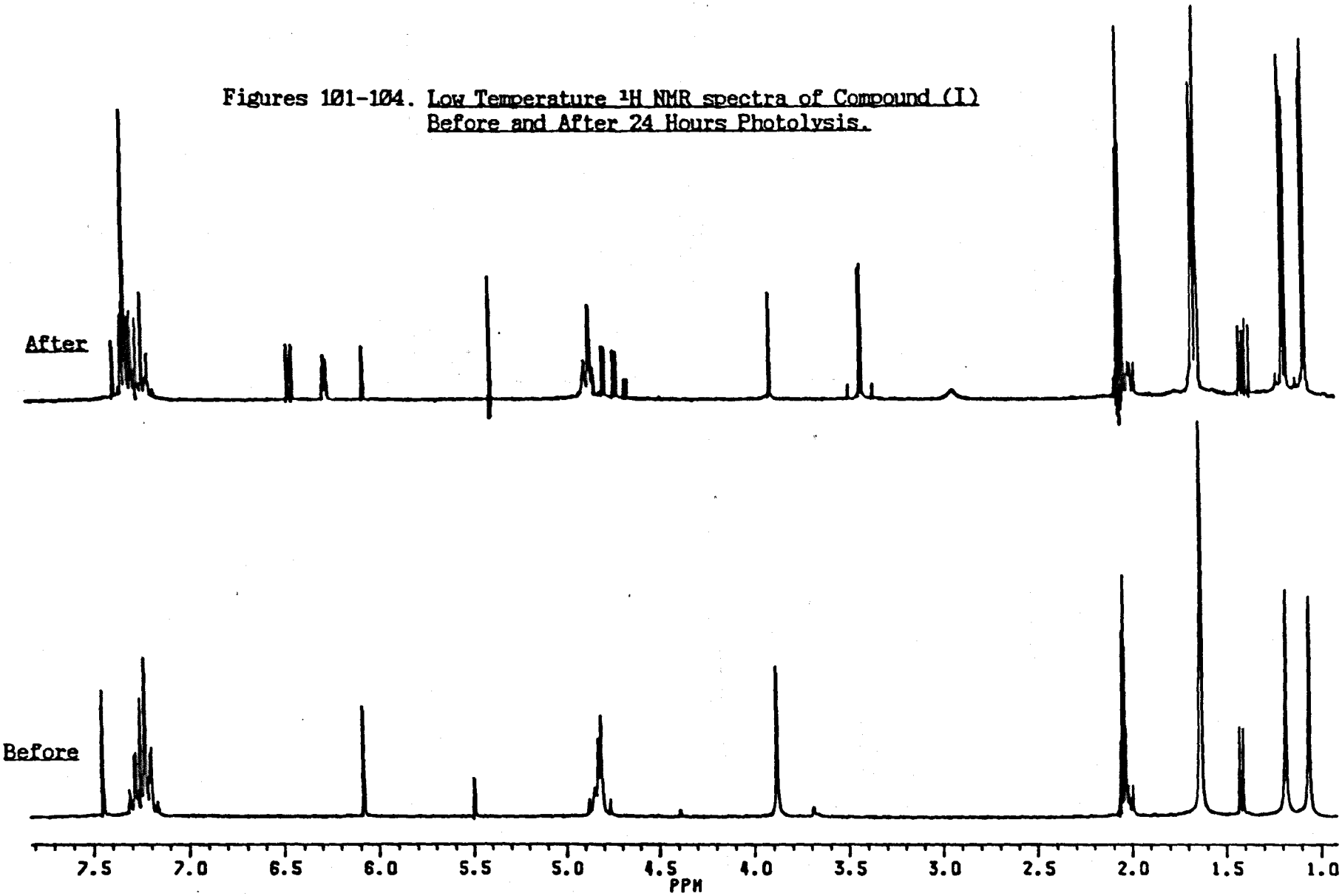
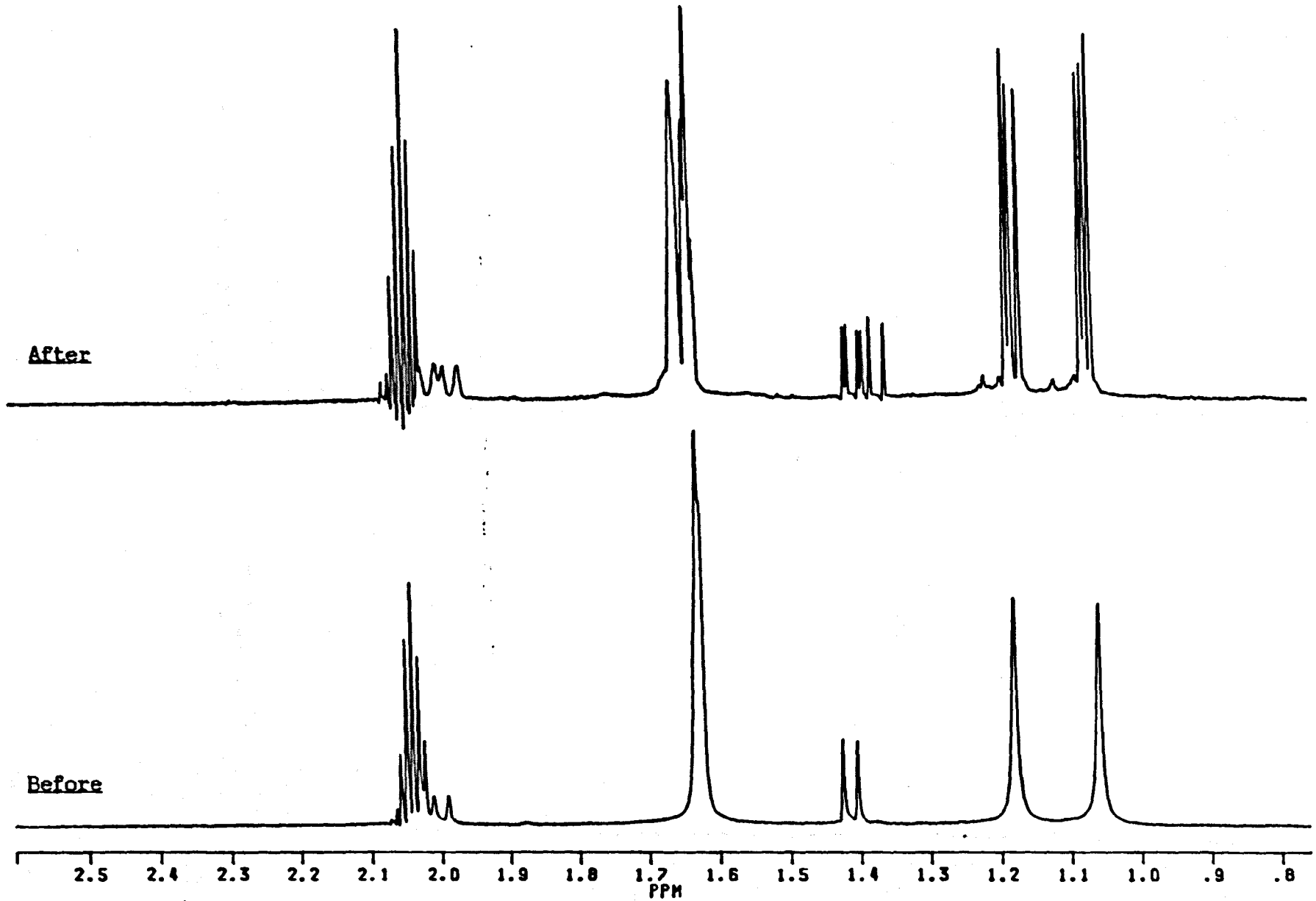


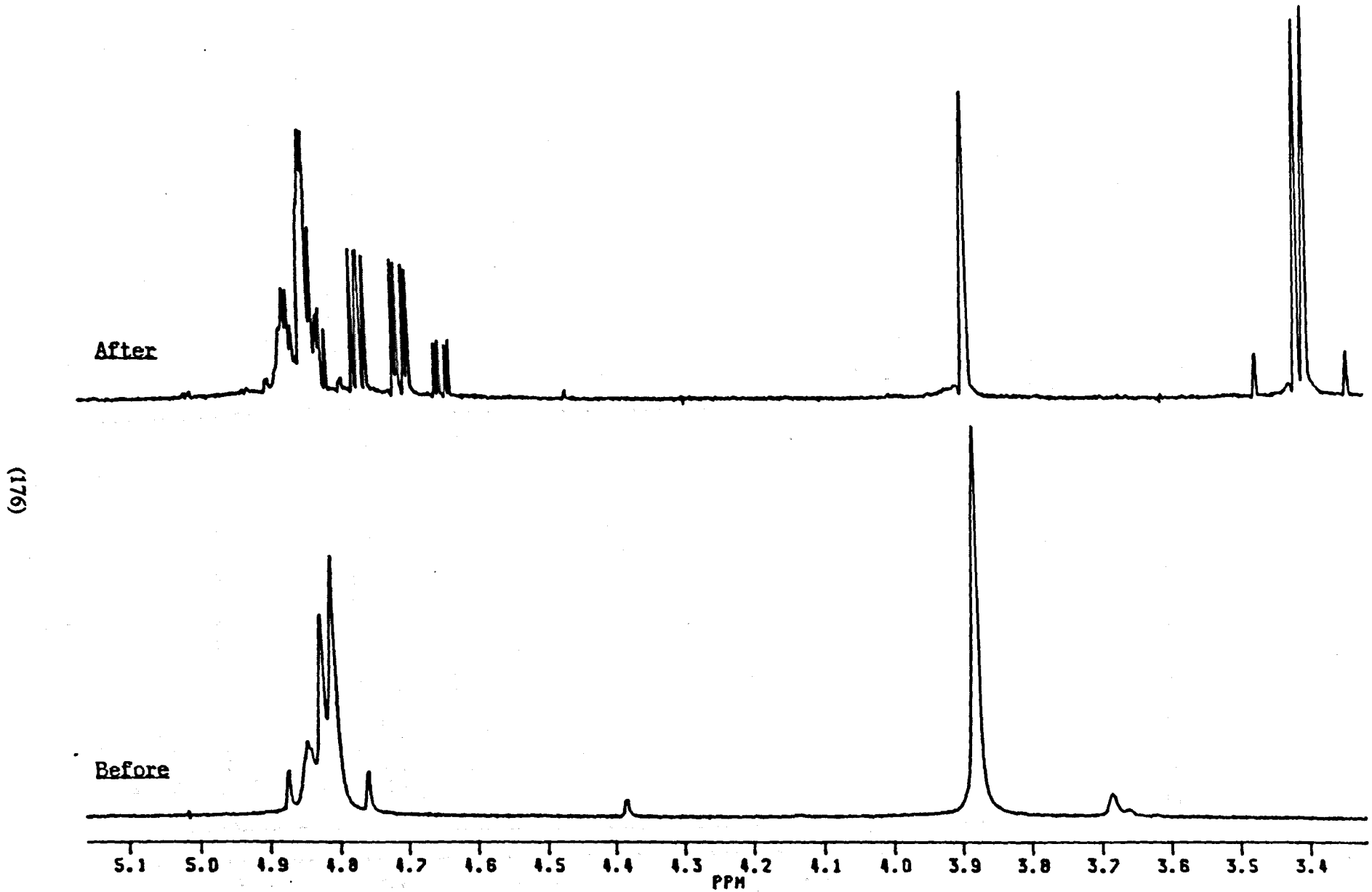
Figure 100 (C) Autoradiogram resulting from the sensitised photo-degradation of 2-14C (I) (10-4M), on silica gel. Sensitiser: (a) & (b): Rose Bengal, (c) & (d): Methylene Blue, (e) and (f): Chlorophyll. Samples (b), (d) & (f) contain β-carotene quencher (10-4M). Wavelength of radiation > 420nm.

Figures 101-104. Low Temperature ^1H NMR spectra of Compound (I) Before and After 24 Hours Photolysis.





(175)


After
Before
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
PPM

(176)

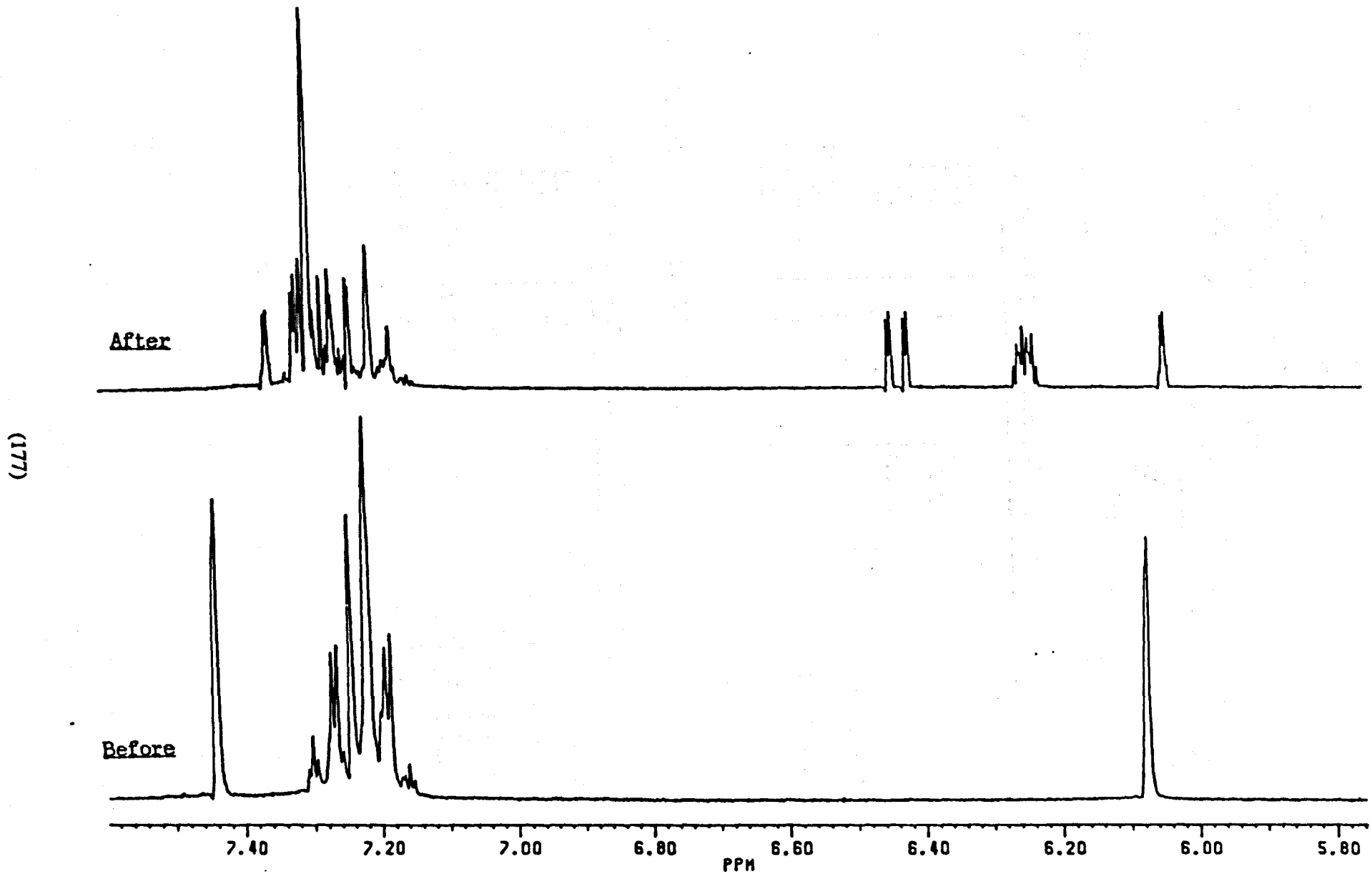
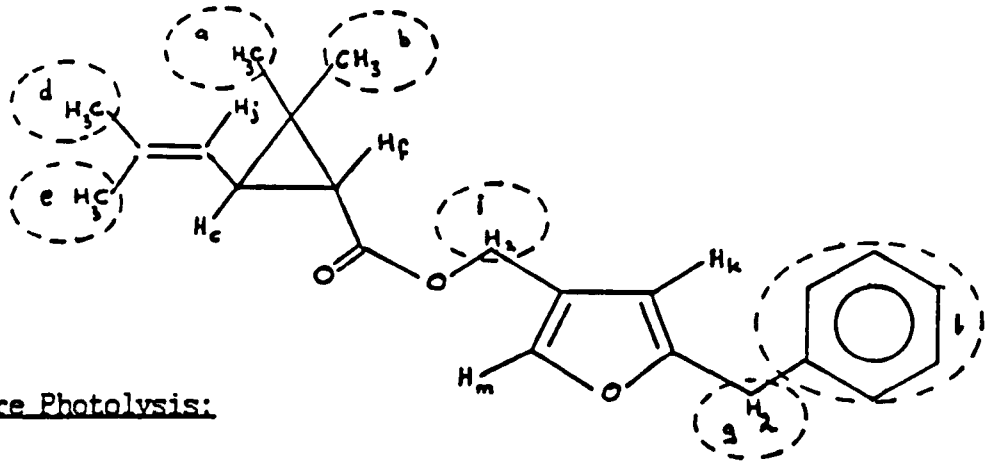

After
Before
7.40
7.20
7.00
6.80
6.60
6.40
6.20
6.00
5.80
PPM

Table 73. Analysis of NMR Spectral Data.



Before Photolysis:

Shift, d(ppm)	Multiplicity; J(Hz)		Assignment
1.05	s		} -CH3 (a,b)
1.19	s		
1.41	d	5.5	-H (c)
1.63	bs		-CH3 (d,e)
1.99	dd	7.1, 5.5	-H (f)
3.88	bs		-CH2- (g)
4.73-4.90	m		-CH2- (i), -H (j)
6.08	s		-H (k)
7.14-7.32	m		phenyl protons (l)
7.44	s		-H (m)

Additional Peaks After 24 Hours:

Shift, d(ppm)	Multiplicity; J(Hz)		Assignment
1.06	s		} -CH3 (a,b) 2 sets
1.17	s		
1.40	d	5.5	-H (c) 2 sets
1.64	bs		-CH3 (d,e)
3.42	d	15	-CH2- (g) 2 sets
4.62-4.85	m - d,d	15,1.4	-CH2- (i) 1 set
	d,d	15,2.6	-CH2- (i) 1 set
4.84-4.92	m - d,q	8,1.5	-H (j)
6.25	q	1.0	-H (k) 2 sets
6.43	d	15	-H (m) 2 sets

CHAPTER 4.

Discussion.

Production of singlet oxygen ($^1O_2$) via energy transfer from a dye photosensitiser involves the following processes:[130,131]

$$\text{Dye } (S_o) \xrightarrow{I_a} \text{Dye } (S_1)$$

$$\text{Dye } (S_1) \xrightarrow{k_f} \text{Dye } (S_o) + h\nu$$

$$\text{Dye } (S_1) \xrightarrow{k_{ic}} \text{Dye } (S_o)$$

$$\text{Dye } (S_1) \xrightarrow{k_{isc}} \text{Dye } (T_1)$$

$$\text{Dye } (T_1) + {}^3O_2 \xrightarrow{k_{O2}} \text{Dye } (S_o) + {}^1O_2$$

If a substrate species (S) that reacts with singet oxygen is present, then the following reactions have to be included in the overall reaction mechanism:

$$^1O_2 \xrightarrow{k_d} {}^3O_2$$

$$^1O_2 + S \xrightarrow{k_r} \text{Products}$$

Application of the steady state principle, to the reaction sequence given by the above mechanism results in the following expression:

$$[-d(O_2)/dt]^{-1} = (1/I_a\Phi_r) + (1/I_a\Phi_r) \times (k_d/k_r) \times (1/[S]) \qquad (18)$$

where $\Phi_r = k_{isc}/(k_f+k_{ic}+k_{isc})$

Plots according to equation (18) for the Rose Bengal sensitised photo-oxidation of compounds (I)-(V) in methanol and methanol/water (1:1) are given in Figures 31-48, 51-54 and 56-69. The linearity of these plots infers that the photo-oxidation of compounds (I)-(V) proceeds via a reaction with singlet oxygen. The ratio of slope/intercept is equal to the ratio k_d/k_r and as k_d is known for a variety of solvents[288], the value of k_r can be determined. A summary of the values of k_r for the photo-oxidation of compounds (I) - (V) is given in Table 77 (Page 183). In order to facilitate discussion of the results the structures of compounds (I) - (V) are shown below the table.

The involvement of singlet oxygen in the reactions studied is

further supported by comparison of the rate constants for the photo-oxidation of compounds (III) and (IV) in deuteromethanol/deuterium oxide and the corresponding rate constants in methanol/water (Table 59). It can be seen from the results in Table 59 that the rate constants for compounds (III) and (IV) increased by a factor of at least 7 upon deuteration of the solvent. The enhancement of the rate arises because the lifetime of singlet oxygen is significantly greater in the deuterated solvent than in the non-deuterated solvent (τ=35μs vs. τ =3.5μs respectively)[288,287] - with the effect that the steady state oxygen concentration is appreciably higher in the deuterated solvent. This consequently results in a faster rate of reaction.

The effect of sodium azide, NaN_3, on the rate constants for the photo-oxidation of compounds (III) and (IV) is shown in Table 62. It can be seen that sodium azide, a well documented singlet oxygen quencher[187], quenched the photo-oxidation of both compounds (III) and (IV) by approximately 30%. Inoue *et al.* [285] examined the effects of sodium azide on the photo-oxidation of various tryptamine derivatives in a (1:1) methanol/water solvent system and the observations of incomplete quenching by sodium azide were taken to indicate that a non-singlet oxygen pathway (a Type I process) was occurring. The Type I processs probably involved reaction of the singlet oxygen or triplet state sensitiser with the substrate to give radicals. It is not expected that this pathway would be quenched by sodium azide. Thus our results would imply that non-singlet oxygen processes played a part in the photo-oxidation of compounds (III) and (IV). This would be in direct conflict with the conclusions drawn from the linearity of the plots according to equation (18) which is a test for deciding if a photo-oxidation proceeds via singlet oxygen. The

simplest explanation for this conflict is that the quencher concentration was only 10^{-4}M, enough to show a marked fall in the rate of reaction if singlet oxygen is present but, probably not enough to quench all singlet oxygen interactions.

Another process which has been reported[285] as occurring in sensitised photo-oxidation performed in polar solvents is the reaction of singlet oxygen with a substrate (S) to give the superoxide ion via electron transfer as shown below:

$$S + {}^1O_2 \longrightarrow S^{\cdot+} + O_2^{\cdot-}$$

For the above process to occur the substrate has to have an oxidation potential less than 0.5 volts, i.e. be electron-rich. If compounds (III) and (IV) have oxidation potentials less than this figure then this may be a contributory reason for the discrepancy between the results obtained from the straight line plots and those from the sodium azide quenching of the photo-oxidations.

Measurement of the rate of photo-oxidation of compounds (III) and (IV) over a range of pH values resulted in the straight line plots shown in Figure 76-81 which were similar to those for the photo-oxidation of compounds (II) and (IV) in methanol/water. The linearity of the plots at low, intermediate and high pH values indicates that the mechanism of the reaction did not alter as the pH was changed and as oxygen was removed from the system via reaction with compounds (III) and (IV). Values for the rate constant, k_r, of the reaction at different pH values are given in Table 58, from where it can be seen that the rate constant increased for compound (III) as the pH was increased, and decreased for compound (IV) as the pH increased. Compound (IV) is chrysanthemic acid and as the pH is increased so the dissociation of the acid into the anionic form will increase. This may

account for the change in the rate constant value. In the case of compound (III), the formation of the anionic form at high pH may account for the increased rate of reaction or the increase in the value of k_r with pH may be due to an increase in the steady-state concentration of singlet oxygen as the pH is raised. This would be in accord with previous findings[273,274] that the efficiency of singlet oxygen production, using dye-sensitisers, is much greater in a basic medium than in an acidic medium.

One form of the Arrhenius equation is shown in Equation (36) below:

$$k_r = A\, e^{-E^*/RT} \qquad (36)$$

where A is the pre-exponential factor, R is the gas constant, T is the temperature and E^* is the activation energy for the reaction under consideration. According to Equation (36) a plot of ln k_r versus T^{-1} should yield a straight line of slope equal to $-E^*/R$. Such plots for the photo-oxidation of compounds (I) - (V) are shown in Figures 35, 40, 45, 50, 55, 60, 65, 70 and 75. The values of E derived from these plots are given in Tables 48 and 49 and are summarised in Table 77.

The Arrhenius equation can also be written in the form of Equation (37):

$$k_r = \frac{k\,T}{h}\, e^{-E^*/RT} \cdot e^{\Delta S^*/R} \qquad (37)$$

where ΔS^* is the entropy of activation for the reaction. The advantage of Equation (37) is that from a measurement of k_r and E^*, the entropy of activation, ΔS^*, can be calculated. The value of ΔS^* so obtained for the photo-oxidation of compounds (I) - (V) are summarised in Table 77.

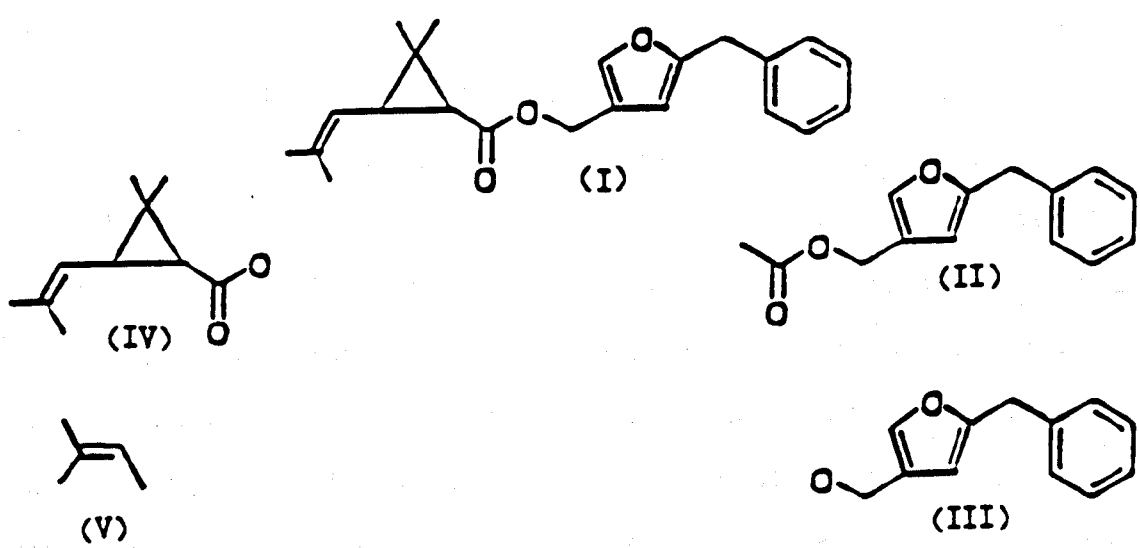
Table 77 - Summary of Results.

Substrate	Methanol			Methanol/water		
	$10^7 k_r$ *	$E^{\neq}$	$\Delta S^{\neq}$	$10^7 k_r$ *	$E^{\neq}$	$\Delta S^{\neq}$
	($mol^{-1}dm^3s^{-1}$)	($KJmol^{-1}$)	($JK^{-1}mol^{-1}$)	($mol^{-1}dm^3s^{-1}$)	($KJmol^{-1}$)	($JK^{-1}mol$)
(I)	5.2	≈0	- 97.9	—	—	—
(II)	8.3	≈0	- 96.5	82	≈0	- 74.8
(III)	3.0	≈0	-102.7	15	≈0	- 87.2
(IV)	—	—	—	2.1	93	209
(V)	0.5	≈0	- 2.0	0.1	≈0	- 133

* Temperature 298K.

--- Compound insoluble in solvent

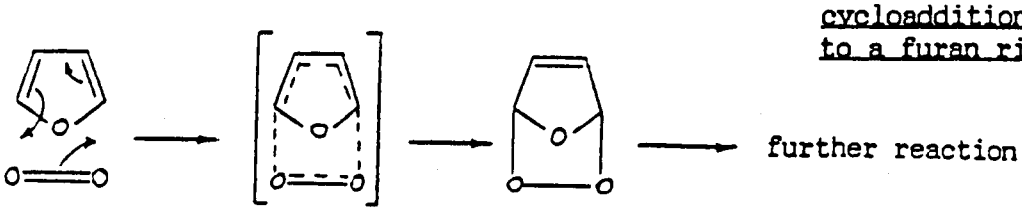
Structures of the substrates used in this study.



A comparison of the rate constants for the photo-oxidations of compounds (I)-(V) indicate that compound (I) reacts at approximately the same rate as the two other analogues possessing the furan moiety - (II) and (III). The rates of reaction of compounds (IV) and (V) are both markedly slower than those of the furan-containing compounds, approaching two orders of magnitude slower. These large differences are consistent with compound (I) reacting preferentially at its furan moiety rather than at its isobutenyl moiety. A comparison of the rate constants for the photo-oxidation of compounds (I) - (III) show that the subtle difference in electron density at the furan diene sysetem does not markedly affect the rate constant for photo-oxidation. Previous studies on furans[152,288,289] have reported k_r values in the range (3-5) x10-8 $mol^{-1} dm^3 s^{-1}$ to be not uncommon, whereas studies performed on isobutenyl-containing compounds *viz.* tetramethylethylene, 2-Methylbut-2-ene, have reported values in the range of 1 $x10^8 mol^{-1}dm^3s^{-1}$ [108,283]. These previous studies are in accord with our results in that the values of k_r for the furan containing compounds are of the order of 10^8 $mol^{-1}dm^3s^{-1}$ in both cases, whilst the values of k_r for the isobutenyl containing compounds are of the order of 10^8 $mol^{-1}dm^3s^{-1}$. This supports the inference that singlet oxygen mechanisms are the predominant photo-oxidation pathways throughout these reactions. It can be seen from Table 77 that for compounds (I), (II) and (III) which contain a furan ring, the enthalpy of activation is approximately zero in each case and the entropy of activation is close to -100 kJ mol^{-1} in each case when methanol is the solvent. These values are in accord with previous studies[152] performed on a wide variey of substituted furans. The negative entropy of activation implies that the transition state is more ordered than the initial reactants, this being indicative of a

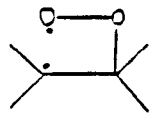
concerted, pericyclic process such as that found in the Diels-Alder reaction. There have been a number of intermediates proposed[233] for the transition state, in such a process, of which the classic (4 + 2) synchronous cyclo-addition is characterised by similar thermodynamic parameters as reported herein. The process is depicted in Figure 95:

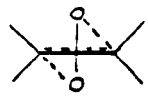
Figure 95 -The proposed(4+2) cycloaddition of $^1O_2$ to a furan ring.

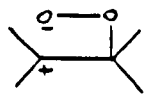


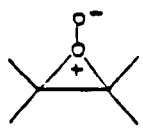
It can be seen from Table 77 that the enthalpy of activation for the photo-oxidation of compounds (I), (II) and (III) is approximately zero in both methanol and methanol/water solvent systems suggesting that the reaction ordinate in the initial stages of the photo-oxidation of the compounds is the same in both solvent systems. However, the entropy of activation for the photo-oxidation of these compounds has a larger negative value in methanol than in methanol/water. This indicates that the transition state in the former solvent system is 'looser' or less-tightly solvent bound than in the latter solvent system.

The entropy of activation for the photo-oxidation of compound (IV) is large and positive (Table 77). This implies that the transition state of the reaction is considerably less ordered than the reactants. It can be deduced from past studies[258] that "electrophilic" singlet oxygen will attack at the isobutenyl C=C bond of compound (IV). It is believed that there are four alternative transition states arising from the attack of singlet on an olefin, as shown below :

(a) biradical transition state 

(b) antarafacial transition state 

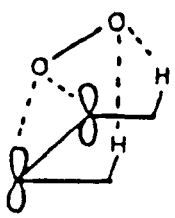
(c) zwitterionic transition state 

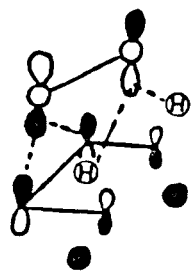
(d) periperoxide transition state 

The large positive entropy of activation for compound (IV) is most readily explainable in terms of either the zwitterionic or periperoxide transition states as neither the biradical nor the antarafacial transition states possess sufficient disorder to explain the large positive entropy of activation. Concerted reaction transition states such as the Diels-Alder type antarafacial transition state have to be well ordered to allow the delocalisation of electrons around the ring - and thus because the transition state is less ordered than the reactants this is not such a process. Previous studies[258,259] have proposed the periperoxide transition state to account for the photo-products isolated from the reaction - our findings reinforce this theory.

Because compounds (IV) and (V) both possess an isobutenyl group one would expect a very similar set of activation parameters and a similar reaction mechanism for both compounds. This was found not to be the case for in both methanol/water (1:1) and methanol the thermodynamic parameters for the photo-oxidation of compound (V) were found to be more similar to those of compounds (I), (II) and (III) than those for compound (IV). This suggests that the photo-oxidation of compound (V) proceeds by a concerted-type reaction rather than by one of the reaction mechanisms proposed for compound (IV). The difference between (IV) and

(V) may be rationally explained by possible steric hindrance in compound (IV) to the oxygen molecule approaching the C=C bond of the acid other than "end-on". Values obtained for the activation parameters $E^{\neq}$ and $\Delta S^{\neq}$ are in agreement with published data[282-284] and would be in accordance with this mechanism. A more likely theory for this difference could be explained by a frontier orbital analysis approach to the reaction between compound (V) and singlet oxygen.





If we consider the singlet oxygen molecule approaching the olefin at a bisecting angle, the olefin HOMO (with the extra $-CH_2$ contribution added in) has the potential for positive interaction between C-H groups and the oxygen. In the absence of severe steric problems, the crowded side with two such interactions would be favoured. Work performed by Schuster and Hurst[270] on compound (V) using laser flash photolysis techniques has given rise to values for an $E^{\neq}$ value of approximately zero and a negative $\Delta S^{\neq}$ value for the above bisecting reaction transition state. The low rates of reaction indicate that many hundreds of interactions between singlet oxygen and (V) are nonproductive. Once aligned in the precise orientation required for a favourable interaction there is no significant enthalpic barrier to completion of the transition state. If a similar frontier orbital analysis was performed on the chrysanthemyl moiety it would soon become apparent that it lacks the *cis*-like arrangement of the methyl protons to combine with the orbitals of the singlet oxygen molecule.

The pyrethroid, Bioresmethrin, of structure (I) contains both a furan ring and an isobutenyl group. It can be seen from Table 77 that in the photo-oxidation of compound (I) the values for the rate constant, the enthalpy of activation and entropy of activation are closely similar to those for compounds (II) and (III) which contain the furan ring only, and markedly dissimilar to those for the compounds (IV) and (V) which contain the isobutenyl group only. This can be taken as conclusive evidence that the photo-oxidation of compound (I) proceeds predominantly via attack of singlet oxygen on the furan ring. Secondary oxidation of compound (I) may occur[258,259], but any contribution to the thermodynamic activation parametersis is masked by preferential reaction at the furan site.

The interaction of singlet oxygen with a substrate can have two outcomes *viz.* physical quenching to produce ground state oxygen or chemical quenching to produce reaction products.

$$^1O_2 + \text{substrate} \begin{cases} \xrightarrow{k_q} {}^3O_2 + \text{substrate} \\ \xrightarrow{k_r} \text{photoproducts} \end{cases}$$

The rate constant, k_{ov}, for the overall quenching (physical and chemical) is given by

$$k_{ov} = k_q + k_r$$

The rate constant, k_{ov}, for the overall quenching in the reaction of singlet oxygen with compounds (I), (II), (III) and (V) was measured using the procedure of Monroe[228] and the results are given in Table 63. The ratio k_q/k_r can be used as an indicator of the relative number of interactions which result in physical quenching as compared to chemical quenching. It can be seen from Table 63 that the value of k_q/k_r for compound (I) is close to 17 and that this value is

significantly higher than the corresponding values for compounds (II), (III) and (V). This can be explained in terms of compound (I) possessing a relatively large molecular framework which can sterically hinder the approach of singlet oxygen to the chemically reactive furan ring site. The consequence of this is that approximately only one interaction in 17 between singlet oxygen and compound (I) results in photo-oxidation of the compound.

It has been reported[180] that singlet oxygen can be produced in the gas phase at atmospheric pressure using a surface-separated-reactor. The authors have shown that singlet oxygen, so generated, can travel distances of up to 1 mm before decaying and can react with substrates in solution which are held at distances less than 1 mm from the site of singlet oxygen generation. This report has important implications for the photo-degradation of agricultural chemicals in the environment in that singlet oxygen could well be generated by sensitisers (e.g. some pollutants) present in the environment and then diffuse in the gas phase to the location of pesticidal or other such material and cause the degradation of the material. In view of this, it was decided to investigate the reaction of exogeneously generated singlet oxygen with compound (I). The advantage of using gaseous singlet oxygen is that the reactions which subsequently occur with the substrate, in solution, should only be caused by singlet oxygen and by no other means.

The capability of the surface-separated-reactor described in the experimental section for producing gaseous singlet oxygen was tested using the imidazole-RNO system[183] as substrate. The presence of singlet oxygen in this system would cause bleaching of the RNO. Conversely, the observation of RNO bleaching proves that singlet

oxygen is being generated in the reactor. Results obtained for the bleaching of RNO are shown in Table 64 and in Figure 86. Clearly the reactor used in our studies produces a significant amount of singlet oxygen.

The results obtained for the reaction of exogeneously generated singlet with compound (I) and (III) in benzene solutions are presented in Tables 65 and 66 and shown in graphical form in Figures 87-90. It can be seen from the tables and figures that there is some degradation of compound (I) in the 'dark' controls where no singlet oxygen is generated, but that the degradation is significantly enhanced when singlet oxygen is produced. The fact that the enhanced degradation arises from the reaction with singlet oxygen is proved by the observation that β-carotene, a known singlet oxygen quencher, causes a reduction in the rate of degradation relative to the situation when it is not present.

If the order of reaction of singlet oxygen with compound (I) was first order with respect to the substrate, as one might expect from a simple photochemical addition reaction, then the following equation would hold:

$$\log (I)_o / (I)_t = (\text{constant}) \cdot t \qquad (35)$$

where $(I)_o$ and $(I)_t$ represents the initial concentration of compound (I) and the concentration of compound (I) at time t respectively. In such a case a plot of $\log(I)_o / (I)_t$ against time would result in a straight line plot. The results of this experiment shown in Table 69 and Figure 97 prove that the exogeneous photo-oxidation reaction under these conditions is first order with respect to the substrate.

Calculation of a rate constant for this first order reaction was thought to be acheivable by the use of either of two kinetic techniques.

The first of these techniques (Method I) involved the use of the Stern-Volmer relationship (c.f. 3.1.4.). This relationship compares two experimental systems identical apart from the fact that one contains an added singlet oxygen quencher. The following equation is derived from the theoretical study of the two systems:

$$\frac{[S]_{t=0} - [S]_{t=t}}{[S]_{t=0} - [S]_{t=t}} = 1 + \frac{k_q}{k_d + k_r[S]} . [Q] \quad (29)$$

where $[S]_{t=\emptyset}$, $[S]_{t=t}$, $[S]_{t=\emptyset}$, $[S]_{t=t}$ represent the respective initial concentrations of S in system (a), the concentration of S at time t in system (a), the initial concentration of S in system (b), the concentration of S at time t in system (b) respectively. These concentrations were determined experimentally and the plot (Figure 98) according to the LHS of equation (29) against [Q] yielded a straight line with an intercept of 1 and a slope equal to $k_q/k_d + k_r .[S]$. The values for the rate constant, k_r, for the reaction of exogeneously generated singlet oxygen with compound (I) were calculated by substituting the values for k_d in benzene[208], k_q and [S] into the expression for the slope of the plot. The average value so obtained is given in Table 72 as 1.5 x 10^{8} $mol^{-1}dm^{3}s^{-1}$ at a temperature of 280K and in benzene solution. This value is the same order of magnitude as the rate constant for the reaction of homogeneously generated singlet oxygen at 298K in methanol *viz.* 0.5 x 10^{8} $mol^{-1}dm^{3}s^{-1}$. Obviously the rate constant values are not directly comparabe because of the different temperatures and solvents, the comparability of magnitude between the rate constant for the reaction involving 'pure' singlet oxygen alone (exogenously generated singlet oxygen) and the rate constant for the dye-sensitised photo-oxidation (homogeneously generated singlet oxygen) could be taken as further evidence that the latter photo-oxidation proceeds predominantly via reaction with singlet oxygen and not other

species.

The second technique, (Method II), for the calculation of the exogeneous rate constant again involved two systems but, this time the only difference between the two was the substrate - one contained compound (I) the other contained a substrate that was known to react with singlet oxygen. A comparison of the two systems showed that the following equation would apply:

$$\frac{-d[S_1]/dt}{-d[S_2]/dt} = \frac{k_1}{k_2} \cdot \frac{[S_1]}{[S_2]} \qquad (34)$$

The rates of removal of substrates S_1 and S_2 were measured at known values of S_1 and S_2 and the ratio of k_1/k_2 was determined (Table 71, Figure 99). Substituting into the equation a value of k_1 [152] for the known substrate S_1, which was 2,5-dimethyl furan, the value of the rate constant, k_2, for the reaction of singlet oxygen with compound (I) was determined and is tabulated in Table 72. The value obtained of $1.0 \times 10^8 mol^{-1}dm^3s^{-1}$ is in agreement, within experimental error, with the value determined by Method (I) described above. It has been reported[218,217] that soils could have the potential to act as sensitisers for the production of singlet oxygen in heterogeneous systems. These reports prompted us to ascertain whether or not soil samples could act as sensitisers for the production of exogeneously generated singlet oxygen. Consequently three soil samples of pH 4.2, 5.5 and 7.5 were tested in the surface-separated-reactor to determine if they could sensitise the photo-oxidation of compounds (I) and (III). The results are given in Tables 67-68 and in the plots of Figures 91-96. It can be seen clearly from these results that the soil samples do act as sensitisers for the photo-oxidation. Although there was some photo-oxidation in the 'control' samples, brought about no doubt by direct UV irradiation of the sample, there is a very real marked

increase in the rate of photo-oxidation relative to the 'control' when a soil sample is used as a sensitiser. Furthermore, the photo-oxidation is inhibited in the presence of the singlet oxygen quencher, β-carotene. This is direct evidence that the soil samples are producing singlet oxygen which traverses the air gap in the surface-separated-reactor to enter the solution containing the compounds (I) and (III) and bring about their oxidation.

The finding that soil samples can produce singlet oxygen is important as it suggests that an agricultural chemical on a soil surface is liable to attack and subsequent degradation by reaction with singlet oxygen which has been generated by sensitisers in the soil. It is probable that the humic acids in soil are the active sensitising agents (284). The reaction of both compounds (I) and (III) with soils of different pH values was studied but, due to different loadings of the soil sensitiser on the plates, no deductions could be made apart from the fact that all three soil samples efficiently generated singlet oxygen.

The present study has shown that the agrochemical, Bioresmethrin, can be photo-oxidised by reaction with either homogeneously generated singlet oxygen. In view of our findings that chlorophyll can act as a sensitiser for the homogeneous generation and that soil samples can act as sensitisers for exogeneous generation, it is quite likely that reaction with singlet oxygen is one of the modes of degradation of Bioresmethrin in the environment. The question arises as to the photoproducts that might be formed when Bioresmethrin degrades by the singlet oxygen mode in the environment. This question led to a study of the products formed in the photo-oxidised degradation of Bioresmethrin.

The pathway to the formation of products is depicted schematically

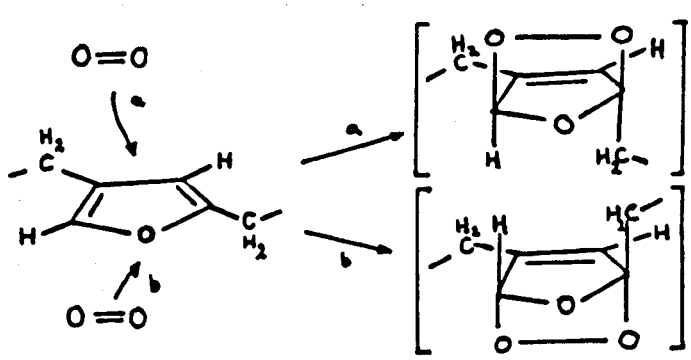
below:

Bioresmethrin + $^1O_2$ ⟶ Intermediate(s) ⟶ Products

The product study was performed in two parts. First, an NMR study of the intermediate(s) formed in the low temperature dye-sensitised photo-oxidation of Bioresmethrin (compound (I)) was undertaken. The study was performed at low temperature in order to stabilise the intermediate(s) formed. The second part of the investigation consisted of an autoradiographic study of the products formed in the photo-oxidation of compound (I) under different conditions using different sensitisers. The two parts of the study are discussed separately in the following.

A solution of Rose Bengal and compound (I) in CD_2Cl_2/CD_3COCD_3 was photolysed at 203K. The proton NMR spectra of the reaction solution before and after 24 hours of photolysis are shown in Figures 101-104 along with assignments in Table 73.

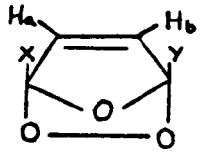
The spectrum after photolysis shows 3 components: starting material (≃20%) and 2 closely related products, the structures of which may be assigned as a pair of diastereoisomers, arising from the attack of singlet oxygen from above or below the furan ring.

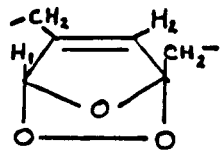


The spectrum of the above endoperoxides is consistent with that

found in previous studies[232] on isolated 2,5-substituted furan endoperoxides. The furan proton chemical shifts for these compounds are compared with those obtained from this study in Table 74.

Table 74. Furan Endoperoxide Chemical Shifts in Selected Compounds.





Compound	Substituent X	Substituent Y	^{1}H Chemical Shifts, δ (ppm)
a	$-CH_3$	$-CH_3$	6.83_a, 6.83_b
b	-H	$-CO_2C_2H_5$	6.77_x, 6.79_a, 6.86_b
c	-C6H5	$-C_6H_5$	5.95_a, 5.95_b
d	-H	$-CH_3$	6.34_x, 6.38_a, 6.48_b
(I)	-H	$-CH_2^-$	6.26_2, 8.43_1

The spectra in Figures 101-104 show no indication of photo-oxidative attack at the chrysanthemyl moiety or cleavage of the ester into its conjugate acid or alcohol. Under these experimental conditions the degradation of compound (I) would appear to proceed solely by a Type (II) process to yield a 1:1 mixture of diastereo-isomeric ozonides as the initial intermediates in the reaction of singlet oxygen with compound (I). This is in agreement with the conclusions drawn earlier from the kinetic studies.

The final products in the sensitised photo-degradation of compound (I) were 'observed' by autoradiography of the mixture of products formed during experiments using ^{14}C-labelled compound (I). The autoradiograms so obtained are shown in Figures 100 (A), (B) and (C). In each of the autoradiograms the 'leading' spot is the one with the longest R_f value, is that of compound (I). It is obvious from the autoradiograms that a complex mixture is formed under all the

conditions used, this being especially so when it is borne in mind that the autoradiograms only show those products carrying the ^{14}C-label. There could be many products formed which do not have the ^{14}C-labelled carbon atom in their structure. The complexity of the product mixtures precluded isolation of individual components and their characterisation by spectroscopic means. Whether the products observed in the autoradiograms were formed during the photolysis time of the sensitisation experiments or were formed on subsequent degradation of such products on the silca gel of the tlc plates is an open question. Notwithstanding this, inferences can be drawn from different experiments as discussed below.

Comparison of the autoradiograms (a) and (b) of Figure 100 (A) which result from the reaction of compound (I) with homogeneously generated singlet oxygen shows quite clearly that the presence of the singlet oxygen quencher, β-carotene, in system (b) has inhibited the degradation of compound (I). Thus, in system (a) compound (I) has completely disappeared whereas in system (b), wich was photolysed under the same conditions, a high percentage of compound (I) still remains. The inhibiting effect of β-carotene is in accord with our findings that singlet oxygen has a predominant role in the sensitised photo-oxidation of compound (I) in homogeneous solution.

The number of products appearing in the autoradiogram of system (a) is clearly greater than those of the other systems (b) - (d). However, this could be due to the fact that in the former system, compound (I) has completely degraded and the concentration of products in this system, and hence spot intensity, will be higher than in systems (b) - (d) where only partial degradation of compound (I) has occurred. Clearly, however, a number of the products formed are the

same for the situations where singlet oxygen is generated homogeneously, heterogeneously and exogeneously.

Comparison of the autoradiograms (c) and (d) of Figure 100 (A) shows that the effect of the presence of β-carotene is to prevent the formation of the product at R_f = 0.4 in the non-quenched raction of system (c). Also, a comparison of the autoradiograms (e) and (f) of Figure 100 (A) shows that the effect of β-carotene is to enhance the formation of the product at R_f = 0.7 in the quenched reaction of system (f). It is not possible to give an explanation of such effects without knowing the compounds involved and whether or not the products arise from direct photo-sensitisation or degradation of the photo-formed products on the tlc plates.

Comparison of the autoradiograms (a) and (b) of Figure 100 (B) which result from the reaction of compound (I) with heterogeneously generated singlet oxygen again shows quite clearly that the presence of the singlet oxygen quencher, β-carotene, inhibits the degradation of compound (I) in homogeneous solution.

The autoradiograms (c) and (d) of Figure 100 (B) are for the products formed in the reaction of exogeneously generated singlet oxygen (soil samples as sensitisers) with compound (I). Comparison of these autoradiograms with those of the autoradiograms (a) and (b) of Figure 100 (B) shows that a similar set of products is found in both systems. This shows that the soil sample acts as a sensitiser in a similar fashion to the dye sensitiser, Rose Bengal, and reinforces the conclusion reached previously that soil can act as sensitisers in the production of singlet oxygen.

The autoradiograms of Figure 100 (C) are for the products resulting from the Rose Bengal, Methylene Blue and chlorophyll

sensitised photodegradation of compound (I), on silica gel (procedure as given in section 3.5.3.). Here again, comparison of autoradiograms, *viz.* (a) with (b), (c) with (d), (e) with (f), shows that β-carotene inhibits the degradation of compound (I). However, in this case, the degradation is taking place homogeneously in benzene or other solvent, and yet the β-carotene is still acting as a quencher of the singlet oxygen produced via the dye and chlorophyll sensitisers.

Comparison across the autoradiograms (c) - (f) of Figure 100 (C) shows that there appears to be no appreciable difference whether the sensitiser be Rose Bengal, Methylene Blue, or chlorophyll. This is not unexpected if the photo-degradation is occurring primarily via reaction with singlet oxygen as these dyes and chlorophyll are standard sensitisers for the production of singlet oxygen.

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POSTGRADUATE STUDIES

Basic Pogramming,	Kingston Polytechic	1986
Pascal Programming,	Kingston Polytechnic	1986
High Performance Liquid Chromatography,	Kingston Polytechnic	1987
Nuclear Magnetic Resonance Spectrometry,	Kingston Polytechnic	1987
Gas Chromatography,	Kingston Polytechnic	1988

Many research colloquia and special lectures have been attended during the course of this project, and a research colloqium has been given.