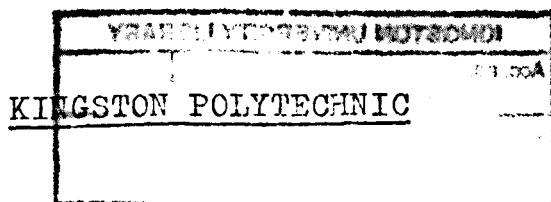


AUTOXIDATION STUDIES OF ORGANOBORANES
AND SELECTED ORGANO-TRANSITION METAL,
SIGMA-BONDED COMPOUNDS

by

J.C. HODGSON

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



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SUMMARY

The preparation and properties of organoboranes have been reviewed with particular reference to their synthetic usefulness. A detailed survey was made of organoborane autoxidations and also of organoperoxyboron compounds, and the literature concerning these systems as vinyl polymerisation initiators considered. A historical survey of the novel σ -bonded organotransition metal compounds has also been made.

The primary initiation of trialkylborane autoxidations was studied by measuring the rate of absorption of oxygen by organoborane solutions whilst under inhibition by galvinoxyl. The reaction was found to be a second order process and rate constants were evaluated as $1.84 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for tri-s-butylborane, $0.94 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for tri-isobutylborane, and $22.8 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for tricyclohexylborane. Previously determined initiation rates were converted into rate constants and comparisons made between results.

The thermal decomposition of di-n-butyl n-butylperoxyborane, di-n-butylperoxy n-butylborane, and di-s-butylperoxy s-butylborane was studied both iodometrically and by their ability to initiate the polymerisation of vinyl acetate. It was concluded that the major route of decomposition was a non-radical intramolecular rearrangement reaction and the first order rate constants were for di-n-butyl n-butylperoxyborane, $k = 6.0 \times 10^3 \text{ e}^{-11,100 \pm 530/RT} \text{ s}^{-1}$; for di-n-butylperoxy n-butylborane, $k = 4.55 \times 10^4 \text{ e}^{-14,300 \pm 1,070/RT} \text{ s}^{-1}$; and for di-s-butylperoxy s-butylborane, $k = 6.46 \times 10^5 \text{ e}^{-15,900 \pm 400/RT} \text{ s}^{-1}$.

A brief study was also made of the reaction between organoperoxyboranes and organoboranes, but it was not possible to draw any definite conclusions concerning this process.

A preliminary investigation was made of the autoxidation of several σ -bonded organotransition metal compounds, tetrakis (trimethylsilylmethyl) titanium, tetrakis (trimethylsilylmethyl) zirconium, hexakis (trimethylsilylmethyl) bimolybdenum, hexaneopentyl bimolybdenum, hexabenzyl bitungsten and tetrabenzyl zirconium. The reactions were extremely vigorous at 20°C and, with the exception of tetrabenzyl zirconium, at -74°C. It was shown that peroxidic intermediates were involved, although the major product was the corresponding alkoxy compound. The effect of various inhibitors was studied and phenothiazine was found to retard the majority of the autoxidations. Because of the great speed of the processes, conclusive evidence concerning the nature of the mechanism was not obtained, but a free-radical chain reaction seemed most probable. The influence of steric shielding and π -bonding ligands on the rate of reaction were discussed, and from this preliminary study the lines for future research are apparent.

PART 1

HISTORICAL SURVEY

CHAPTER 1

ORGANOBORON COMPOUNDS

1. Introduction.

The major part of the work presented in this thesis is concerned with the reaction of oxygen with selected σ -bonded organometallic compounds. The well known organoboranes were chosen for an intensive study, and the experience accumulated during this period was then applied to certain less well characterised early transition metal compounds.

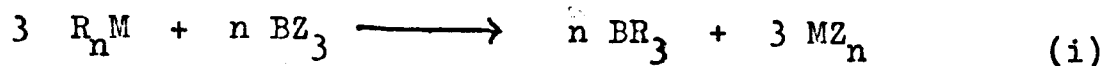
The organic chemistry of boron has developed with remarkable speed during the last ten years, probably prompted by an interest in their possible uses as rocket fuels. Although interest in this aspect has declined, the interest of research groups in these compounds has expanded. Accompanying this upsurge of interest, there has been, of course, a large volume of published material; fortunately, there are now several excellent reviews and books available, notably those of Gerrard¹, Davies², Lappert³, Coates⁴, and Niedenzu⁵. However, a brief review of the more recent literature relating to those properties of organoboranes

pertinent to the synthetic and mechanistic aspects of this thesis will now be given.

2. Synthesis.

The synthesis of organoboranes has been achieved by either of two main preparative procedures; firstly by transmetallation, and secondly by hydroboration which is the reaction between diborane and an olefin.

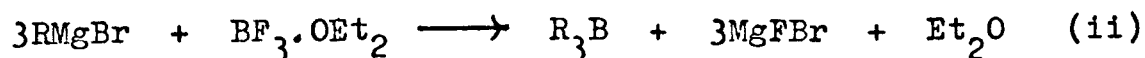
The process of transmetallation involves the reaction between an organometallic compound and a boron halide or ester, the general equation for which, is:-



where $M = Zn^{6,7}, Mg^8, Li^9, Al^{10}$

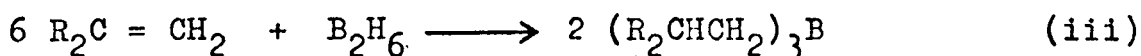
$Z = OR^{11,12}, Cl^7, F^{13}$

The most convenient method, and the method used in this study, was that of Hennion, McCusker et al.¹⁴, which was the reaction of the appropriate Grignard reagent with boron trifluoride etherate:-

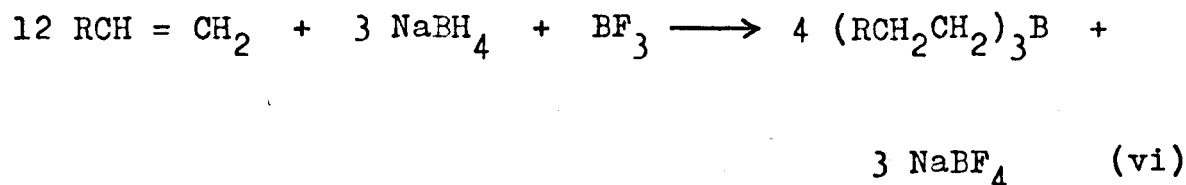
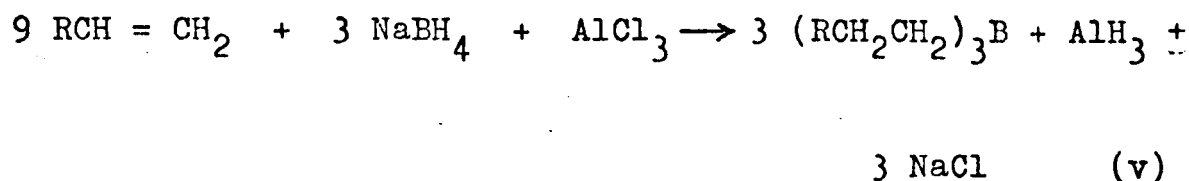


Yields were usually excellent.

Hydroboration is the reaction between an olefin, or acetylene, and diborane.



This reaction was first investigated by Hurd¹⁵ in 1948 and he found that it was very sluggish, requiring high temperatures and long reaction times. Subsequent work, however, by Brown and co-workers showed that the reaction could be catalysed by the use of ethers as solvents, and these major routes were reported by Brown and Subba Rao in 1956¹⁶ and 1957¹⁷:-

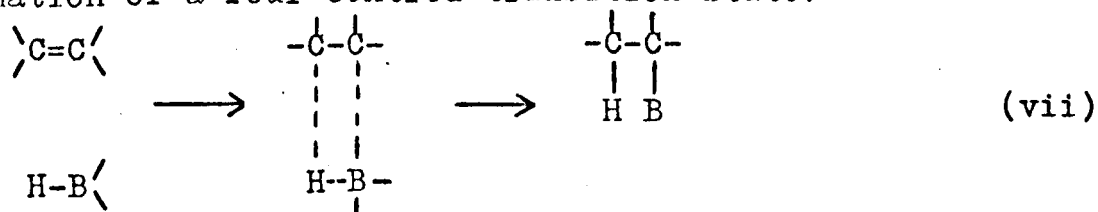


All of these reactions were carried out in an ether of convenient boiling point so that the organoborane was readily separated. The yields were usually in excess of 90%. There are now many experimental procedures available for hydroborating an olefin, so that reaction conditions

may be tailored for a particular olefin; these are fully described by Brown and Zweifel.^{18,19}

If the olefin for hydroboration was unsymmetrical, then the boron atom attached itself to the least substituted of the two carbon atoms of the double bond.²⁰ This was satisfactorily explained in terms of electronic factors; the terminal carbon atom of an unsymmetrical olefin has a slight negative charge due to hyperconjugation, whilst the boron atom, because of an inductive effect, has a slight positive charge, hence the observed directive effect. If diborane is used as the hydroborating agent, steric effects are not normally noticed, but if mono- or dialkylboranes are used, then steric factors can play an important part in determining the rate and direction of addition. Thus, the hydroboration of 1-pentene and styrene by diborane yielded 94% and 80% respectively of the terminal borane, whereas using the dialkylborane derived from 2-methyl-2-butene (given the contracted name "disiamylborane"¹⁸) as the reagent, this figure was in excess of 98% for both olefins.²¹

By studying the hydroboration of a number of selected olefins, and in particular norbornene, Brown and his co-workers were able to show that the hydroboration reaction almost certainly occurred with cis-addition.^{22,23} To explain this, it was suggested that the reaction involved the formation of a four-centred transition state:²²



3. Physical Properties.

With respect to their melting and boiling points, solubilities etc., the organoboranes usually resemble the corresponding hydrocarbons.

The orbitals used in bonding by the boron atom in a simple trivalent compound are considered to be sp^2 hybrids, and since the compounds are invariably monomeric, the organic groups occupy a planar configuration around the central boron atom with bond angles of 120° . However, the boron atom can also make use of sp^3 hybrid orbitals in order to achieve a covalency of four, in such ions as $(BH_4)^-$, or in simple co-ordination compounds when the boron accepts electrons from a donor, for example, $(CH_3)_3B:NH_3$. This ability of boron to switch from three to four co-ordination is a property of special relevance to this work.

The determination of the structures of organoboranes has been greatly facilitated in recent years by the application of spectroscopic techniques. The infra-red spectra of organoboranes are now well documented and several reviews have been published.^{24,25} Some of the more common group frequencies are given in Table 1.

Natural boron consists of two isotopes, ^{10}B (18.8%) and ^{11}B (81.2%), both of which have nuclear spins, and thus it is possible to obtain boron magnetic resonance spectra.

In the latter spectra, complicated splitting patterns can arise because the two boron isotopes have different

TABLE 1

Infra-red Spectra of Organoboranes. Common Group Frequencies.

COMPOUND	GROUP	VIBRATION	FREQUENCY (CM ⁻¹)
B-ALKYL	B-Me	ASYM. DEFORMATION	1405 - 1460
		SYM. DEFORMATION	1280 - 1330
	BC ₂	ASYM. STRETCH	1110 - 1175
		SYM. STRETCH	770 - 830
B-ARYL	B-ARYL	STRETCH	1125 - 1280
	ARYL		1430 - 1440
B-O	B-O	STRETCH	1310 - 1380

nuclear spins, that of ¹⁰B is 3, while that of ¹¹B is 3/2. However, for general purposes, this can be considered as a first-order effect, and thus it does not show up in the spectra of trialkylboranes only in those compounds with a proton directly bonded to the boron atom.

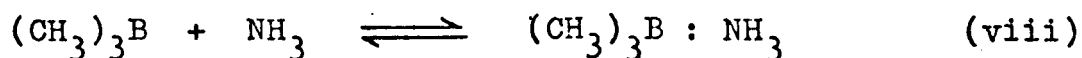
Boron magnetic resonance spectra are most commonly based on the ¹¹B isotope and the effect occurs, in a constant field strength of 14,092 gauss, at a frequency of 19.25 MHz. The spectra obtained are complicated by substantial line broadening since the isotope does possess a nuclear quadrupole moment. In spite of this, the technique is very useful, for example the change of a boron atom from three to four co-ordination is accompanied by a large chemical shift.

This subject is now well documented and reviewed^{26,27,28}.

4. Chemical Properties.

(a) Lewis Acidity.

As mentioned previously, a trivalent boron atom shows a strong tendency to accept electrons in order to achieve a more stable octet. This ability of organoboranes to react with bases was first noted by Frankland:²⁹

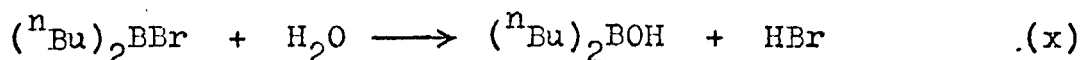
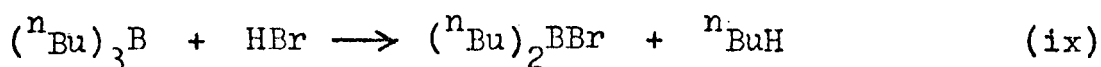


Brown has since made use of these addition compound forming reactions in order to study steric effects^{30,31}, and there is now a considerable amount of thermodynamic data available concerning the reactions of organoboranes with bases³². More recently, Ingold, Davies et al. have made use of this property in order to obtain absolute rate constants for the propagation step in the reaction of trialkylboranes with oxygen, since the concentration of available borane (unco-ordinated) at any one time, is very small^{33,34}.

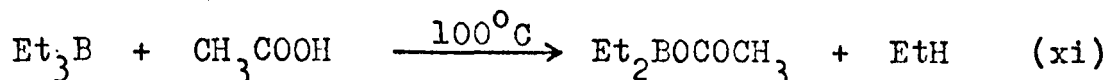
(b) Protonolysis.

The organoboranes were reasonably stable towards water³⁵, hydrogen sulphide³⁵, alcohols and phenols⁴⁰, quite vigorous conditions being required to bring about reaction. The hydrolysis of trimethylborane with water at 180°C, over a period of seven hours, only removed one alkyl group, producing 69% of dimethylboronic acid³⁵.

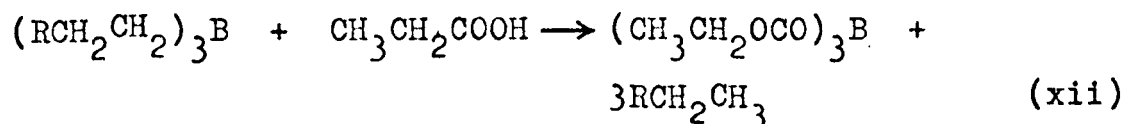
Hydrolysis by mineral acids was somewhat easier, though even so, only one of the alkyl groups could be removed. For example, heating tri-n-butylborane with 48% hydrobromic acid to reflux for 1 hour produced a quantitative yield of di-n-butylboronic acid¹¹:



In contrast, the action of carboxylic acids on organoboranes resulted in the removal of alkyl groups with surprising ease. Triethylborane was readily converted into diethylboron acetate and ethane by reaction with acetic acid³⁶:



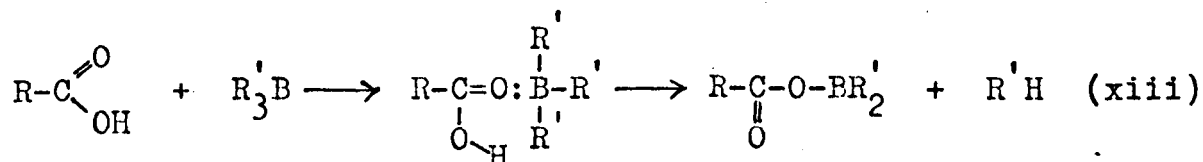
Further, it has been shown that all three alkyl groups could be removed from the organoborane by refluxing with excess propionic acid in diglyme for two to three hours³⁷:



It can be seen that one of the products of this reaction is the alkane which is produced in almost quantitative amounts. Thus a simple route for the conversion of an olefin into an alkane, by a non-catalytic method, is provided by a

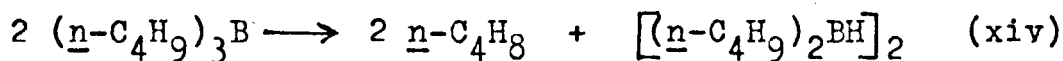
combination of hydroboration and protonolysis.

The mechanism for this reaction is not entirely clear, although it was suggested that it involved co-ordination followed by an intra-molecular attack on the boron to carbon bond by the proton¹⁸:

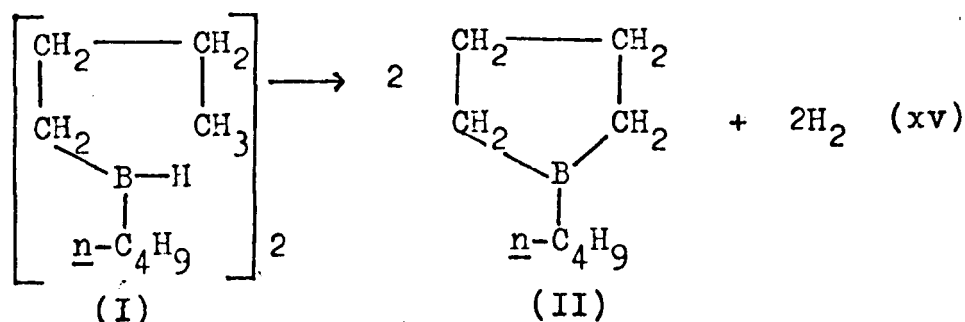


(c) Thermal Behaviour.

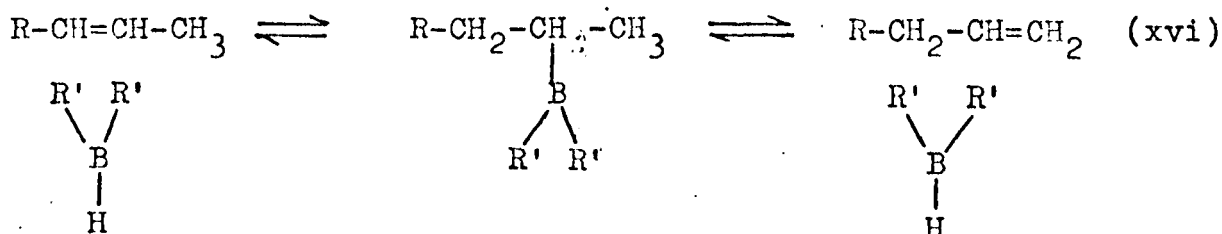
When trialkylboranes are heated at reflux, they tend to decompose to form dialkylboranes and olefins, i.e., retro-hydroboration. Thus heating tri-n-butylborane at 110°C resulted in the formation of n-butylborane and butene³⁶:



If the reaction was carried out in an autoclave at 300°C, the products were butene, hydrogen and a cyclic borane, 1-n-butyl boracyclopentane³⁷. The reaction probably involved the prior formation of the alkylidiborane(I), which then lost hydrogen to yield the cyclic product(II):

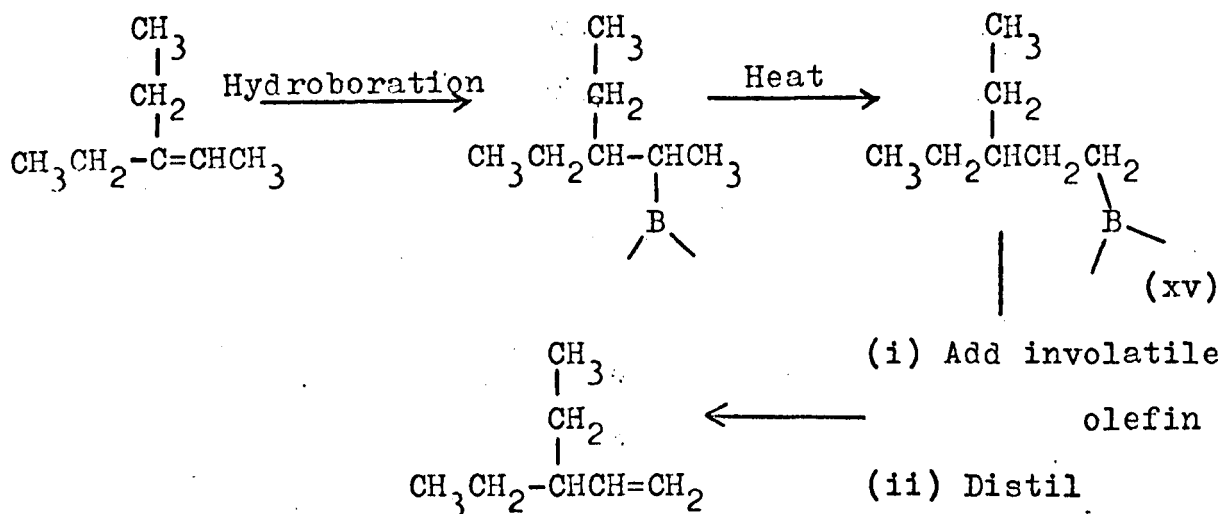


Another important thermal reaction is isomerisation at moderate temperatures, a reaction which is catalysed by diborane. For example, tri-sec-butylborane thermally isomerised to give tri-n-butylborane; in the absence of diborane the required conditions were 210°C for 48 hours¹⁴, but with a trace of diborane the reaction proceeded quickly at 120°C¹⁷. A possible mechanism for this process involves the formation of a series of labile equilibria:



Thus the boron atom is considered to move freely about the carbon structures of the alkyl groups of the organoborane, and finishes in the least hindered position. This is illustrated by the isomerisation at 125°C of the organoborane derived from 3-hexene.³⁸ In the original organoborane, the boron atom was almost exclusively attached at the 3- position, but after heating for eight hours at 125°C the product consisted of 82% of the 1-isomer.

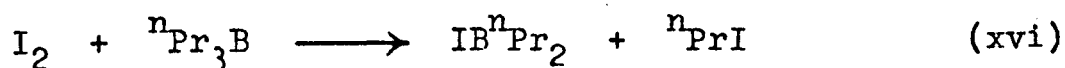
Evidence for the mechanism suggested in (xvi) was provided by the observation, that, if a second less volatile olefin was added to an organoborane, the original olefin could be distilled out.¹⁷ This is of synthetic importance since the contrathermodynamic isomerism of an olefin may be readily achieved:



(d) Halogenation.

The direct reaction of trialkylboranes with the halogens was very slow although the lower members reacted vigorously with resulting substitution in the alkyl chain.

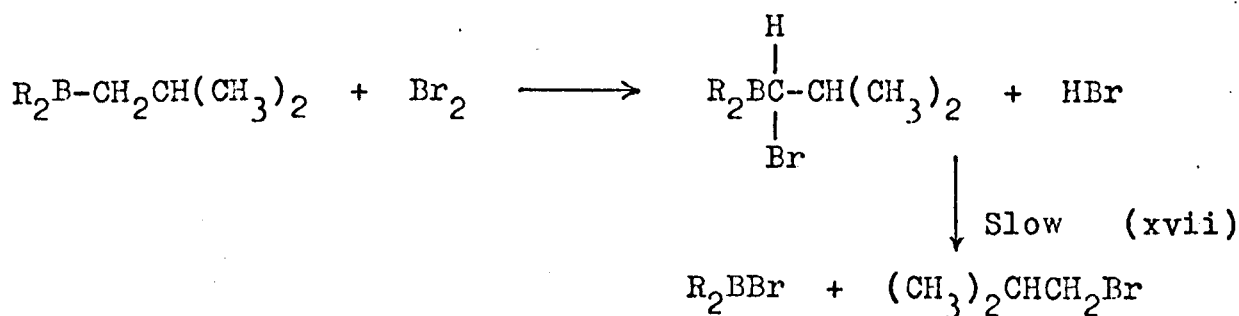
Trimethylborane reacted with chlorine in the gas phase at -95°C to produce chloromethyldimethylborane.³⁹ Direct substitution of an alkyl group by a halogen was difficult and usually only one alkyl group could be removed. For example, the reaction of iodine with tri-n-propylborane at 150°C yielded only iodo di-n-propylborane:⁴⁰



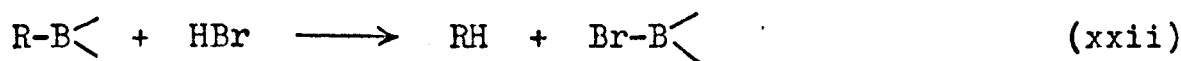
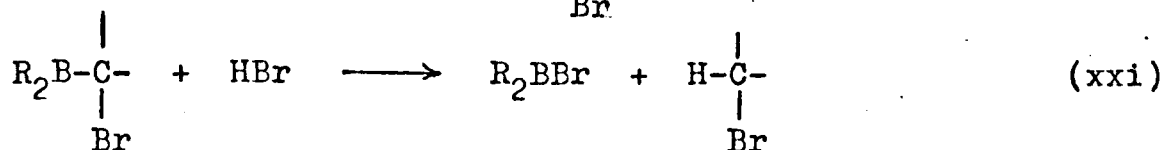
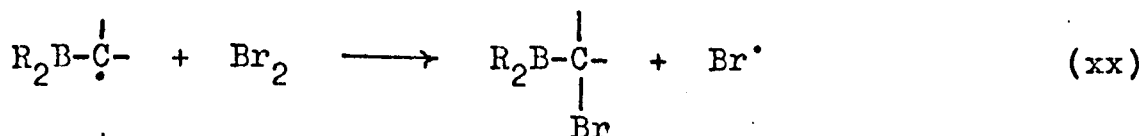
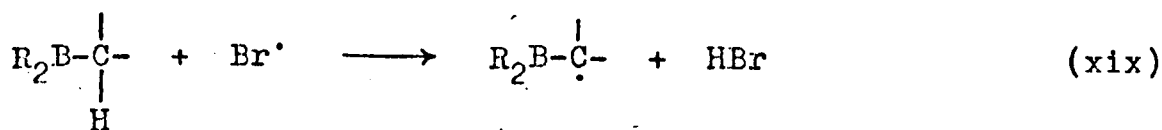
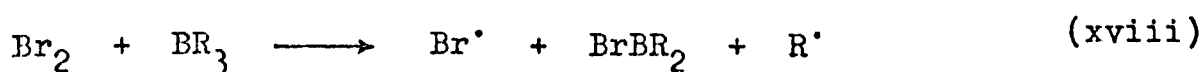
Any attempt to force the reaction further only resulted in substitution in the alkyl group.

More recently, Brown has studied the reaction of bromine with organoboranes in the dark and concluded that the reaction involved the prior attack by bromine at the α -position in the alkyl chain, followed by cleavage of the

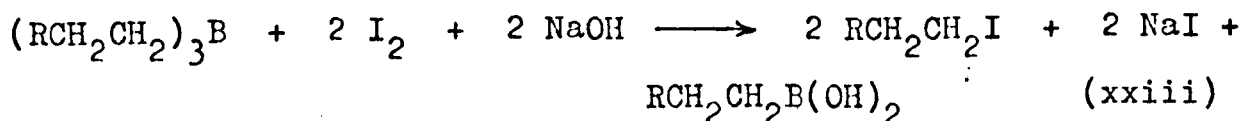
boron - carbon bond by the hydrogen bromide formed:⁴¹



The mechanism postulated for this reaction was one involving free radicals:



If the reactions were performed in the presence of base, two alkyl groups could be removed very quickly, even at 0°C. Iodination was easily achieved in the presence of sodium hydroxide:⁴²



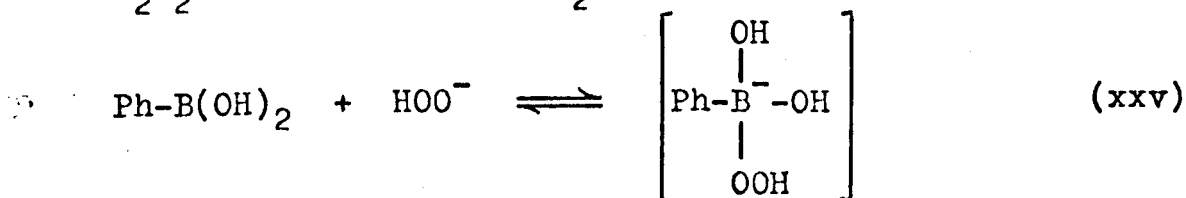
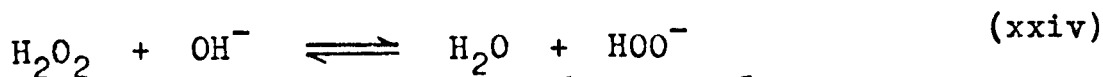
For bromination, it was found preferable to use sodium methoxide as the base, to avoid oxidative side-reactions due to the formation of sodium hypobromite in sodium hydroxide.⁴³

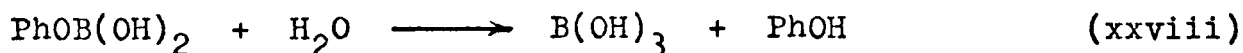
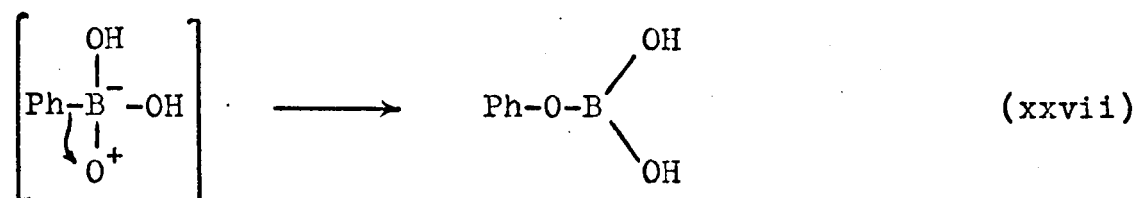
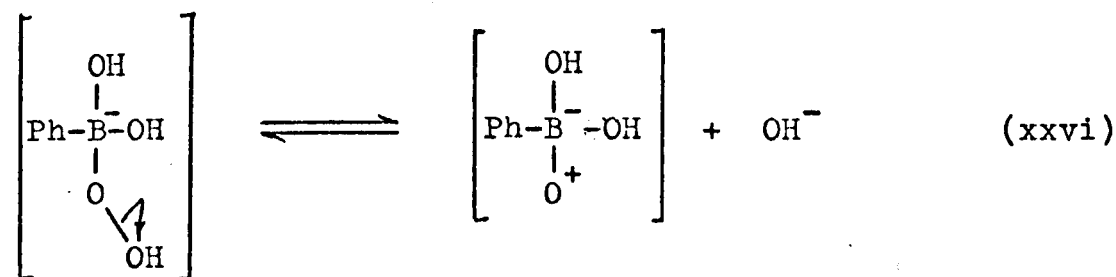
These reactions again are of synthetic value, since they result in the anti-Markovnikov hydrohalogenation of the original olefin.

(e) Oxidation

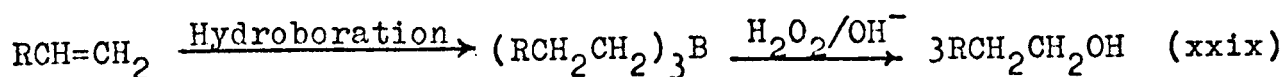
The fact that the organoboranes are very sensitive to oxygen has long been known. Because of the relevance of the autoxidation of organoboranes to this thesis, this property will be dealt with at length in the following chapter.

Oxidation has also been achieved with alkaline hydrogen peroxide, chromic acid, or amine oxides. The reaction of organoboranes with alkaline hydrogen peroxide was first investigated by Johnson et al.,⁴⁴ and they found that the final products consisted of boric acid and the corresponding alcohol. Kuivila and Armour studied the similar reaction of phenylboronic acid and alkaline hydrogen peroxide and they suggested the following mechanism:⁴⁵





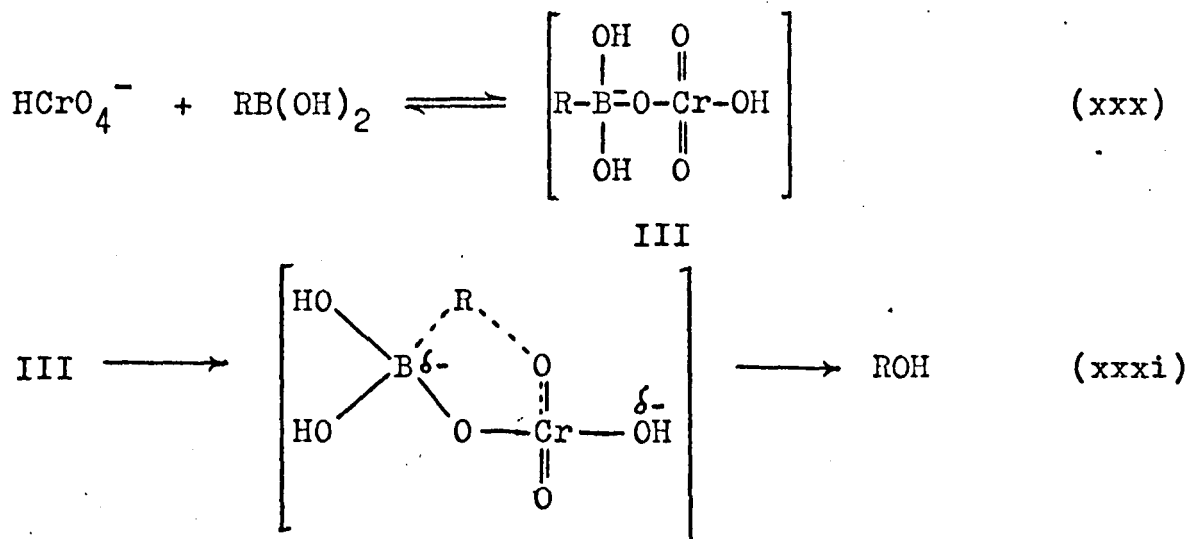
Thus, it can be seen, that basically the reaction involved co-ordination followed by a 1,2 nucleophilic shift of the phenyl group from boron to oxygen. Further evidence was provided by Davies and Roberts who reported that the diethanolamine ester of optically active 1-phenylethylboronic acid was oxidised to 1-phenylethyl alcohol with retention.⁷² Brown has since developed this reaction as a method for the synthesis of alcohols, obtaining almost quantitative yields under mild conditions:⁴⁶



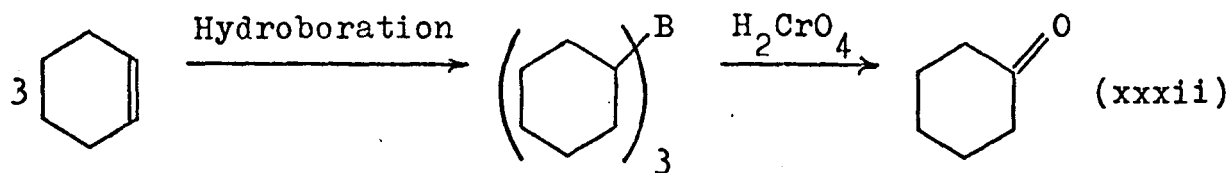
It is clear that, similarly to the halogenation reactions, the alcohol obtained is the anti-Markovnikov product.

Chromic acid oxidations were studied in some detail by Ware and Traylor.⁴⁷ They found that the attacking species involved were HCrO_4^- and H_3CrO_4^+ and that from pH 3 to 7 the major product was the alcohol. At higher acidity the alcohol

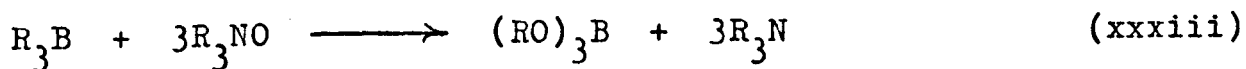
was oxidised further to produce ketone. It was also observed that the structure of the alkyl group influenced the rate of reaction. This was in contrast to alkaline hydrogen peroxide oxidations and hence they postulated a mechanism involving a nucleophilic 1,4 alkyl rearrangement:



Again, Brown developed this reaction as a method of ketone synthesis from organoboranes derived from secondary olefins:⁴⁸

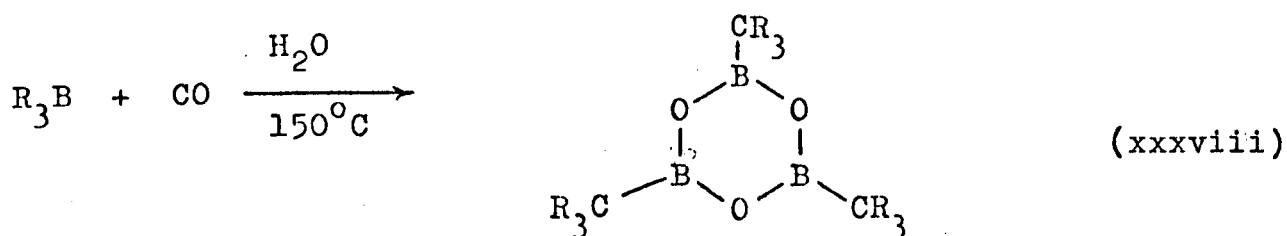


Oxidations using N-oxides of tertiary amines resulted in the smooth transformation of all boron-carbon bonds into boron-oxygen-carbon:

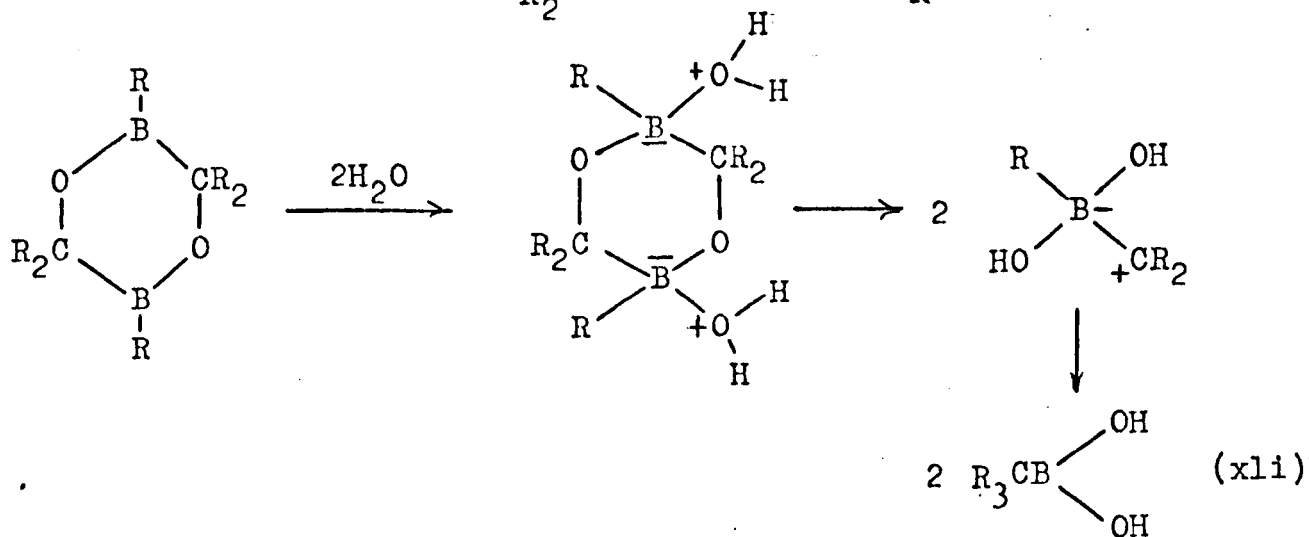
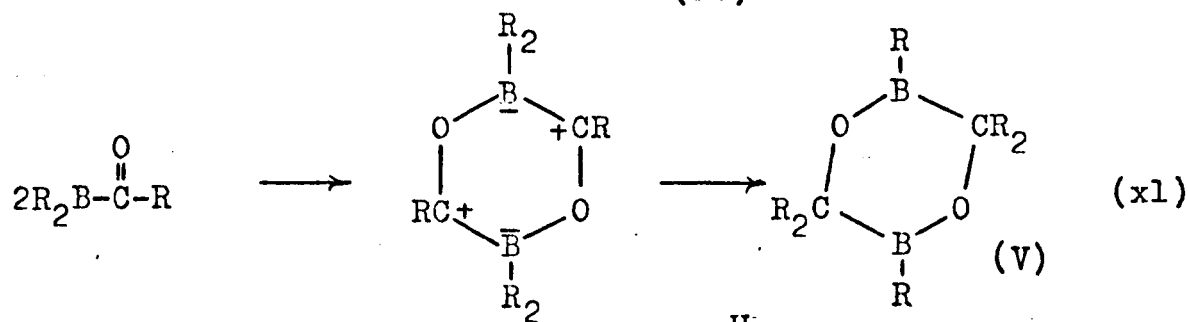
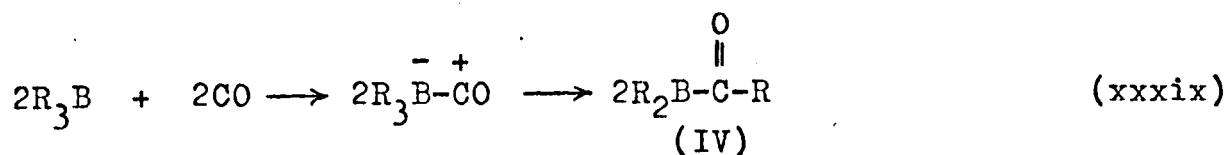


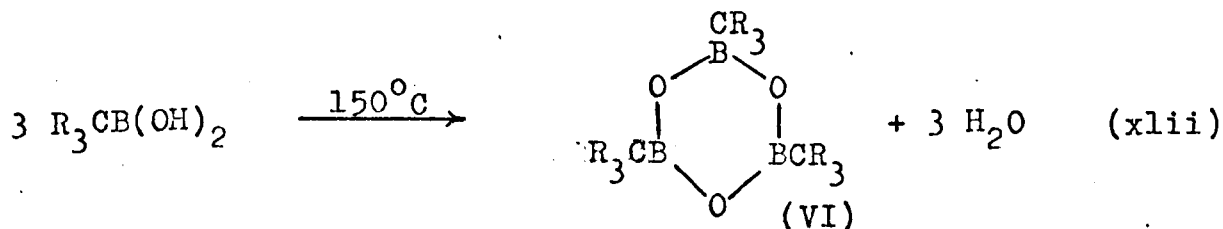
From their studies on the reaction between 1-phenylethylboronic acid and trimethylamine N-oxide, Davies and Roberts concluded

was a trialkylcarbinyboroxine.⁵⁸



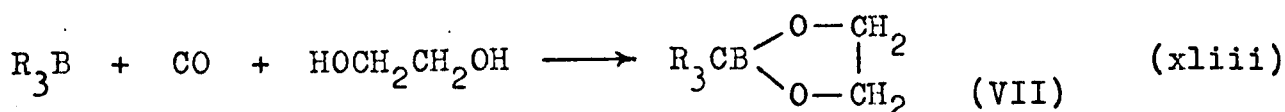
The mechanism Hillman proposed for this reaction was the formation of a carbon monoxide-organoborane adduct which rearranged, presumably by a 1,2 alkyl shift, to give an acylboron compound (IV). This in turn rearranged to give a hexa-alkyl-2,5-diboradioxane (V) which then reacted with water to give a boronic acid. This compound then broke down at the temperature of the reaction to give the trialkylcarbinyboroxine (VI):



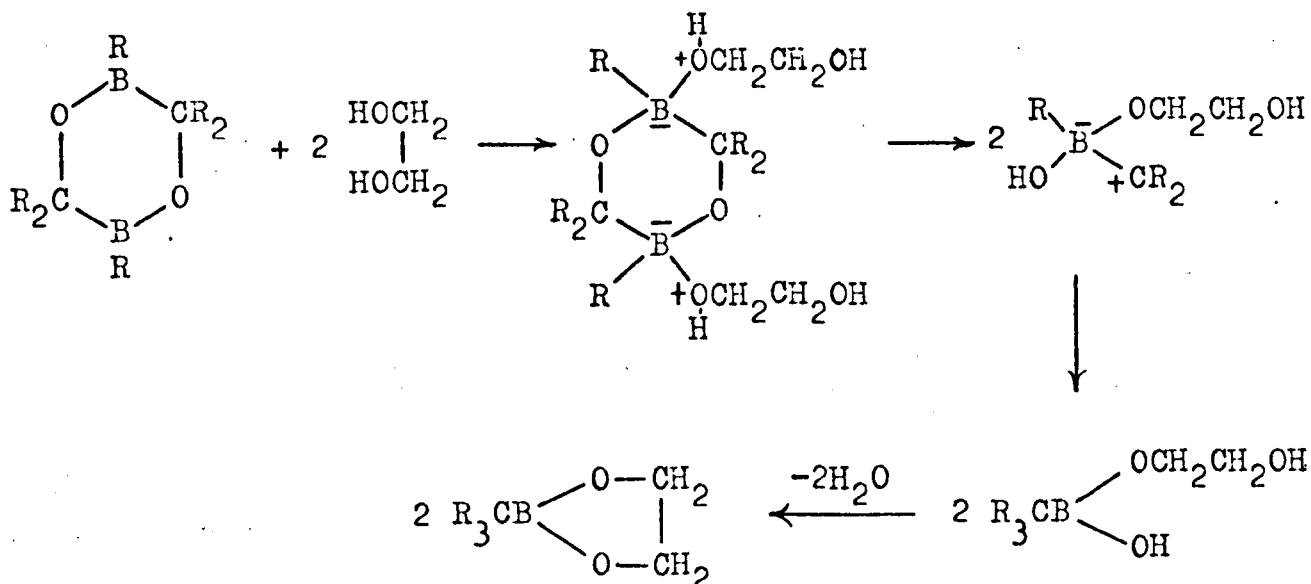


Later, Hillman also found cyclic boron compounds could be obtained if the reaction was performed in the presence of glycols or aldehydes.

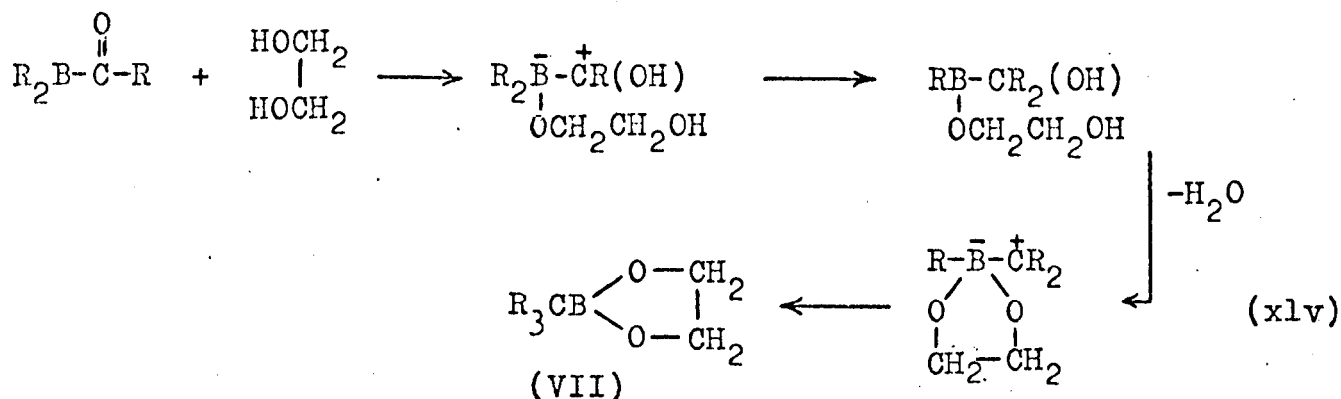
The high pressure reaction with glycols produced cyclic esters of trialkylcarbinyboronic acids⁵⁹(VII):



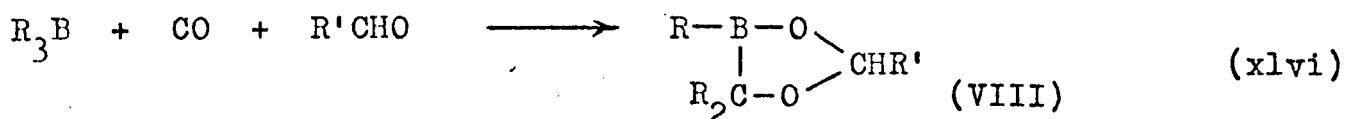
Two mechanisms were postulated for this reaction, the first being analogous with that above and involving the reaction of the glycol with (V):⁵⁹



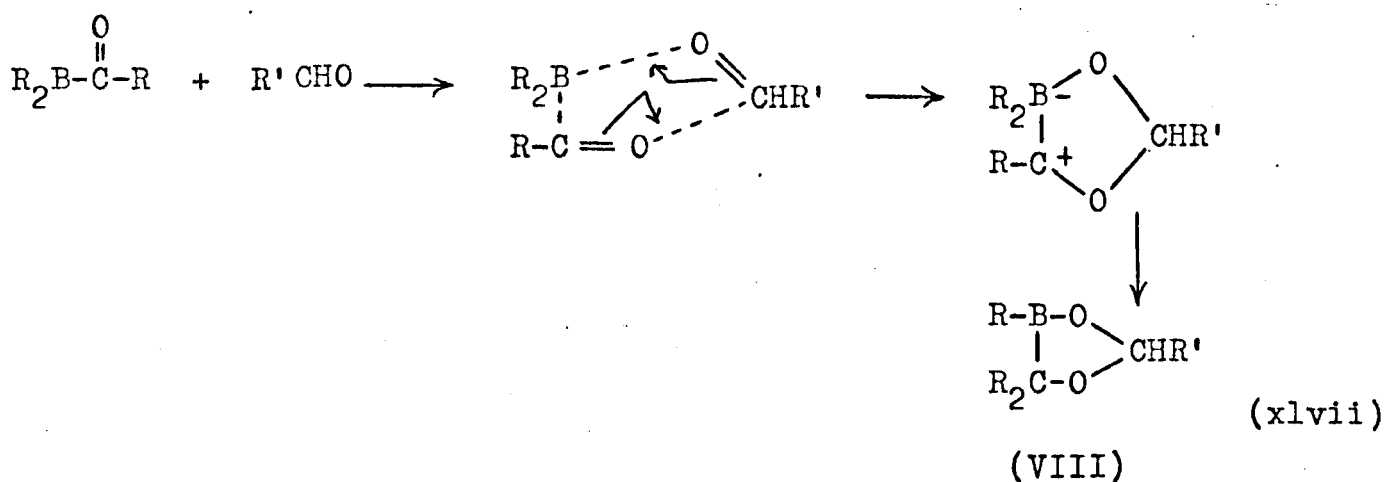
Alternatively, he suggested that the process could involve the reaction of glycol with (IV):⁵⁹



The involvement of (IV) was also suggested for the reaction with aldehydes, the products of which were novel 4-bora-1,3-dioxolanes⁶⁰(VIII):



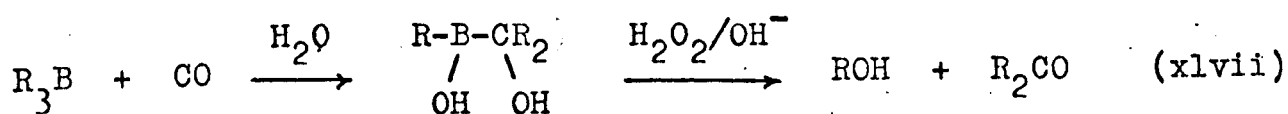
The mechanism for this reaction involved a 5-centre transition state:⁶⁰



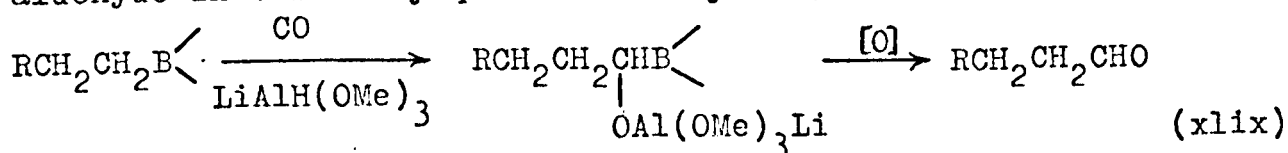
The big disadvantage with these reactions, was that very high pressures (up to 800 atmospheres) were required. Brown and Rathke, however, found that if reactions were

performed in ethereal solvents the carbonylation proceeded smoothly at atmospheric pressure^{61,62}. It had been previously noted by Hillman^{58,59}, that oxidation of the cyclic boron compounds, (VI) and (VII), produced trialkylcarbinols, and now that carbonylation could be easily achieved, the synthetic usefulness of these reactions to produce trialkylcarbinols in good yields, was realised.⁶¹ This can be shown by the following example; by a combination of hydroboration, carbonylation, and oxidation, cyclohexene was converted into tricyclohexylcarbinol in 80% yield.⁶¹ A classical synthesis via the Grignard gives a 10% yield.⁶³

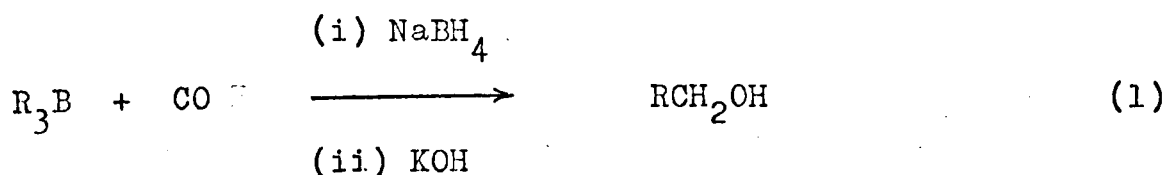
It was also observed that if a trace of water was added to the reaction mixture during carbonylation, only two of the alkyl groups would migrate from the boron to the carbon⁶²; subsequent oxidation of this intermediate produced the ketone in good yield:



If the carbonylation reaction was performed in the presence of a reducing agent such as lithium trimethoxyaluminumhydride, subsequent oxidation gave the aldehyde in virtually quantitative yield:⁶⁴



In the presence of a stronger reducing agent, for example lithium borohydride, the methylol derivative was obtained:⁶⁵

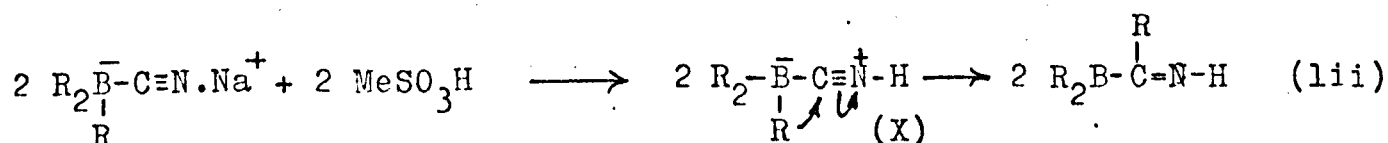
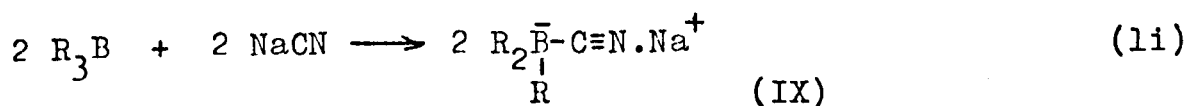


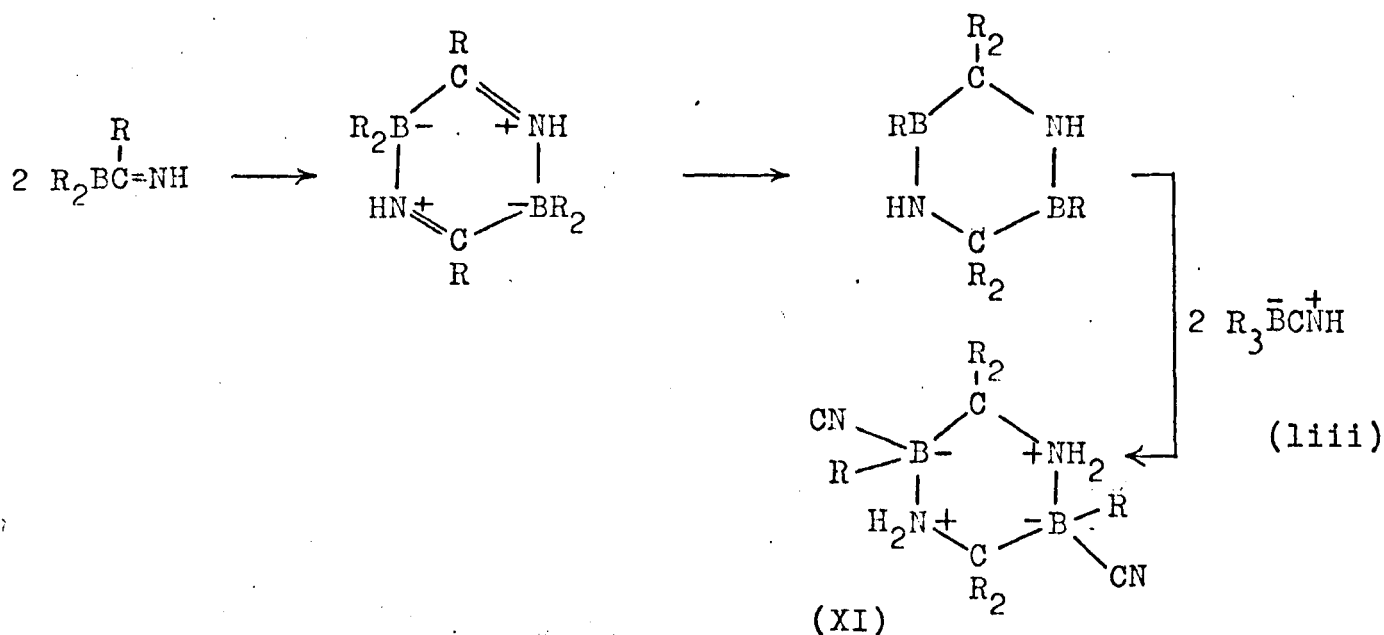
Under the chosen reaction conditions, it is not unreasonable to suggest that the aldehyde is initially produced, and this is then reduced by excess borohydride.

(h) Cyanolation.

The reaction of sodium cyanide with an organoborane produced a stable salt, (IX). If this salt was treated with an electrophilic reagent, a series of rearrangements occurred to produce an intermediate which, on treatment with alkaline hydrogen peroxide, produced the ketone.⁶⁶

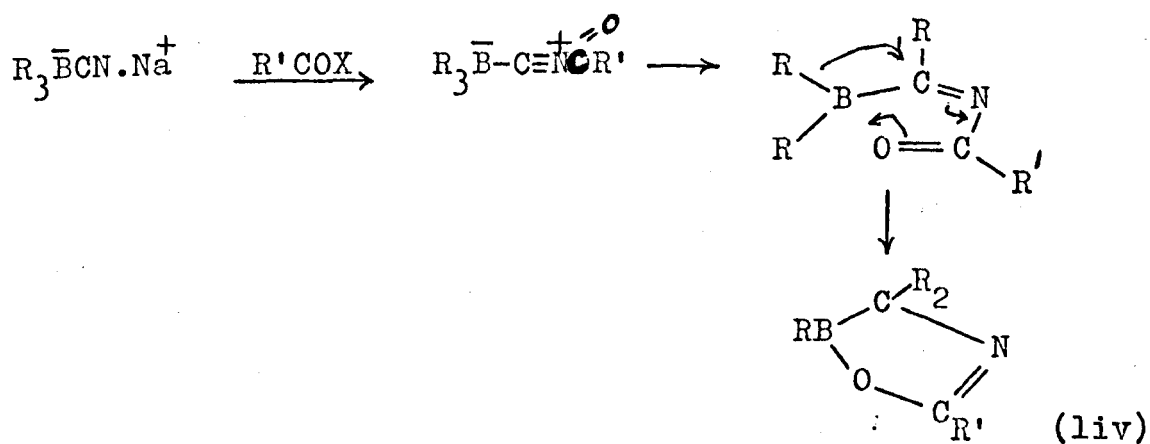
The intermediate produced and the mechanism of the rearrangement was dependent upon the electrophile chosen. The action of proton acids induced a 1,2 alkyl shift in the salt to produce an intermediate which then underwent cyclisation and produced a stable adduct (XI) after further reaction with the ylide (X):





It will be noted that this mechanism is not dissimilar to that suggested for the carbonylation reaction (equations (xxxix) to (xli)).

Since the last step involved the abstraction of hydrogen cyanide from the ylide (X), the potential yield of the ketone was limited to 50%. If, however, benzoyl chloride or trifluoroacetic acid were used as the electrophile, a different reaction occurred from which the ketone could be obtained in yields in excess of 85%.



(1) Other Reactions.

The number of synthetically useful reactions of the organoboranes is ever increasing, and only those of major interest or of relevance to this thesis have been described above. Table 2 is a summary of the main synthetic uses of these compounds.

TABLE 2

Synthetic Uses of Organoboranes

Product from $(RCH_2CHR)_3B$	Reagent and Conditions.	Ref..
Isomerisation of $RCH=CHR$	Heat; add less volatile olefin; distil.	17
Alkane, RCH_2CH_2R	Heat with carboxylic acid.	37
Primary halide, RCH_2CHRX	Add halogen + base.	42,43
Primary alcohol, RCH_2CH_2OH	Treat with alkaline H_2O_2	46
Higher alcohol, $RCH_2CH_2CH_2OH$	Carbonylation in the presence of $LiBH_4$; oxidation.	65
Tertiary alcohol, $(RCH_2CHR)_3CHOH$	Carbonylation; oxidation	61
Aldehydes; $RCH_2CHRCHO$	Carbonylation in the presence of $LiAlH(OMe)_3$; oxidation.	64

Product from $(RCH_2CHR)_3B$	Reagent and Conditions	Ref.,
Ketones; RCH_2COR	Oxidation with chromic acid.	48
$(RCH_2CHR)_2CO$	(i) Carbonylation in the presence of H_2O ; oxidation.	62
	(ii) Cyanolation; addition of benzoyl chloride; oxidation.	66
Hydroperoxide; $RCH_2CHROOH$	Autoxidation at room temperature; addition of H_2O_2 .	51
Coupling; $RCH_2CHRCHRCH_2R$	Treat with alkaline $AgNO_3$	56
Primary amines; RCH_2CHRNH_2	Treat with o-hydroxylamine sulphonic acid.	67
Secondary amines; $(RCH_2CHR)_2NH$	Reflux with alkyl azide in xylene.	68
Tertiary amines; $(RCH_2CHR)_3N$	Treat with dimethylchloramine.	69
Sulphides; RCH_2CHRSR'	Treat with R'_2S_2 in presence of O_2	70
Dialkyldisulphides; $(RCH_2CHR)_2S_2$	Heat with sulphur at $130^\circ C$.	71

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CHAPTER 2

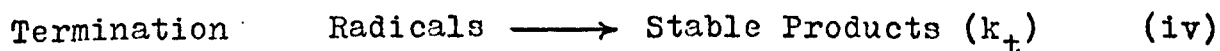
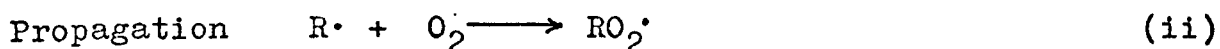
THE AUTOXIDATION OF ORGANOBORON COMPOUNDS.

An autoxidation process is one in which a compound reacts with molecular oxygen, and although it has long been known that most organoboron compounds do so with striking effects, significant advances in the study of these processes have only been made in the last decade. Because comparisons and references are to be made to the analogous reactions of carbon containing compounds, a brief resumé of the autoxidation of hydrocarbons is now given.

1. The Autoxidation of Hydrocarbons.

The nature of a compound can have a very large effect on the ease with which this reaction occurs, hydrocarbons being considerably less reactive than compounds containing a hetero atom. The industrially important process for converting cumene to cumene hydroperoxides occurs readily at temperatures about 60°-100°C, but acetaldehyde will form an explosive peroxide by reaction with oxygen at 0°C.

It is now established that these reactions occur by a free radical chain mechanism^{1,2} and the general reaction scheme may be written as:^{1,2}



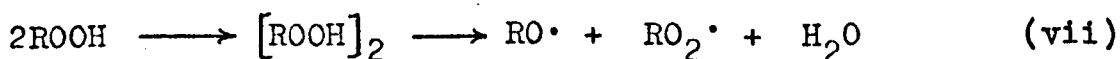
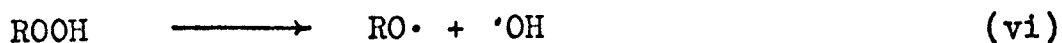
The assumption that the chains are long and that there is a steady concentration of peroxy radicals allows the derivation of a simple rate equation:¹

$$\frac{-d [\text{O}_2]}{dt} = k_p [\text{RH}] \left(\frac{\text{R}_i}{2k_t} \right)^{\frac{1}{2}} \quad (\text{v})$$

This equation only applies at relatively high oxygen pressures (greater than 100mm) when termination occurs almost exclusively between peroxy radicals.

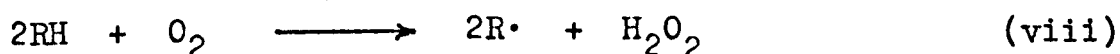
Initiation and Propagation.

The initiation step involves the formation of a free-radical from the hydrocarbon. If sufficient attention is not given to purification of the hydrocarbon, trace quantities of hydroperoxide impurity will break down to give radicals which then initiate a chain reaction. The breakdown of the hydroperoxide may occur by either a uni- or a bimolecular mechanism:³



As the autoxidation proceeds the peroxide concentration increases, which results in a greater rate of initiation and hence the characteristic auto-acceleration of these processes.

It has been frequently observed that even the most carefully purified hydrocarbons will autoxidise to some extent and various reasons have been suggested, including the presence of trace metals⁴, glass surfaces⁵, and a direct molecular reaction between oxygen and the hydrocarbon.^{5,6,7} This last reaction is a termolecular process:

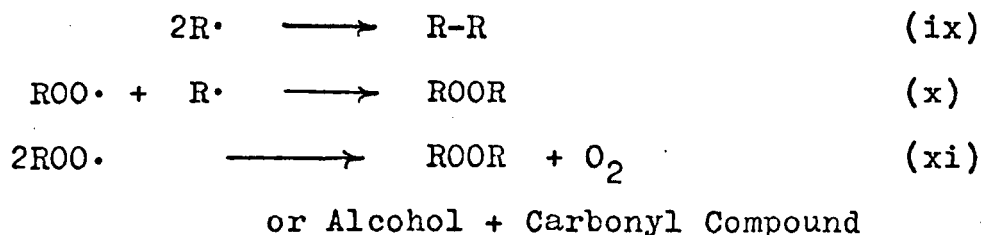


For kinetic studies it is generally more convenient to induce initiation, and this is done by adding small amounts of organic peroxides or azo compounds which by, thermal or photochemical means, break down to give radicals at a constant rate.

The propagation steps involve the reaction of the alkyl radical with oxygen to produce a peroxy radical, (ii), which subsequently attacks the hydrocarbon to produce an alkyl radical and the hydroperoxide, (iii). Reaction (iii) is an example of an S_H^2 reaction (substitution, homolytic, bimolecular)⁸ at hydrogen.

Termination.

The termination reactions and the products of autoxidation tend to be complex, but the three principal routes for the removal of radicals from the system are:



At low oxygen pressures, or if the alkyl radical is highly stabilised, reaction (ix) predominates, while at high oxygen pressures or if the alkyl radical is very reactive, route (xi) is favoured. The majority of the products obtained are due to the breakdown of the hydroperoxide formed in the propagation steps. This can give rise to a wide variety of products including acids, alcohols, carbonyl compounds and esters.

Hydroperoxides may be isolated in appreciable yield from alkane autoxidations in a few cases.^{9,10}

The rate of spontaneous initiation has been measured by Robb and Carlsson⁵ by determining the rate of oxygen absorption during the very early stages of reaction. They found that this was a termolecular reaction (viii), in agreement with Emanuel et al.⁷

Much kinetic work has been devoted to the determination of k_p , and, from equation (v), it is obvious that an accurate knowledge of R_i and k_t is required in order to evaluate this rate constant from oxygen absorption measurements. As has been mentioned previously, kinetic experiments are usually done in the presence of an initiator, in order to achieve a constant rate of initiation. Although the rates of homolysis of initiators are well known, these values cannot be taken as the rates of initiation because a proportion

of the radicals produced are removed by, for example, cage recombination reactions. Hence, it is necessary to measure the rate of chain initiation under the experimental conditions. This is easily achieved by adding a known amount of inhibitor, and determining the induction period produced. Equation (xii) then applies:¹¹

$$\text{Induction Period} = \frac{n [\text{Inhibitor}]}{R_i} \quad (\text{xii})$$

n = number of radicals destroyed by one molecule of inhibitor. Values of k_t are usually obtained via the rotating sector technique.¹² Essentially this involves causing fluctuations in the radical concentration of a photo-initiated process, by 'flickering' the illumination with an interposed rotating sector. By relating the sector speed to the rate of reaction, it is possible to determine the chain lifetime and k_t :¹³

$$\text{Chain Lifetime} = \frac{\text{Population}}{\text{Birth Rate}} = \frac{[\text{RO}_2\cdot]}{R_i} = \frac{1}{(2k_t R_i)^{\frac{1}{2}}} \quad (\text{xiii})$$

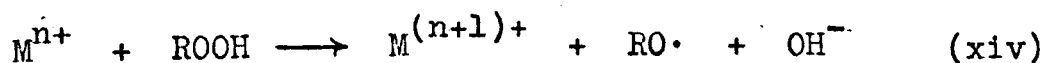
More recently, it has been found possible to determine values of k_t for alkylperoxy radicals by electron spin resonance.^{12,14}

Thus, with a knowledge of k_t and R_i , values of k_p can be obtained from equation (v) by measuring the rate of oxygen absorption. Values of k_p for many hydrocarbons are now available.¹³

Inhibitors.

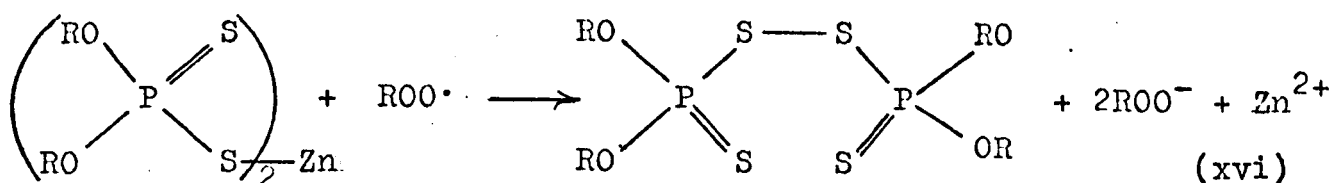
The various types of inhibitor and their modes of action have been well reviewed.^{15,16} The autoxidation of a hydrocarbon can be inhibited either in the initiation stage or during propagation, and this affords a ready classification of anti-oxidants. Initiation suppressors can be further sub-divided into three categories.

Metal-ion deactivators operate by either complexing the metal to its maximum co-ordination number, or by altering its redox potential, so stabilising one valence state. This then reduces the ability of the transition metal ions, such as Fe^{2+} , Co^{2+} , or Cu^{+} , to initiate by such reactions as:

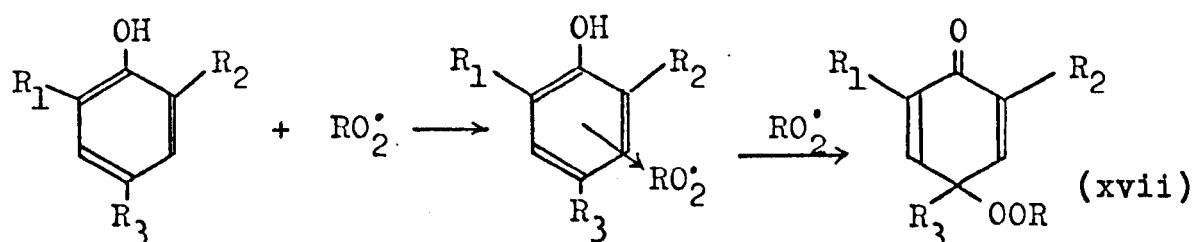


Ultra-violet light stabilizers suppress initiation by absorbing the radiation and then disposing of it by a non-radical mechanism, hence reducing the possibility of photo-chemical initiation.

The third sub-division in the class of initiation suppressors concerns peroxide destroyers. These compounds do exactly what their name suggests and reactions (vi) and (vii) cannot therefore occur. Frequently, compounds in this group can also act as propagation suppressors by removing peroxy radicals^{17,18}, for example, Burn proposed the following reactions for zinc dialkyldithiophosphates:

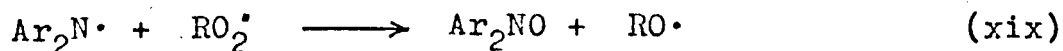
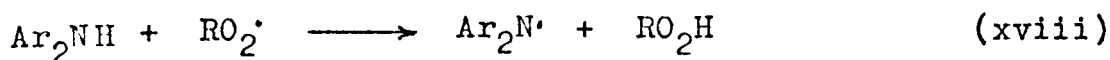


Propagation suppressors operate by removing the propagating radicals, producing either radicals of lower reactivity, or molecular products. Phenolic compounds are the most common in this class and one molecule of a phenol will usually remove two peroxy radicals from the system¹⁹ forming stilbenes, quinones, bis-phenols or biphenylquinones.²⁰ The mechanism by which they remove peroxy radicals to give such products may be written as:¹⁹



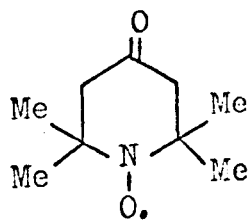
There are many factors which influence the effectiveness of a particular phenol as an inhibitor, suffice it to say here that electron releasing groups increase the reactivity and that it is preferable to have a bulky ortho substituent to minimise chain transfer effects. Detailed discussions are given by Scott¹⁶ and Ingold.²¹

Amines also fall in this category, and appear to remove up to three peroxy radicals per molecule of inhibitor.¹⁵ The mechanism by which they remove radicals is:^{22,23}

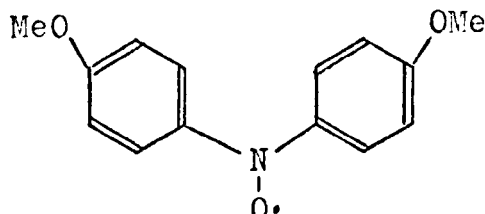


In some cases the nitroxide produced by reaction (xix) can also remove a radical from the system.

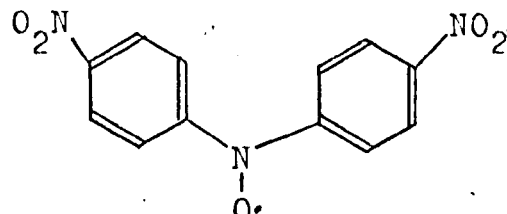
The last group of compounds that will be considered, is the stable free radicals. Ingold and Brownlie have studied nitroxides in some detail²⁴, mainly as a result of trying to gain an understanding of amine anti-oxidant activity. They found that (I) only trapped alkyl radicals, and although (II) and (III) also reacted with peroxy radicals, the authors concluded that these compounds were less effective than phenols or amines.



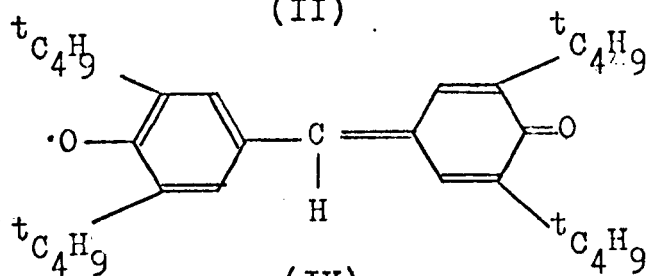
(I)



(II)



(III)



(IV)

A stable free-radical which is highly efficient is galvinoxyl (IV). This compound was shown by Bartlett to be a very efficient scavenger for cyano-iso-propyl and t-butoxy radicals²⁵, and also was one of the very few compounds capable of inhibiting the autoxidation of trialkylboranes.²⁶ This implies that it also traps peroxy

radicals which are the propagating species in the borane autoxidation chains. Galvinoxyl has also been used to inhibit the autoxidation of several other organometallic compounds.²⁷

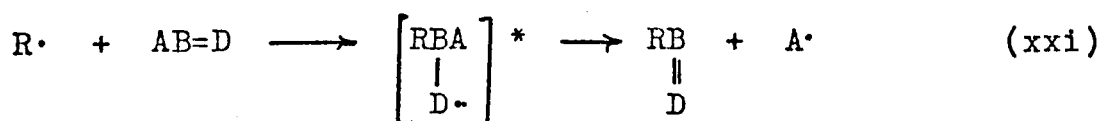
2. S_H² Reactions.

The homolytic bimolecular (S_H²) reaction has some similarity to the well known heterolytic, nucleophilic S_N² reaction. It involves the displacement of a radical from a molecule by a second incoming radical. The general reaction is:

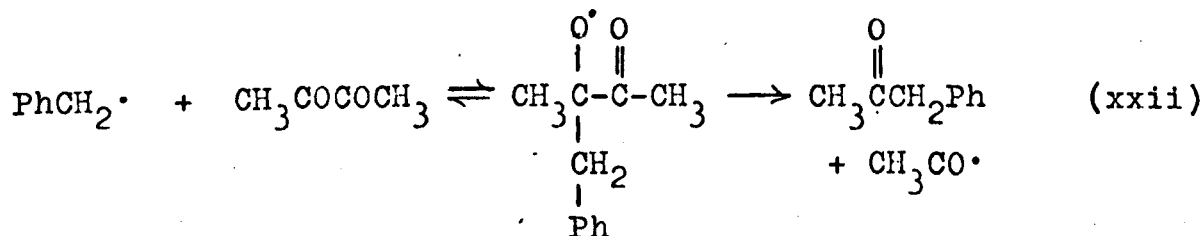


Many radical processes involve reactions of this type but it is only recently that they have been recognised and drawn together under the classification S_H².⁸ The most common S_H² reaction occurs when R· attacks a univalent atom, such as hydrogen in a molecule to give RH and this has generally been known as abstraction. Substitutions at multivalent centres are also known and occur readily providing the multivalent atom is multiply bonded or is co-ordinatively unsaturated. Both of these requirements allow the formation of a transition state* (or intermediate) with little activation energy.

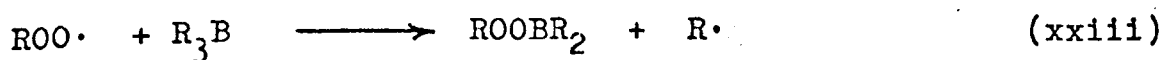
The general reaction at a multiply bonded centre is:



A reaction of this type will typically occur at an sp^2 hybridised carbon atom, and may well be involved in the relatively facile autoxidation of acetaldehyde mentioned earlier. A more specific example is the attack on biacetyl by benzyl radicals²⁸:



S_H^2 reactions at co-ordinatively unsaturated centres are most frequently found in organometallic chemistry and have low activation energies providing the atom under attack has available vacant low energy orbitals which allow it to increase its co-ordination number. There are many examples of this type of reaction but one that is particularly relevant occurs during the autoxidation of trialkylboranes, and involves the attack of a peroxy radical at a boron centre:^{29,30}

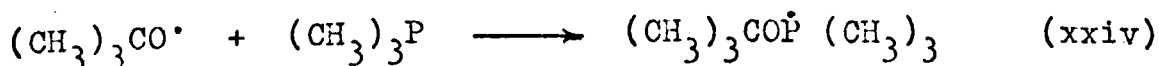


The transition state presumably involves a four co-ordinate organoboron radical.

Two different types of S_H^2 reactions are possible, synchronous and stepwise.⁸ In a synchronous process the

loss of B \cdot [reaction (xx)] occurs with the approach of R \cdot and (RAB)* is only a transition state. A stepwise mechanism involves the formation of an intermediate (RAB)*, which has a finite lifetime, and which then subsequently undergoes a unimolecular decomposition. As can be seen the only distinction lies in the lifetime of (RAB)*. and when this is particularly long it is possible to observe the intermediate radical using electron spin resonance spectroscopy.

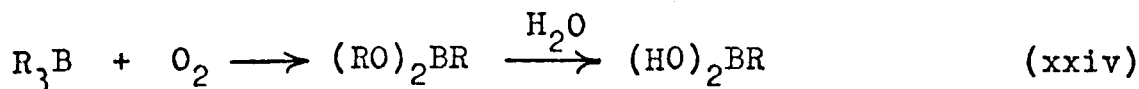
The t-butoxytrimethylphosphoranyl radical has been identified in the reaction of trimethylphosphine and t-butoxy radicals:³¹



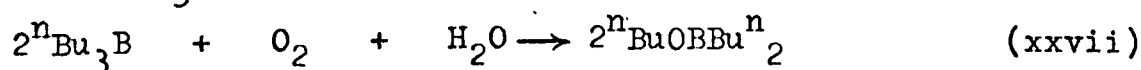
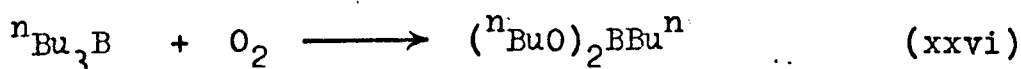
Further examples of the S_H² reaction will occur later in this thesis.

3. Early Studies on the Autoxidation of Organoboron Compounds.

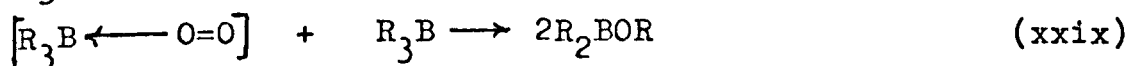
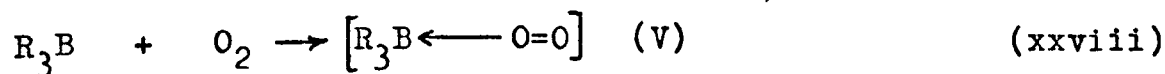
The most striking property of trialkylboranes is the remarkable ease with which they react with atmospheric oxygen. This fact was first noted by Frankland over 100 years ago, when he reported that both trimethyl and triethyl boranes were spontaneously inflammable in air.³² The facile autoxidation was also noted by other workers.³³ Krause et al. found that by controlling the oxidation, they could obtain boron oxides, which, on crystallisation from water, gave the acids in pure form:³⁴



Johnson and co-workers observed that water affected these autoxidations.^{35,36} Dry tri-n-butylborane absorbed almost one molecular equivalent of oxygen to yield di-n-butyl n-butylboronate, whilst in the presence of water, only 0.5 moles were absorbed and the major product was the corresponding borinate:³⁶



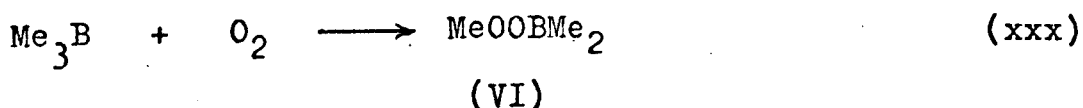
These authors also suggested a mechanism for the autoxidation, and proposed that initially a boron-oxygen adduct (V) was formed. This intermediate then underwent a redox reaction with unreacted trialkylborane to produce the borinate ester:



The possibility of a peroxide intermediate was first demonstrated by Grummitt³⁷ in his studies on trialkylboroxines $[(RBO)_3]$. He found that the partially autoxidised liquids liberated iodine from acidified potassium iodide and initiated the polymerisation of vinyl acetate. He also observed that boroxine autoxidations could be inhibited by the addition of 0.1% phenyl-2-naphthylamine,

but not by quinol, and in fact he drew comparisons between this reaction and the autoxidation of benzaldehyde, which was known to be free-radical.³⁸ In spite of this he favoured the non-radical mechanism proposed by Johnson and Van Campen.³⁶

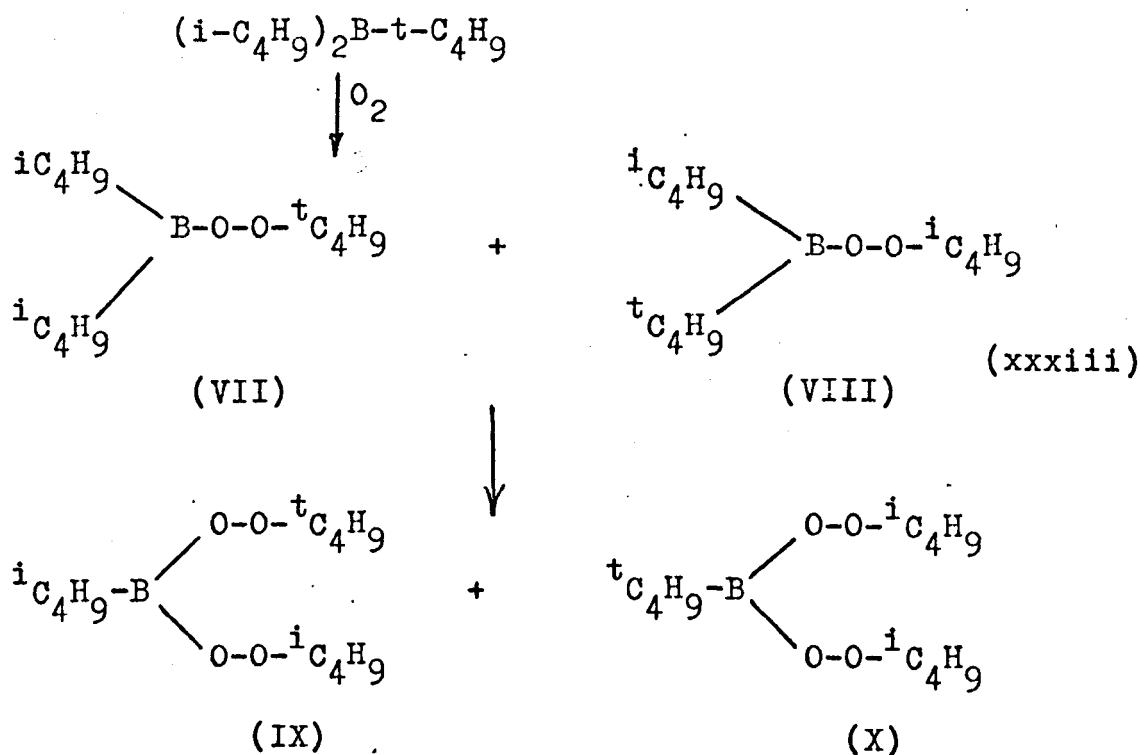
In 1953, it had been demonstrated by Walling and Buckler, that the product obtained from the autoxidation of Grignard reagents was an alkylperoxymagnesium compound.³⁹ Thus it was not unreasonable to expect a similar compound to be produced from the autoxidation of organoboranes, and in 1956, Petry and Verhoek made the first positive identification of an organoperoxyborane.⁴⁰ It was prepared by the reaction of trimethylborane and oxygen in the gas phase and at low pressure. They confirmed the structure by iodometry and mass spectrometry as a dimethyl methylperoxyborane (VI):



At about the same time, Davies and Moodie published details of the preparation of boron peroxides via nucleophilic substitution^{41,42}, rather than autoxidation. In this way, the existence of organoperoxyboranes was well established.

Previous to this, Bamford and Newitt had concluded, from a kinetic study of the gas phase autoxidation of boron and zinc alkyls, that a chain reaction was involved⁴³.

Davies et al., studying the liquid phase autoxidation of tributylboranes, found that there was no induction period

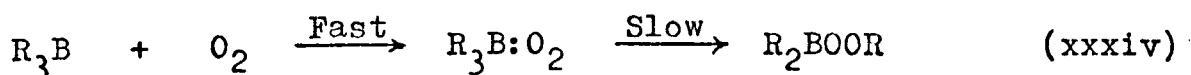


After the uptake of the first mol. of oxygen the product was shown to consist of 69% of compound (VII) and 31% of compound (VIII). The ultimate product after the absorption of two mols. of oxygen consisted of 99% of compound (IX) and 1% of compound (X); the structure of compound (IX) was confirmed by its proton magnetic resonance spectrum.

The mechanism proposed in equation (xxxi) was the same as that suggested by Walling for the autoxidation of Grignard reagents.⁴⁷

Evidence for the borane-oxygen intermediate was provided by Zutty and Welch.⁴⁸ After passing one molecular equivalent of oxygen through a solution of tri-n-butylborane and thoroughly flushing with nitrogen, the solution was periodically analysed for peroxide. It was found that the peroxide concentration increased from 25% to 60% over a period of three hours, and they postulated the formation of

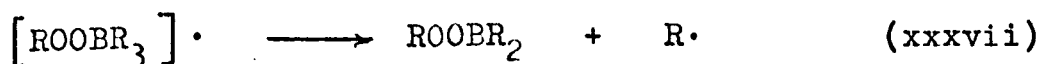
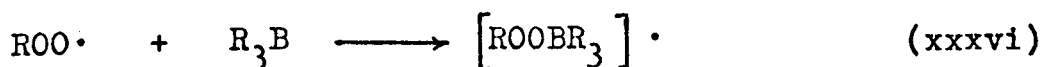
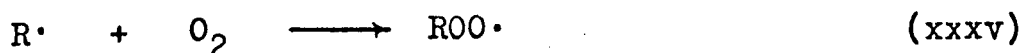
a non titratable boron-oxygen complex which slowly rearranged to a peroxide:



Davies and co-workers failed to reproduce this work⁴⁹, and Hansen and Hamann reported that in the autoxidation of triethylborane, all the peroxide was formed within fifteen seconds.⁵⁰

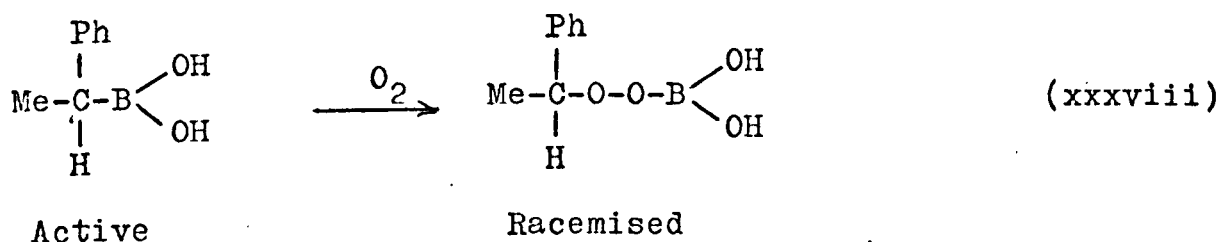
4. Recent Studies.

A free-radical mechanism was first suggested by Davies and Coffee in 1966⁵¹. They observed that during the autoxidation of trialkylboroxines, small amounts of boric acid were produced and non- stoichiometric amounts of oxygen were absorbed. Further, they suggested that the evidence in favour of the ionic mechanism was not compelling and could be applied equally to their proposed free-radical chain mechanism:



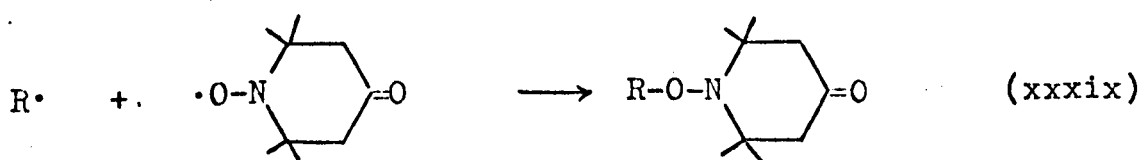
In this same year positive evidence for such a mechanism

was provided by Davies and Roberts from their studies on the autoxidation of optically active 1-phenyl^{ethyl}boronic acid.^{29,53} The reaction resulted in a racemised product, dihydroxy-1-phenylethylperoxyborane, which indicated the involvement of a symmetrical intermediate:

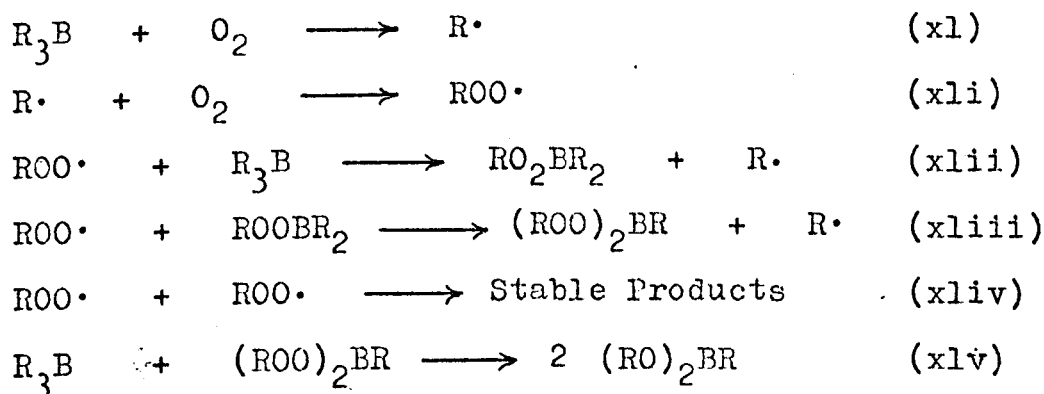


The autoxidation was inhibited by small amounts of copper (II) N,N-dibutyldithiocarbamate, or galvinoxyl. A short time after this, Allies and Brindley published similar results for the autoxidation of optically active di-iso-pinocamphenyl-sec-butylborane.⁵⁴ They too observed extensive racemisation in the product and showed the reaction could be inhibited by galvinoxyl, phenothiazine or copper (II) N,N-dibutyldithiocarbamate. They later extended their studies to include the tributylboranes and again found that galvinoxyl produced significant induction periods.²⁵

Allies and Brindley, in a later paper, examined a large range of possible inhibitors,³⁰ but none were found to be superior to galvinoxyl. In this paper they also reported the isolation of an adduct formed by the trapping of alkyl radicals by 2,2,6,6-tetramethylpiperid-4-one-nitroxide:



Further, the difference in activation energies for the absorption of the first and second mols. of oxygen by tributylboranes was clearly demonstrated. At -74°C the rate of absorption of the second mol. of oxygen was considerably reduced, and in the case of tri-n-butylborane was negligible. The following stepwise scheme was postulated for the autoxidation process:



Reactions (xlii) and (xliii) are both $\text{S}_{\text{H}}2$ reactions at a boron centre, and the differences in activation energies for these two reactions result from a $p\pi$ electron back donation from the α -oxygen atom to boron.

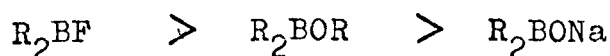
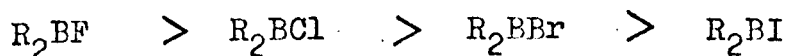
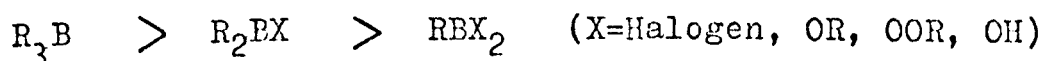
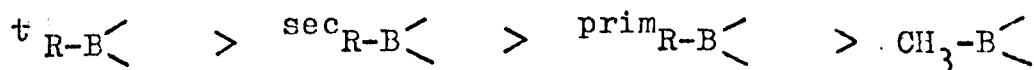
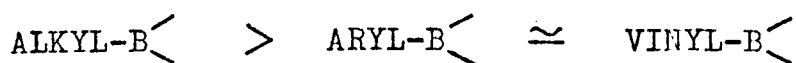
Following this work, the autoxidation of triethylborane was studied by Grotewold and co-workers both in the liquid⁵⁵ and gas phases⁵⁶ and they further substantiated the autocatalytic free-radical chain mechanism. It is interesting to note that they found iodine was a successful inhibitor in solution, in quite small quantities, in contrast to the work of Hansen and Hamann.⁵⁰

5. Kinetic Studies.

The relative rates of autoxidation of organoboron compounds have been reported by many authors and the main features are summarised in Table 3⁵⁷.

TABLE 3

Relative Rates



These results may be a rough reflection of the speed of the $\text{S}_{\text{H}}2$ reaction occurring at the boron atom during the propagation step. One of the major factors influencing the rate is the degree of $p\pi$ electron back donation from the α -atom to the boron - the greater this contribution, the slower is the rate. Steric factors can also affect the rate of autoxidation; thus trimesitylborane was completely inert to oxygen and tri-1-naphthylborane, at 25°C , only absorbed

0.5 mol. of oxygen in 50 days⁵⁸. The effect of one factor that is difficult to judge is the stability of the displaced radical. Obviously, a very stable radical will give a considerable 'thermodynamic drive' to the reaction.

The series given in Table 3 are basically correct, but many measurements produced anomalous results because early experiments were frequently performed under conditions where the rate determining step was the rate at which oxygen diffused into the solution. The importance of really efficient gas-liquid mixing was not appreciated until quite recently.³⁰

Since the discovery that galvinoxyl was an efficient inhibitor of organoborane autoxidations, it has been possible to evaluate rates of initiation by making use of formula (xii), noting that for galvinoxyl, $n=1$.^{30,59,60}

An alternative method, described by Brown et al.⁶¹, utilised the fact that iodine in high concentration is an effective inhibitor. Essentially the technique involved estimating the alkyl iodide produced from the trapping of alkyl radicals by the iodine.

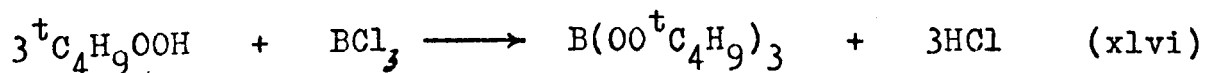
A most thorough kinetic study of organoborane autoxidations has been made recently by Ingold, Davies et al.⁵⁹, and Ingold et al.⁶⁰. In these papers, absolute rate constants for the S_H2 propagation reactions (xli) are listed.

Because of the great relevance of all these kinetic studies to this thesis, they will be dealt with, at length, in later chapters.

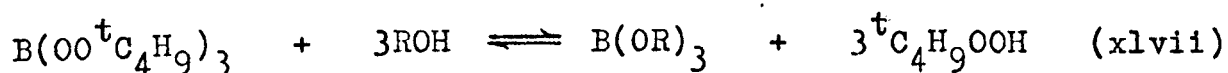
6. Organoperoxyboron Compounds.

The evidence for the existence of organoperoxyboron compounds which had been suggested as intermediates in the autoxidation reactions became increasingly strong,³⁷ and in 1956 and 1957 compounds of this class were prepared and isolated both from autoxidation⁴⁰ and nucleophilic substitution reactions.⁴¹

Nucleophilic substitution was used to prepare triperoxyborates which could not be obtained from autoxidation. Tri-t-butylperoxyborate was prepared by the reaction of boron trichloride with t-butylhydroperoxide at room temperature:⁴¹

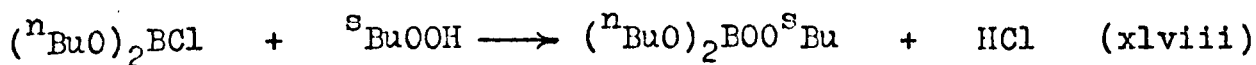


It was found that this peroxide was very susceptible to hydrolysis and alcoholysis:



This reaction was an equilibrium and by adding excess hydroperoxide to a borate, it was possible to prepare the peroxide.

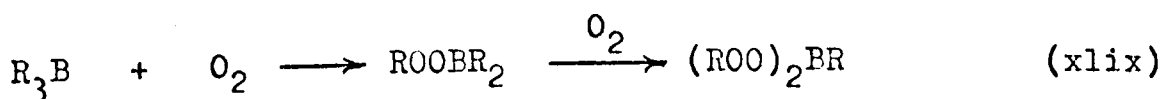
Recently, Russian workers have devoted much attention to the synthesis of mono and diperoxyborates by nucleophilic substitution. In a typical experiment, di-n-butoxy s-butylperoxyborate was prepared from di-n-butoxychloroborane and s-butyl hydroperoxide:⁶²



The structure of the compound was confirmed using infra-red and proton magnetic spectroscopy.

Maslennikov et al. described an alternative method of preparation using the sodium salt of the hydroperoxide.⁶³ This resulted in the precipitation of sodium chloride which was filtered off to leave a solution of the peroxyborate.

The autoxidation of trialkylboranes in solution produced the alkylldiperoxyboronates, and yields were virtually quantitative providing the reaction was done in dilute solution and with efficient gas/liquid mixing.^{46,49,30}



The peroxide could be isolated by removal of solvent and their structures have been satisfactorily confirmed, e.g.⁴⁶

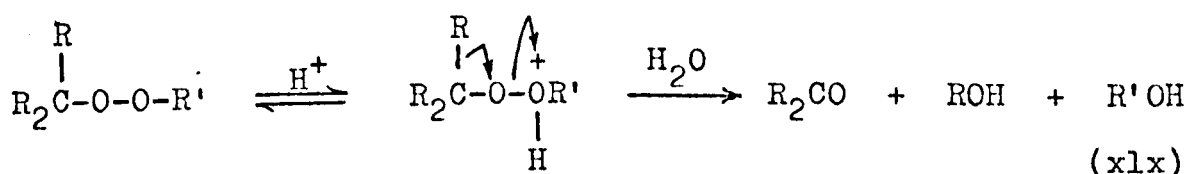
At room temperature the diperoxide was quickly formed, but Allies and Brindley have shown that at -74°C the autoxidation of the tributylboranes slows considerably after the absorption of one mol. of oxygen.³⁰ Although never isolated, it seemed beyond doubt that the product at this stage of the reaction was the butylperoxy dibutylborinate.

Rearrangement and Decomposition Reactions.

Organoperoxyboranes, other than the peroxyborates, have a remarkable ability to undergo nucleophilic rearrangements

in the absence of other reagents, and this has been a serious obstacle to their isolation. Organic peroxides undergo a variety of similar reactions, which have been well studied, as well as the more familiar homolysis of the oxygen-oxygen bond.

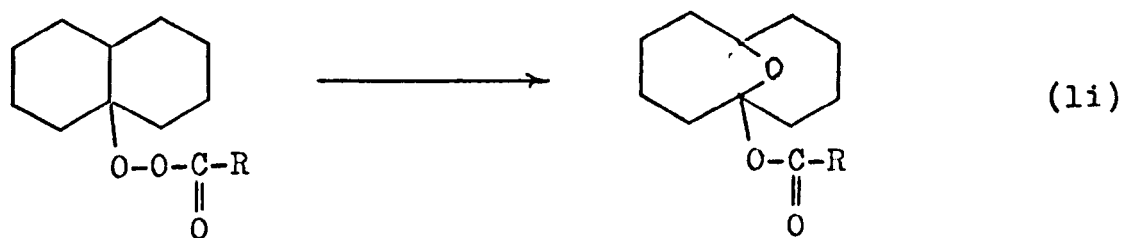
Alkyl hydroperoxides and dialkyl peroxides readily rearranged when treated with a trace of sulphuric acid in acetic acid solution:⁶⁴



It has been shown that the migration of R occurred either simultaneously or very soon after the loss of R'OH.⁶⁵

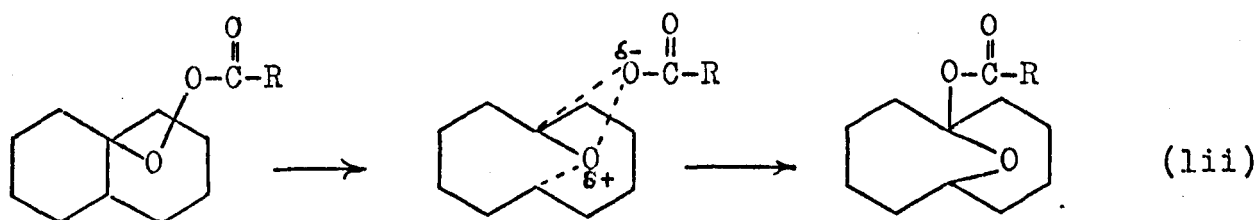
A detailed study by Kooyman and Van Steveninck confirmed this and their evidence appeared to favour an intramolecular mechanism.⁶⁶

Peroxyesters rearranged in a similar manner and in some cases the reaction occurred in the absence of acid catalysis. Esters of decahydro-9-naphthyl hydroperoxide rearranged on standing to give the isomeric ester:⁶⁷



The rate of reaction increased with an increase in the strength

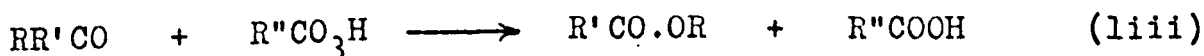
of the acid, RCO_2H , and also with the dielectric constant of the solvent. This led Criegee and Kasper to suggest a synchronous intramolecular process by analogy with the Beckmann and pinacol-pinacolone rearrangements:



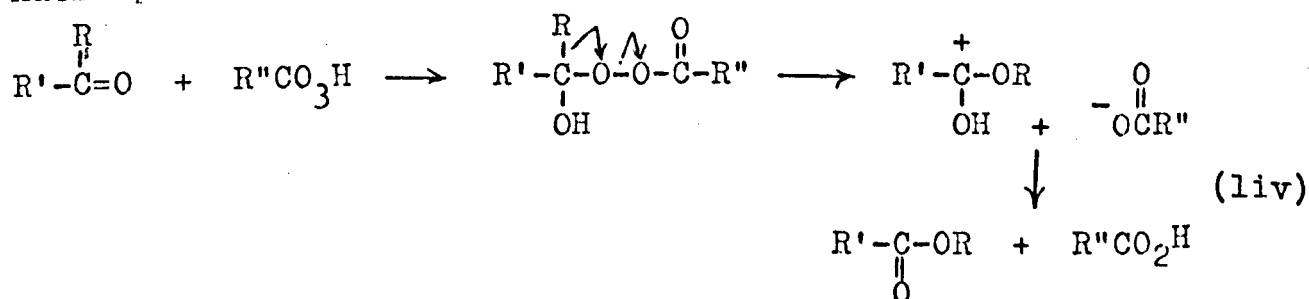
The rearrangement was subject to slight acid catalysis.

Simple alkyl peroxyesters were much less prone to this rearrangement and generally required warming with a trace of perchloric acid.⁶⁸

The Baeyer-Villiger reaction for the conversion of a ketone to an ester involved a similar peroxidic rearrangement. The production of the ester was achieved by treating the ketone with hydrogen peroxide or more usually a peroxyacid:



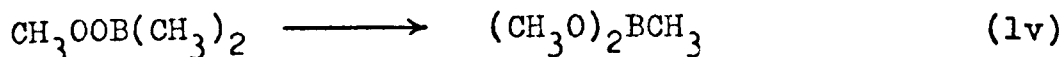
The mechanism proposed for this reaction was the formation of a hydroxy peroxyester which then decomposed by a nucleophilic 1,2 alkyl shift:^{67,69}



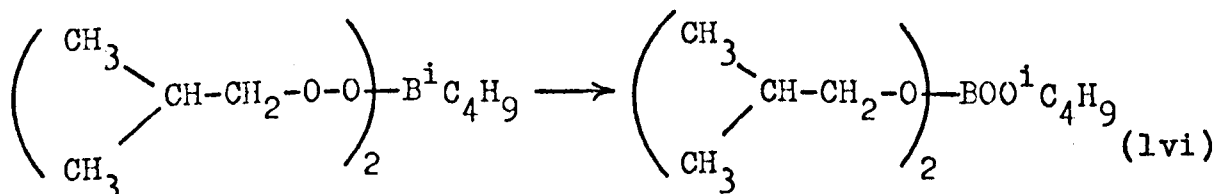
Similarly to reaction (li), polar solvents increased the rate and the reaction was subject to acid catalysis.⁷⁰

Hawthorne and Emmons also found that the nature of R" influenced the migratory aptitudes of R and R',⁷⁰ and this was good evidence that the rearrangement was a synchronous process.

The rearrangement of organoperoxyboranes was first noted by Petry and Verhoek during their studies on methylperoxy dimethylborane.⁴⁰ This compound rearranged, both in the gas phase and solution, by a first order reaction to give dimethoxy methylborane. The half-life in the gas phase at room temperature was 60 days.

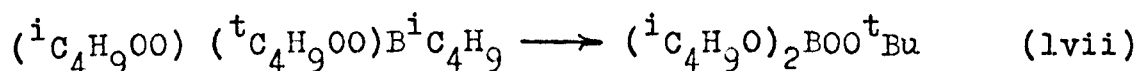


Davies et al. studied the rearrangement of iso-butyl di-iso-butylperoxyborane using proton magnetic resonance spectroscopy.⁷¹ The doublet due to the methylene peroxy group gradually diminished and a new doublet appeared at a slightly higher field, and this was attributed to the methyleneoxy group:

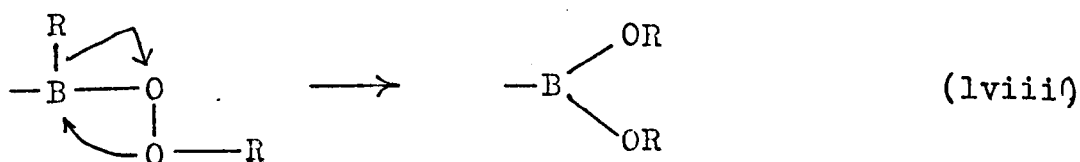


In a later paper, Davies and co-workers showed that in

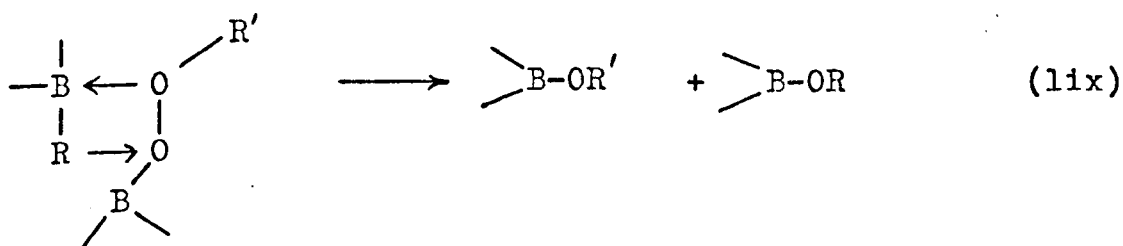
the compound iso-butylperoxy t-butylperoxy iso-butylborane, the iso-butyl group was preferentially reduced:⁴⁶



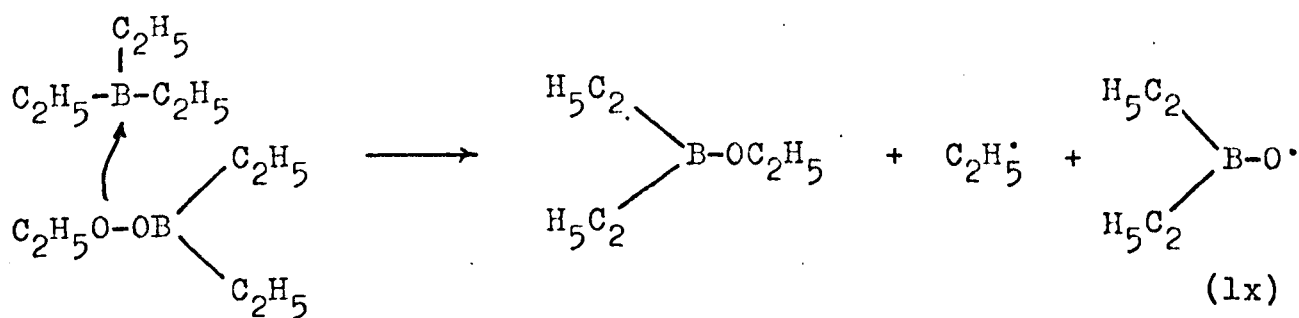
Davies suggested that this evidence was consistent with a 1,2 nucleophilic rearrangement and he favoured an intramolecular rearrangement by analogy with the Baeyer-Villiger reaction previously mentioned:



Murviss favoured an intermolecular mechanism, because of evidence from his studies on the effect of trialkylboranes on peroxides. If, during the autoxidation reaction the concentration of trialkylborane was increased, the final concentration of peroxide was markedly lowered.⁷² Also, the addition of excess tri-n-hexylborane to a partially autoxidised solution of tri-n-butylborane led to a large reduction in the peroxide concentration.⁷³ Murviss proposed the following mechanism to account for these reactions:



The reaction between borane and organoperoxyborane was also studied by Hansen and Hamann,⁵⁰ who found that a mixture of triethylborane and the peroxide initiated free-radical polymerisations. In the presence of iodine, ethyl iodide was formed and this was suggested as further evidence for an initial induced decomposition into radicals:



To account for the formation of borate ester, and the fact that less than an equivalent amount of iodine was consumed, a fast radical combination reaction, between the ethyl and organoboron-oxy radicals, within a solvent cage, was invoked.

The reaction between borane and peroxyborane accounts for the failure to detect peroxide in many of the early organoborane autoxidations. Most of the reactions were performed under conditions of oxygen starvation, and in many cases in the absence of solvent. Thus, as soon as any peroxide was formed, it was reduced by the excess borane. It is now clear that the conditions required for maximum peroxide yield are very efficient gas-liquid mixing, high dilution and low temperatures.

The homolysis of the oxygen-oxygen bond is a familiar

reaction of organic peroxides, but it is only recently that the comparable reaction of organoperoxyboranes has received any attention, and only those compounds unable to undergo the nucleophilic rearrangements are suitable for study.

Maslennikov and co-workers followed the decomposition of di-n-butoxy s-butylperoxyborane in nonane solution.⁶² The reaction proceeded at a measurable rate at temperatures above 100°C and was first order, with an activation energy for the spontaneous decomposition of 30 kcal.mole⁻¹. No rate constant was quoted. Similarly, tri-n-butylperoxyborane decomposed with first order kinetics and an activation energy of 32.6 kcal.mole⁻¹.⁷⁴ These values are quite similar to those found for organic peroxides, which were usually in the range 30-40 kcal.mole⁻¹. Typically, the decomposition of di- α -cumyl peroxide was first order and the activation energy determined was 34.5 kcal.mole⁻¹.⁷⁵

7. Organoboron Compounds as Polymerisation Initiators.

As we have seen, the first indication that organoboron compounds could bring about vinyl olefin polymerisations was made by Grummitt in 1942.³⁷ A considerable degree of polymerisation occurred when vinyl acetate was heated in air with partially oxidised tri-n-butylboroxine for a few hours.

After this somewhat qualitative beginning, Furukawa et al., in 1957, extended the work to include a variety of vinyl monomers.⁷⁶ Triethylborane was added to the nitrogen flushed monomers and the polymer produced was weighed after precipitation.

An ionic mechanism was suggested for these polymerisations. Federova and Kolesnikov made similar observations using tributylborane as the initiator.⁷⁷ In contrast to the work of Furukawa et al., they found that the borane would not initiate the polymerisation of acrylonitrile. Rather than this reflecting differences between the initiating abilities of the two boranes, it was probably a result of differing techniques, since the role of oxygen was not then understood.

The idea that these polymerisations involved a free-radical mechanism was first tentatively suggested by Ashikari,⁷⁸ and in the following year he and Nishimura provided positive evidence for this.⁷⁹ They determined reactivity ratios for a number of vinyl monomer combinations initiated by tri-iso- butylborane.

The values obtained were very similar to known values for free-radical polymerisation processes. Ashikari and Nishimura made a further important observation by stating that, although the experiments were performed under nitrogen, it was most probable that residual oxygen played an important role in the initiating mechanism.

The Importance of Oxygen.

By 1958 it was becoming increasingly clear that oxygen played an important part in borane initiated polymerisations. Ashikari showed both di-iso-butylboron chloride and di-iso-butyl iso-butyloxyborane would effectively initiate the polymerisation of several vinyl monomers in the presence of air, but if precautions were taken to exclude air the

extent of polymerisation was reduced by half.⁸⁰ The precautions taken only involved flushing the monomer solution with nitrogen and quite probably residual oxygen remained. More elegant work by several schools in the early 1960's demonstrated that in the total absence of oxygen no polymerisation occurred,^{81,82,83} although Fordham and co-workers found that vinyl chloride would still slowly polymerise (1%/hour), even after having taken very vigorous precautions against the inclusion of air.⁸⁴ It may well have been that in this case the residual polymerisation occurred by a non-radical mechanism, or possibly it was the result of catalysis by impurities in the materials.

Nevertheless, the importance of oxygen was now clearly demonstrated and the attention of workers was turned to the mechanism of the initiation.

The Initiating Species.

At this time it was well known that boron peroxides existed and Davies et al. demonstrated that the newly synthesised triperoxyborates were effective initiators for styrene and methyl methacrylate polymerisations.⁴¹

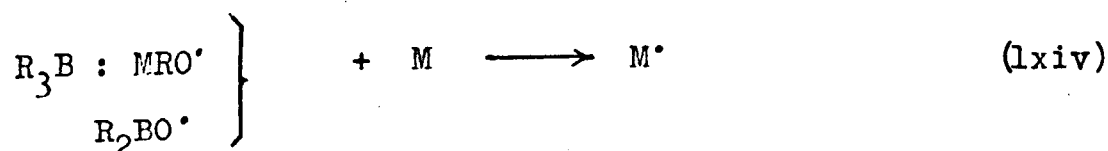
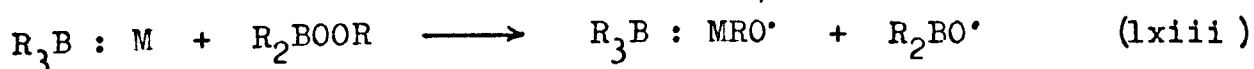
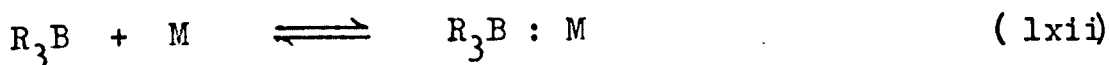
Furukawa took up this theme and suggested the role of oxygen in borane initiated polymerisations was to bring about the formation of an organoperoxyborane.⁸⁵ This prior formation of peroxide was also regarded by Bawn and co-workers to be an important step in the initiating mechanism.⁸⁶ In a short paper, these workers reported on methyl methacrylate polymerisations initiated by tri-n-butylborane and an

autoxidised solution of the borane. This latter solution was stated to be the monoperoxide but with the benefit of hindsight it was more likely to have been a mixture of mono and diperoxides with boron esters. The polymerisations were followed dilatometrically and a satisfactory rate equation was derived, namely,

$$\left(\frac{-d[M]}{dt} \right)_{\text{Initial}} = K [R_3B]^{\frac{1}{2}} [R_2BOOR]^{\frac{1}{2}} [M] \quad (1xi)$$

Where $[M]$ = concentration of monomer.

They proposed a mechanism having as its first step the formation of a borane-monomer adduct which then reacted with the peroxide to produce the initiating radicals:

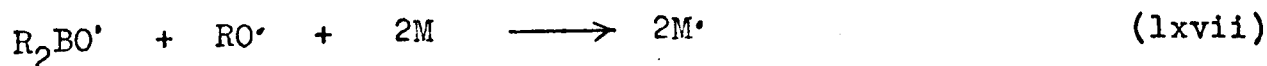
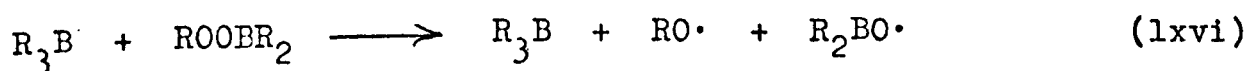
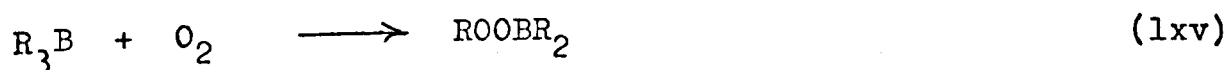


Peroxide or borane alone were found to be ineffective catalysts.

About the same time, Zutty and Welch suggested a reaction between the boron alkyl and autoxidised boron alkyl as the initiating species in trialkylborane-oxygen catalysed polymerisations.⁸² These workers were not convinced that the

co-catalyst was a boron peroxide, but proposed that it could be a transitory intermediate in the formation of the peroxide from the organoborane.

The idea that an organoborane-organoperoxyborane reaction was the pertinent factor of trialkylborane-oxygen initiated polymerisations was further substantiated when Welch published the results of a detailed study.⁸³ The bulk polymerisation of methyl methacrylate, initiated by triethylborane-oxygen mixtures, was followed by product analysis and Welch proposed the following scheme to account for the initiation:



i.e., a prior formation of peroxide followed by an induced disproportionation reaction which produced the initiating radicals. At high oxygen to borane concentration ratios the polymerisation ceased after low conversion and he explained this as being a result of almost 100% peroxide production which almost eliminated the disproportionation reaction (1xvi)

A similar effect was noted at the other extreme of concentration ratios, and this he explained by considering that any peroxide formed was rapidly destroyed by excess borane, reaction (1xvi), which would not give sustained initiation. The maximum rate of polymerisation occurred when the concentrations of borane and oxygen were about equal, conditions under which reaction

(lxvi) would proceed to its greatest extent. Some years later, Hansen⁸⁷ published work of a very similar nature to this and agreed with the general conclusions found by Welch. Welch had achieved varying concentration ratios by altering only the concentration of oxygen, but Hansen extended this to include varying triethylborane concentrations. Although the kinetics were complicated, at low oxygen to borane ratios the following rate equation was found to apply:

$$\left(\frac{\ln. \frac{[M]_0}{[M]}}{[M]} \right)_{\text{Initial}} = K [O_2]^{\frac{1}{2}} ([R_3B]_0 - [O_2]_0)^{\frac{1}{2}} . t \quad (\text{lxviii})$$

$[M]_0$ = initial monomer concentration.

$[M]$ = monomer concentration at time t.

The square root dependence on oxygen concentration had been noted previously by both Welch⁸³ and Bawn⁸⁶. This equation predicted a maximum initial rate at $[Et_3B] = 2 [O_2]$ and Hansen showed this to be approximately correct, which was a contrast to Welch's findings of a maximum rate at

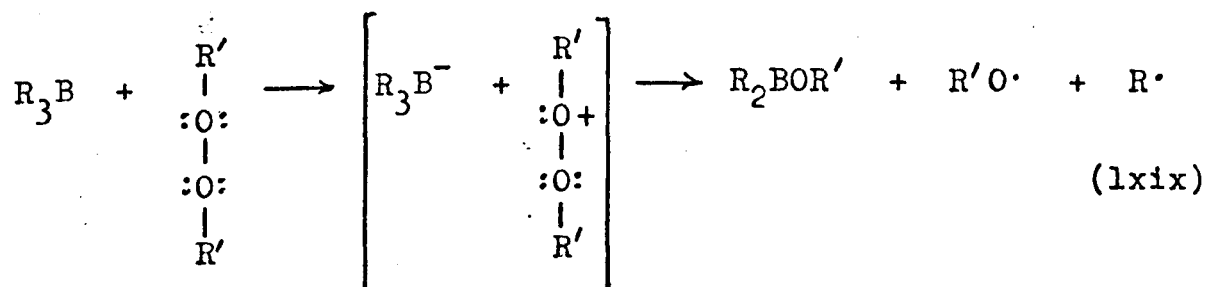
$[Et_3B] = [O_2]$. The energy of activation for the polymerisation was determined and had a value of $2.4 \text{ kcal.mole}^{-1}$ in good agreement with Welch's value of 4 kcal.mole^{-1} ⁸³, but in contrast with that found by Bawn of $12.9 \text{ kcal.mole}^{-1}$.⁸⁶

Finally, Davies found that di-iso-butylperoxy iso-butylborane initiated the polymerisation of acrylonitrile equally as well as a mixture of tri-s-butylborane and oxygen.⁴⁶ However, he did qualify these findings by suggesting that the decomposition of the peroxide may have been induced by complex

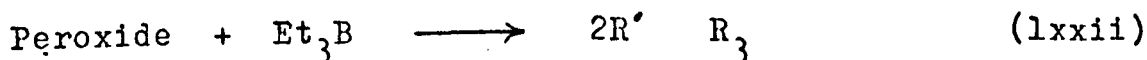
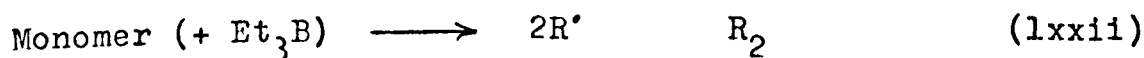
formation with the acrylonitrile.

Borane - Organic Peroxide Initiators.

Meanwhile, the usefulness of this kind of initiation system had been investigated by Furukawa et al. They found that a mixture of triethylborane and an organic diperoxide was an effective initiator for vinyl chloride polymerisations. A redox reaction was suggested as being responsible for the production of initiating radicals:



For the next ten years little work of significance was done on the initiating ability of this system. Recently, Grotewold and co-workers have studied the polymerisation of methyl methacrylate using triethylborane - organic peroxide mixtures.⁸⁹ The system worked satisfactorily, and from the polymerisation data, they were able to deduce information concerning the nature of the reaction of borane and peroxide. Three initiation reactions were postulated:

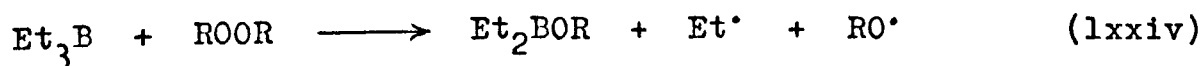


and expression (lxxiii) was derived:

$$R_3 = (R_p^2 - R_1^2 - R_2^2)^{\frac{1}{2}} \quad (\text{lxxiii})$$

where R_p = rate of polymerisation.

At low triethylborane, high peroxide concentrations, the stoichiometry of reaction (lxxii) was 1:1, and when the peroxide was di-t-butylperoxide, the reaction had an activation energy of 10 kcal.mole⁻¹. Although unable to detect free-radicals from reaction (lxxii) Grotewold et al. suggested a similar mechanism to that of Furukawa:



Initiation by Borane - Donor Complexes.

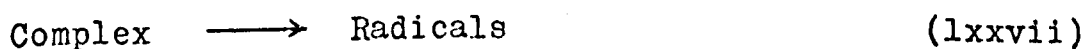
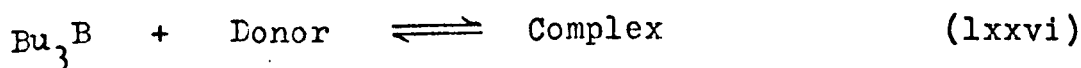
Several authors have explored the possibility of using these complexes because they are much easier to handle than the free borane. Although he gave no details, Ashikari stated that compounds of the type >N:BR_3 had no initiating ability.⁸⁰ He suggested that this was due to their inability to form the borane-oxygen adduct previously discussed (p 42). The results of this work were completely contradicted by Noro and Kawazura.⁹⁰ These workers reported that the triethylborane-ammonia complex readily initiated vinyl polymerisations in the presence of air. The complex was found to be as effective as the free borane, except at low temperatures, when presumably the complex was virtually

100% associated. Borsini went further and reported that under conditions of excess oxygen the complexes were more effective than free borane.⁹¹ In the absence of donors, and as the oxygen to borane ratio was increased, the rate of polymerisation of vinyl chloride increased to a maximum at $[O_2] / [R_3B] = 0.3$ after which any further increase resulted in inhibition, in agreement with other workers.^{83,87} In the presence of pyridine or diethyl ether, the rate again reached a maximum but any further increase in the oxygen concentration did not inhibit the reaction, the rate of polymerisation staying constant. Borsini et al. suggested that this was because the complex interfered with the mechanism through which the free-radicals originated.

In a more recent paper the rates of polymerisation of methyl methacrylate, initiated by tributylborane-oxygen in the presence of a variety of donors, have been reported.⁹² Kojima and co-workers showed a satisfactory rate equation was:

$$R_p = k \cdot [\text{Complex}]^{\frac{1}{2}} [M] \quad (1xxv)$$

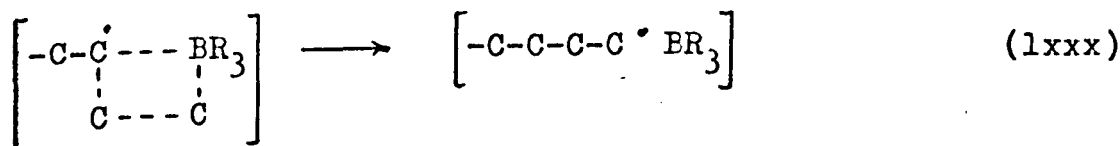
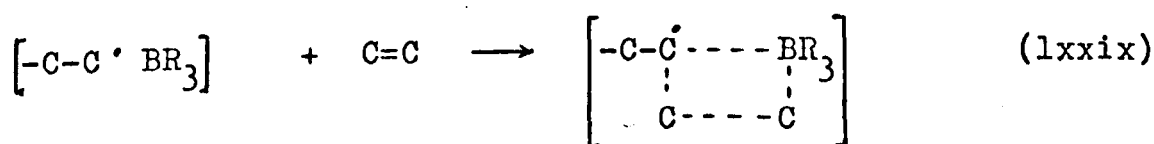
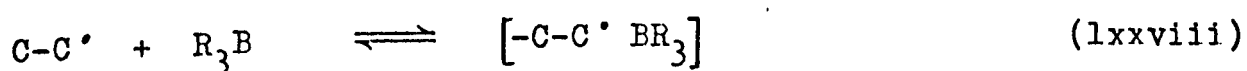
although there was no mention of the effect of varying oxygen concentration. The results indicated that pyridine and substituted pyridines accelerated the rate of polymerisation relative to initiation by uncomplexed borane and oxygen.



For a series of methyl substituted pyridines, the reactivity was found to be the reverse of the basicity, and Kojima and co-workers suggested that this was due to reaction (lxxvii) becoming more facile.

Inhibition of Borane - Oxygen Initiated Polymerisation.

Arimoto found that a variety of vinyl monomers could be polymerised by a borane-oxygen or borane-peroxyborane initiating system, even in the presence of large amounts of inhibitors, such as various amines, phenols, quinones or phenothiazine.⁹³ He further reported that, whereas azo bis-iso-butyronitrile (A.I.B.N.) would not initiate polymerisation in the presence of these inhibitors, if a small amount of borane was added, under nitrogen, polymerisation readily occurred. This led him to suggest a mechanism involving a borane-propagating radical complex which facilitated polymerisation even in the presence of inhibitors:



Brindley and Pearson questioned this mechanism.⁹⁴ In an earlier paper, Brindley and Allies had shown that the inhibitors

used by Arimoto were not effective in inhibiting trialkylborane autoxidations,³⁰ and Brindley and Pearson therefore pointed out since autoxidation still occurred, polymerisation would be readily initiated by chain transfer. They further reported that galvinoxyl, an effective borane autoxidation inhibitor, successfully inhibited polymerisation for a number of hours. The A.I.B.N.-borane initiated polymerisations could have resulted from a low concentration of cyano-iso-propyl radicals displacing a radical from the borane (an S_H^2 reaction) and hence giving a growing polymer chain.

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CHAPTER 3.

σ - BONDED ORGANOTRANSITION METAL COMPOUNDS.

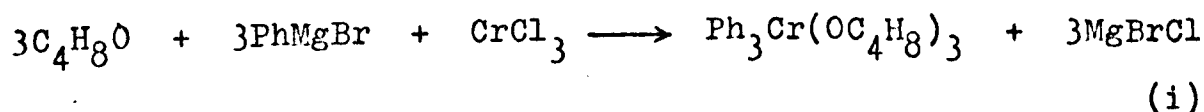
Of the many compounds which can be classed as organotransition metal compounds, this and subsequent chapters will deal with those compounds containing only σ -bonded alkyl groups, and attention will be focussed on the early transition metals (Groups IVa to VIa). Except for a few isolated examples, stable compounds within this class have only become known in the last two or three years and this can be attributed to a basic lack of understanding of the reasons for their apparent instability. The existence of σ -bonded organotransition metal compounds as labile intermediates in catalytic processes, has often been postulated.

1. Introductory Survey.

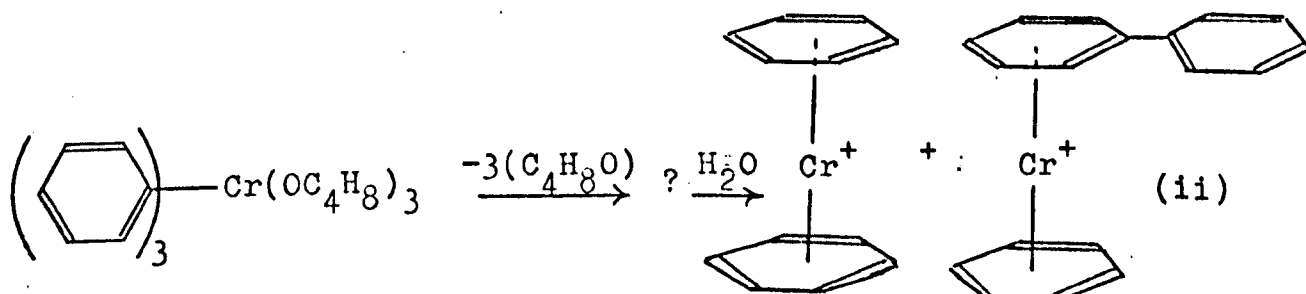
In the 1930's following a lack of success in the preparation of σ -bonded transition metal organometallics, their existence was thought unlikely. Indeed a review was published providing a theoretical explanation for the apparent instability of covalent transition metal to carbon bonds.¹

However, some twenty years later some degree of success was achieved with the isolation of phenyltitanium tri-isopropoxide

This was the first compound prepared containing an early transition metal to carbon bond. It was quite stable but subsequent attempts by these workers to form compounds of the type $\text{Ph}_n\text{TiX}_{4-n}$ showed that the stability decreased drastically as n was increased to two and three.³ In fact, stable compounds were only formed when n was less than two, and X was a highly electronegative group, such as halogen or alkoxide.³ A similar affect was noted for the methyl titanium chlorides.^{4,5} Also during this period of time, work by Zeiss et al. on phenylchromium π -complexes,⁶ generated interest in σ -bonded phenyl chromium compounds.^{7,8} Most of these compounds were stable only in the presence of donor solvent molecules. For example, the reaction of phenylmagnesium bromide with chromium (III) chloride in tetrahydrofuran gave tris-(tetrahydrofuran) tri-phenylchromium:⁹

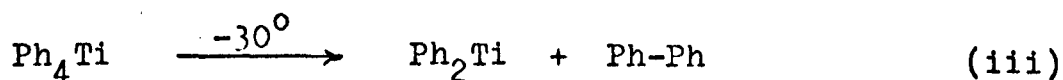


This was a bright red complex, shown by magnetic measurements to be a sigma complex, but on removal of the co-ordinated tetrahydrofuran, it rearranged to a black solid, which on hydrolysis yielded π -complexes:



The analogous mesityl compound was more stable and did not rearrange on removal of the solvent.⁸

The first fully alkylated compound to be prepared was tetramethyltitanium which was extremely unstable and decomposed above -10°C .⁵ The analogous phenyl derivative was similarly found to be very unstable decomposing to biphenyl and diphenyltitanium at temperatures above -30°C .¹⁰ The latter compound was found to be more stable than its quadrivalent analogue.



It would be instructive at this point to consider the reasoning put forward during this period in order to explain the instability of these compounds. The theory proposed by Coates drew comparisons between the formation of a titanium chlorine bond and a titanium-carbon bond.¹¹ The titanium 3d and 4s orbitals are relatively diffuse compared to the compact orbitals of carbon or chlorine, and therefore, in the absence of other effects good overlap and strong bonding would not occur. The effect of the large electronegativity difference between titanium and chlorine causes considerable polarisation - a contraction of the titanium orbitals and an expansion of the chlorine orbitals - and consequently good overlap occurs between these atoms, giving strong bonds. He further suggested that such polarisation would not occur to such an extent between the electronegatively similar atoms of titanium and carbon, and

thus it was not surprising that strong bonds were not formed. This argument also applied to the increase in stability on replacing alkyl groups with halogen or alkoxide groupings, since a degree of polarisation would be expected thus facilitating the formation of a relatively strong titanium-carbon bond.

In 1968 Green made a very important contribution by pointing out that the kinetic stability must be considered as well as the thermodynamic stability of transition metal to carbon bonds.¹² Thermodynamic stability relates to the intrinsic strength of a bond whereas the kinetic stability is concerned with the rate of decomposition of such bonds. Thus, it is perfectly possible to have a thermodynamically unstable compound with a long lifetime, because of its slow rate of decomposition. This chemical principle is well known but Green was the first to relate it to early transition metal organometallic compounds. In his article he agreed with Coates that it was probable that these bonds were thermodynamically unstable, the reason being that on decomposition carbon ions or radicals would be produced which would readily form stable products and this should give rise to a large decomposition energy. These facts are summarised in the potential energy diagram, Figure 1. Green therefore suggested that factors affecting the kinetic stability would probably play the most important role in determining the thermal stabilisation of early transition metal organometallics. Kinetic stability is primarily determined by the mechanism of the decomposition, and Green suggested rather than a purely homolytic dissociation, the

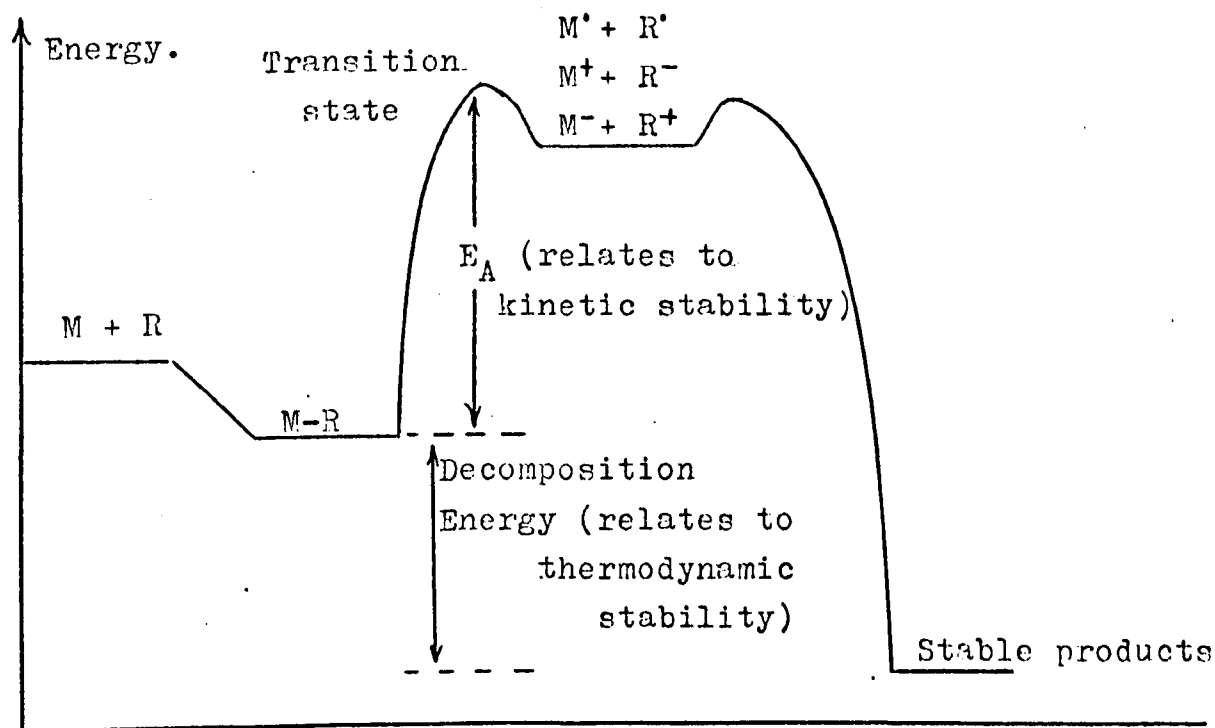
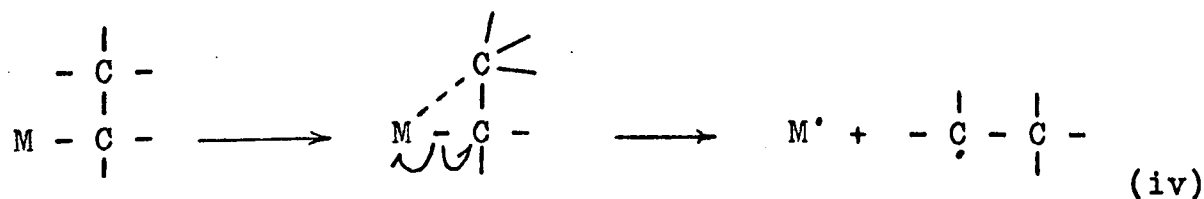


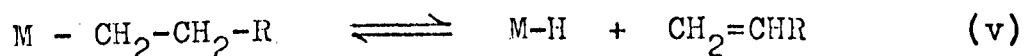
Figure 1. Potential Energy Diagram for the Formation and Decomposition of a Transition Metal Alkyl.

decomposition could well involve β - interactions giving rise to a transition state of very low energy (Figure 1):



Wilkinson¹³ extended the theories proposed by Green. Firstly, he suggested, with respect to the thermodynamic stability, there was no reason for believing that early transition metal to carbon bonds should be any weaker than bonds to nitrogen or oxygen, and compounds containing such bonds were quite stable, e.g., the dialkylamides, $M(NR_2)_n$ ^{14,15} Secondly, considering the kinetic stability, Wilkinson proposed

that the most common mechanism for the destruction of transition metal to carbon bonds involved the elimination of an olefin:



This then was the heart of the argument; viz., organic groups unable to form olefins should form the most stable early transition metal organometallic compounds. Wilkinson et al. substantiated this suggestion by the isolation of many stable organotransition metal derivatives of the trimethylsilylmethyl group $[(CH_3)_3SiCH_2-]$.^{13,16} These compounds, in the absence of oxygen, were considerably more stable than the methyl or phenyl derivatives described earlier, and could be stored for weeks at room temperature. In a later paper, Wilkinson et al. also reported the preparation of several stable neopentyl derivatives.¹⁷

Evidence for this idea was also provided by Tamura and Kochi who had prepared many dialkyl manganese compounds and studied their decomposition 'in situ'.¹⁸ The benzyl, methyl, and neopentyl derivatives were by far the most stable, and obviously these groups forbid reaction (v).

Lappert et al. also prepared several stable trimethylsilylmethyl transition metal compounds, although apart from the tetra substituted titanium and zirconium derivatives, additional stabilising ligands, such as cyclopentadienyl, were incorporated into the molecule.¹⁹

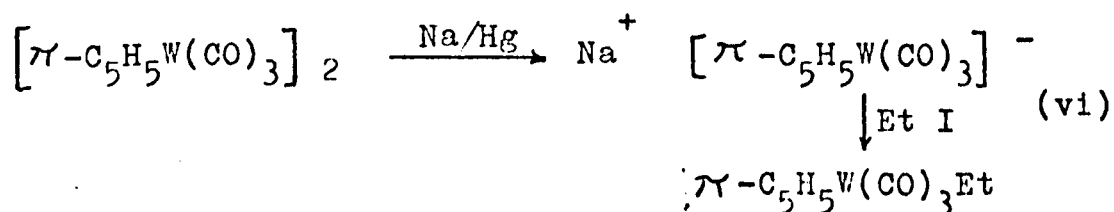
Prior to the work of Wilkinson, stable benzyl derivatives

of titanium and zirconium had been prepared, although any theoretical explanation for their stability was not proposed.²⁰ In a later paper, these workers published details of the properties of these compounds.²¹

2. Synthesis

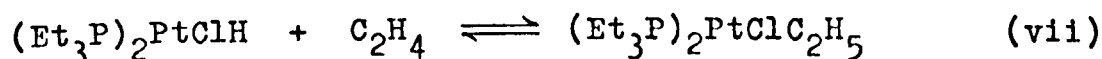
A feature of all of the preparative methods is the great necessity to exclude oxygen during all stages of the reaction. There are three major preparative routes and the most common of these is transmetallation. This invariably involves the interaction of a transition metal halide with the Grignard or organolithium reagent. For the less stable alkyls, such as tetramethyltitanium, this reaction was done at low temperature, usually below -50°C , and the pure alkyl was obtained by removing the solvent.⁵ The elimination prohibiting compounds were prepared at room temperature, and after removal of the solvent, purification was achieved by column chromatography.¹⁶ In some cases the alkoxides have been used in place of the metal halides.²

The second technique involves the reaction of an organic halide with a complex metal anion and has only been used to prepare σ -bonded compounds containing other ligands. The most common method required treating a solution of a metal carbonyl with sodium amalgam, and reacting the resultant complex metal anion with the appropriate alkyl or aryl halide at low temperature:²²



This technique is not applicable to the production of fully alkylated derivatives.

The last general method involves the reaction of an alkene with a metal hydride, and is analogous to the hydroboration reaction discussed previously for the preparation of organoboranes (p.3).



This reaction was done at 95°C and at 40 atmospheres pressure.²³ However, it is obviously the reverse of reaction (v) and is only useful for the preparation of σ-bonded complexes containing stabilising ligands, as in the above example.

There are of course other methods which have been used in isolated cases, but the major routes available for the introduction of a σ-bonded organic group are those outlined above.

3. Properties.

Because of their somewhat recent discovery, our knowledge of these compounds is limited. Those compounds containing stabilising ligands have been more fully studied, and in some

aspects it is probable that the properties of the fully alkylated derivatives will resemble them quite closely.

Bonding and Structure.

Wilkinson et al. investigated the structure of hexakis (trimethylsilylmethyl) bimolybdenum using X-ray diffraction, and they concluded that each metal atom had a distorted tetrahedral structure.¹⁷ They gave the following bond angles, Mo-Mo-CH₂ 100.6°, and Mo-CH₂-Si 121.1° and found the metal-metal bond was 2.167 Å in length. In a later publication,¹⁶ Wilkinson, using a simple molecular orbital treatment, discussed the bonding in this compound and proposed that the metal-metal bond was a triple bond, formed by the six d electrons, with d_{z²} as the σ-bond and d_{xz} and d_{yz} as π-bonds.

X-ray diffraction was also used by G.R. Davies and co-workers to study the structures of the benzyl derivatives of the Group IVA transition metals.^{24,25} All of the structures were found to be distorted tetrahedra. For tetrabenzyl zirconium the bond angles were, CH₂-Zr-CH₂ 95° (mean value), and Zr-CH₂-C 92° (mean value). They proposed that this distortion was the result of a π-interaction between the aromatic rings and vacant orbitals on the metal atom.

The orbitals used in bonding in these d⁰ tetrahedral structures is not clear because the three p orbitals and the three d orbitals (d_{xy}, d_{xz}, and d_{zy}) are of the same symmetry class and thus they mix with each other. Crudely, the bonding orbitals may be considered as a mixture of sp³ and sd³ hybrids.

There is little data concerning the structures of bis (η -cyclopentadienyl) dialkyl complexes of titanium and zirconium, although it seems probable that they will closely resemble the corresponding dihydrides and dichlorides.¹²

In these compounds the cyclopentadienyl (Cp) rings are non-parallel, and the Cp-M-Cp bond angle can range from 135° to 175°. The bonding involved in cyclopentadienyl complexes is discussed fully and clearly by Green,¹² suffice it to say here that it can be envisaged as an overlap between filled η -orbitals of cyclopentadiene and vacant orbitals on the metal, of suitable symmetry.

Thermal Stability.

Many papers have been devoted to the study of the mechanism of the decomposition of organotransition-metal compounds, which were usually prepared and studied 'in situ'.^{18,26,27,28,29} From all of these papers it was generally concluded that the products of decomposition consisted of alkanes, alkenes, and usually a metal hydride. Four major decomposition processes were detected for the break down of alkyl chromium systems.^{27a,b}

- (a) β -metal hydride elimination,
- (b) α -metal hydride elimination,
- (c) Hydrogen transfer from solvent to an alkyl group,
- (d) Hydrogen transfer from the β -position of one alkyl group to the α -position of another,

Sneeden and Zeiss summarised these fragmentation modes for a dimeric chromium compound as follows:^{27b}

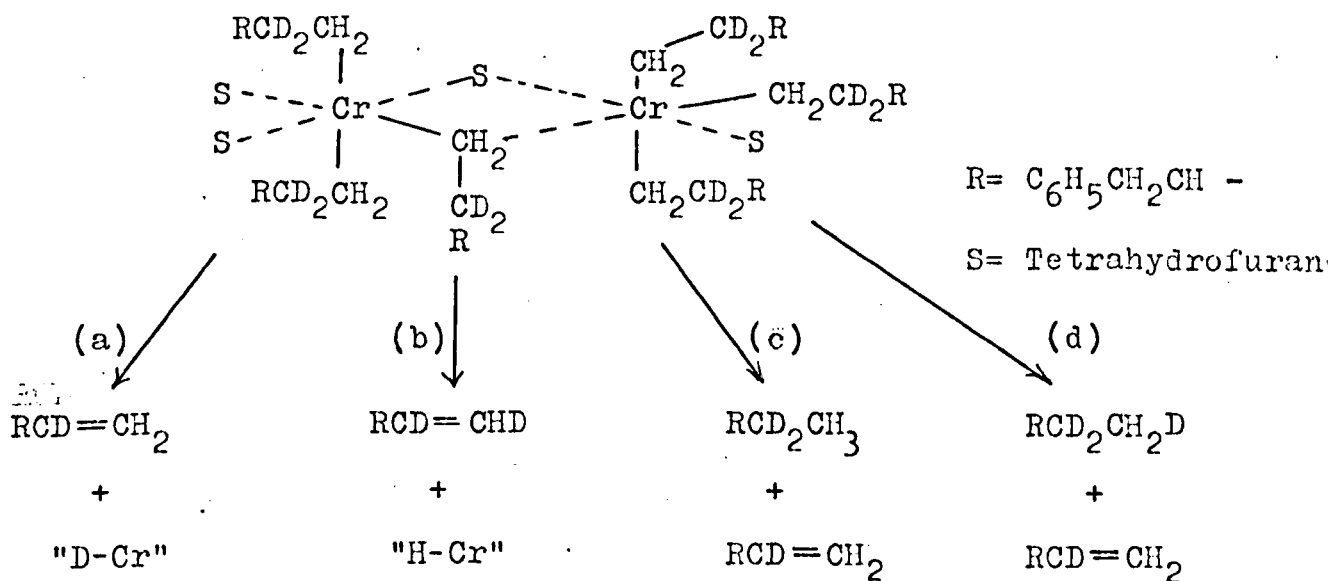
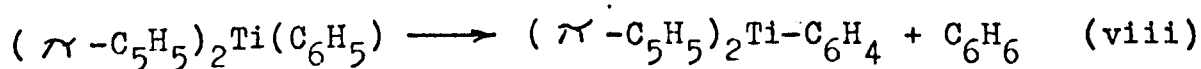


Figure 2. Decomposition Routes of a Dimeric Organochromium Compound.

Wilkinson suggested that route (a) appeared to be the most common and the most facile mechanism of decomposition.¹⁶

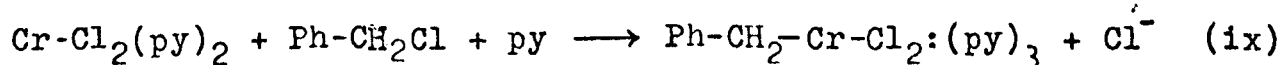
Tetramethyl titanium decomposed at room temperature to give a black precipitate and a metallic mirror.³⁰ This black precipitate had been observed previously and was found to be pyrophoric,³¹ and it may well have been dimethyltitanium by analogy with the decomposition of tetraphenyltitanium which yielded diphenyltitanium and biphenyl¹⁰ (equation iii). The thermal stability of this biphenyl derivative was much increased, relative to the tetraphenyl compound, and it was at low pressure and 200°C that it decomposed to yield biphenyl and metallic titanium.¹⁰ Diphenyl dicyclopentadienyl titanium

similarly decomposed to yield biphenyl and dicyclopentadienyl titanium (II).³² This reaction was thought to be a simple homolysis of the two titanium carbon bonds, but a more recent study by O'Brien et al. has shown it to be somewhat more complicated.³³ It appeared that the first phenyl radical would abstract a proton from the second phenyl group rather than from the solvent to yield benzene and a titanium phenylene derivative:



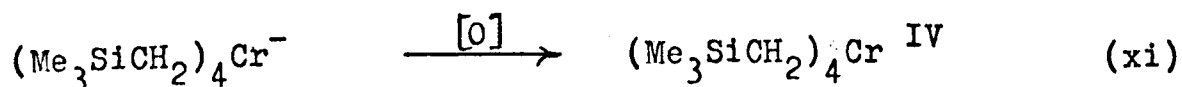
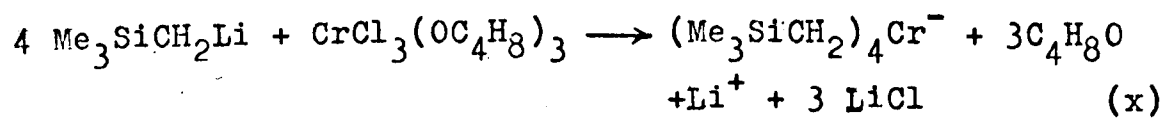
The nature of the phenylene derivative was not clear.

The trimethylsilylmethyl compounds were much more stable, and it has been reported that in hydrocarbon solution and in the absence of oxygen, the molybdenum and tungsten derivatives were stable for a week at room temperature, whilst the vanadium analogue was stable indefinitely at -30°C .¹⁶ Tetrabenzyltitanium and tetrabenzylzirconium did not degrade at all in the solid phase, but slowly decomposed in hydrocarbon solution at room temperature.²¹ These two compounds were effected adversely by light.²¹ In complete contrast, tribenzylchromium was very unstable decomposing in solution to give toluene, 1,2-diphenylethane and other hydrocarbon products rapidly at room temperature.³⁴ In a later paper Sneed et al. reported the preparation of dichlorobenzyl chromium (III) compounds as stable pyridine (py) adducts:³⁵



Ortho- and para- dichlorobenzyl derivatives were prepared similarly, and all of these complexes were stable for months at -5°C under nitrogen.

Wilkinson et al. also observed the unusual behaviour of chromium (III) alkyls.¹⁶ An attempted synthesis of tris (trimethylsilylmethyl) chromium was found to yield the tetrakis (trimethylsilylmethyl) chromate (III) ion, which they were unable to isolate as a salt. Mild oxidation of this compound by a trace of air allowed the isolation of tetrakis (trimethylsilylmethyl) chromium (IV):¹⁶



Autoxidation.

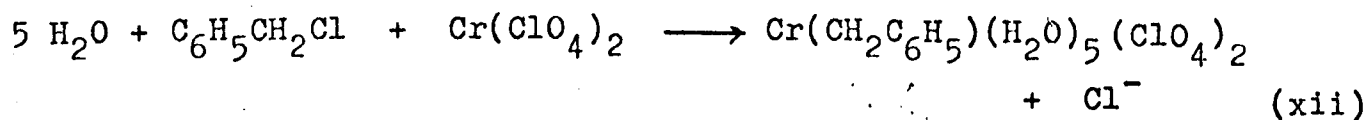
A very distinctive feature of many of these compounds is their facile reaction with oxygen. Diphenyltitanium was very reactive and in the solid state it ignited, the reaction in solution was less vigorous and phenol and biphenyl were found among the products.¹⁰ Tetramethyl- and tetraphenyl-¹⁰ titanium were equally reactive. Wilkinson and co-workers noted that all the trimethylsilylmethyl compounds were sensitive to air.¹⁶ The solid molybdenum and tungsten derivatives were reported as being stable for short periods in air, but soon darkened and the end product appeared to be

the metal oxide. The vanadium compound was particularly reactive and inflamed in air. It was stated that on passing a solution through a cellulose column (presumably nitrogen filled), during chromatographic purification, they obtained the oxo derivative, $[(CH_3)_3SiCH_2]_3VO$. Whether this was formed as a result of reaction with the column packing or residual oxygen was not clear. A more detailed study of the reaction of oxygen with σ -complexes, was made by Giannini et al. who showed that both tetrabenzyltitanium and tetrabenzylzirconium reacted with two mols. of oxygen.²¹ Following hydrolysis they obtained benzyl alcohol, though only in 50% yield based on the benzyl groups originally present.

Those compounds containing stabilising halogen ligands were also very susceptible to oxidation, and the autoxidation of the titanium derivatives has been reviewed.³⁶ Typically, the autoxidation of methyltitanium trichloride was found to proceed rapidly in solution and 0.5 mol. of oxygen was absorbed with the production of methoxytitanium trichloride.⁵ The introduction of cyclopentadienyl groups considerably stabilised these compounds towards oxygen and dicyclopentadienyl methyltitanium chloride remained unchanged over a period of weeks in contact with atmospheric oxygen.³⁷

The autoxidation of some chromium compounds has also been investigated. Thus the yellow compound bis-O-methoxyphenylchromium, formed by the reaction of O-methoxyphenyllithium and a chromium (II) halide, was found to be pyrophoric in air.³⁸ An interesting compound was formed by the reaction of benzyl chloride with an aqueous

solution of chromium (II) perchlorate in perchloric acid:³⁹



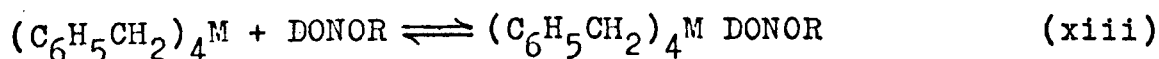
This compound reacted with oxygen to form benzaldehyde which may well have resulted from an initial alkoxide formation which gave benzyl alcohol, and this was then oxidised 'in situ' by perchloric acid to yield benzaldehyde.

Adduct Formation.

Since all the early transition metals have vacant orbitals, it is not suprising that these σ -bonded complexes should behave as Lewis acids. Tetramethyltitanium formed a number of 1:1 and 1:2 adducts with a variety of monodentate⁴⁰ and bidentate⁴¹ ligands. The formation of these complexes appeared to increase the thermal stability of the tetramethyltitanium. Thus, various diamine complexes were stable for hours at 0°C⁴², in contrast to free tetramethyltitanium which would rapidly decompose at this temperature.⁵ It has been suggested that the increased thermal stability was due to the transition metal atom more closely approaching an inert gas configuration⁴³ although Wilkinson thought it more likely to be a result of the blocking of sites required for decomposition reactions.¹⁶ A similar effect has already been mentioned for the arylchromium (III) compounds.⁹

More recently, Felton and Anderson have studied quantitatively the formation of adducts of tetrabenzylzirconium and tetrabenzylhafnium with a variety of donors using nuclear

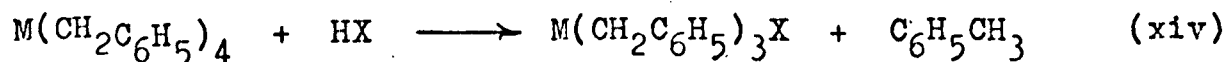
magnetic resonance spectroscopy⁴⁴. They found 1:1 adducts were formed with pyridine, quinoline, trimethylphosphine and tetrahydrofuran, and that these compounds existed in equilibrium with the dissociated species:



The equilibrium quotient for the reaction between pyridine and tetrabenzylzirconium was 12.6 at 40°C. There was no evidence for the formation of a 1:2 complex with pyridine which was in contrast to tetramethyltitanium³⁸ and presumably resulted from increased steric crowding around the central metal atom. However, with 2,2'-bipyridyl both the zirconium and hafnium compounds formed insoluble red complexes, and the authors suggested, but did not establish, that the bipyridyl functioned as a bidentate ligand to form a six co-ordinate complex. The tetrabenzyltitanium formed a similar derivative and this has in fact been used as a method of isolation.⁴⁵

Reactions with Protonic Species.

Attempts to cleave the metal-carbon bond with water, acids, or alcohols have provided a number of seemingly conflicting results, although as more data is accumulated perhaps the reasons for these differences will become clear. Giannini et al. studied the reaction of several protonic species with tetrabenzylzirconium and titanium, and the general reaction may be written as:²¹

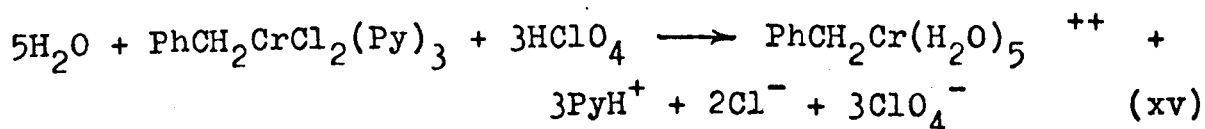


Where $X = F, Cl, Br, I, OEt$.

With excess reagent, all of the organic groups were replaced. Tetramethyl- and tetraphenyltitanium behaved similarly, releasing methane and benzene respectively.⁴¹ These reactions are presumably examples of nucleophilic substitution at the metal centre.

In contrast, water and dilute acids did not attack hexakis (trimethylsilylmethyl) dimolybdenum, but, strangely, the tungsten analogue reacted rapidly, but no information was given concerning the nature of the products. The molybdenum compound was, however, readily attacked by glacial acetic acid to give a quantitative yield of molybdenum (II) acetate. Also these authors reported that tetrakis (trimethylsilylmethyl) vanadium was decomposed by water and alcohols, but the chromium (IV) analogue appeared remarkably inert.¹⁶

Benzylchlorochromium (III) tripyridine reacted slowly with water or methanol to produce toluene and chromic salts. Dilute perchloric acid produced a penta-aquo benzylchromium(III) salt:³⁵



This compound had been previously reported and was found to be stable for about 56 hours in solution.³⁹ Several of these compounds are known^{46,47} and the majority were prepared by the reaction of an alkyl halide and an acidic solution of chromium (II) ions.

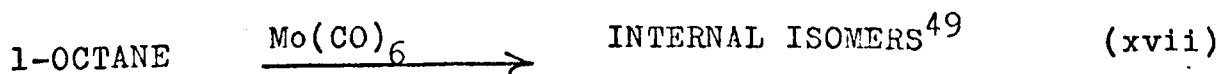
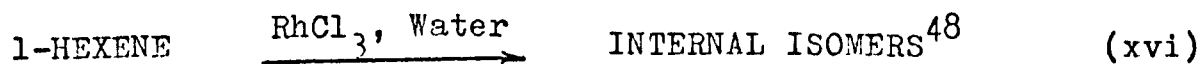
In the above sections an attempt has been made to draw together the available material concerning fully σ -bonded early transition metal organometallic compounds. Much of the work so far has been shallow and unrelated and hence it is difficult to draw comparisons or indicate general trends. However, it would appear that in comparison with other more well known organometallic compounds such as those of boron, aluminium, lithium, etc., the Group IVa alkyls and aryls are fairly typical, but the Groups V and VI transition metal derivatives appear somewhat different in several aspects.

4. Organotransition-Metal Compounds in Catalytic Processes.

Much of the work mentioned in the previous sections has been done in order to achieve an understanding of the role of transition metals in catalytic reactions, and in this section a brief review will be made of these processes. There are indeed many such processes but this survey will be confined to the major reactions, including the isomerisation of olefins, the hydrogenation of olefins, the polymerisation of olefins, hydroformylation, the Halcon process for the production of epoxides, and oxidations.

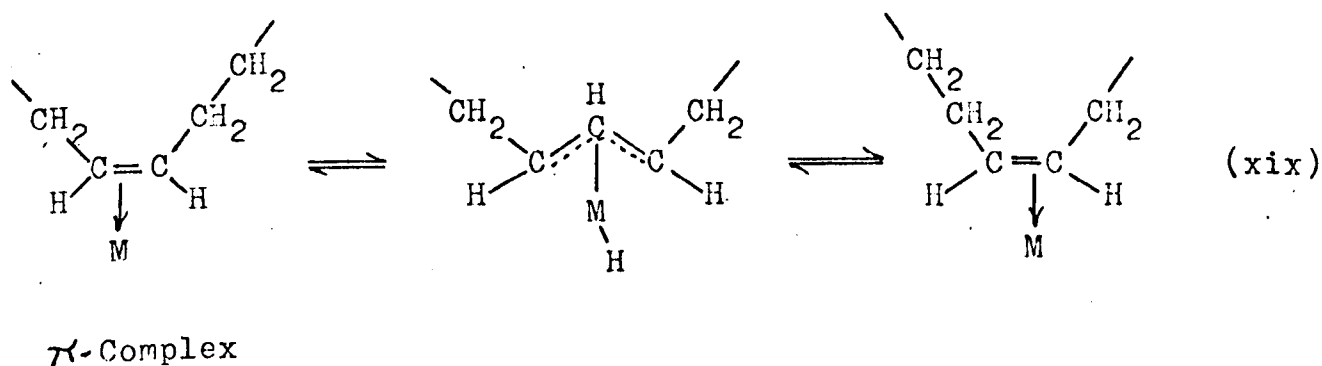
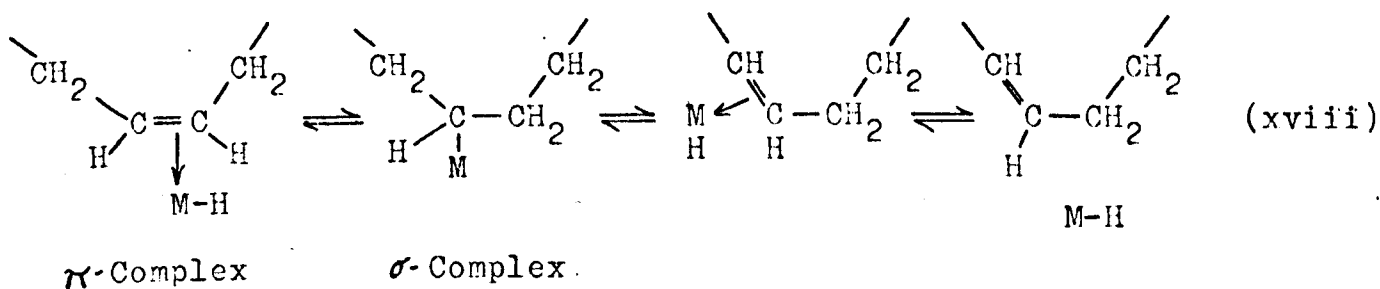
Isomerisation.

Most transition metals have the ability to isomerise olefins, and it appears irrelevant in which oxidation state or to what ligands the metal is attached. The reaction is invariably performed homogenously and thus it is necessary to have the transition metal in a soluble form. Typical reactions are:



The product was the thermodynamically more stable olefin, and it has been shown that for a range of products, the distribution was related to their relative stabilities.^{49,50}

It was a general feature of all postulated mechanisms that there is involved a reversible reaction between metal and olefin producing a σ -bonded organometallic intermediate which gives rise to the isomerised olefin. Two popular mechanisms are:^{49,50,51.}

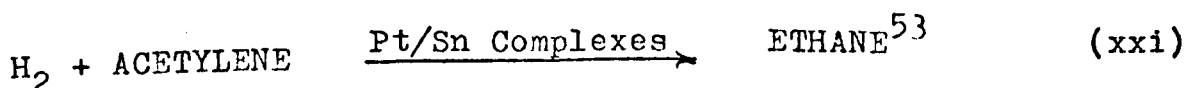
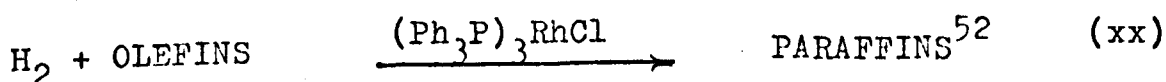


Scheme (xviii) necessitates the prior formation of a metal hydride (cf. isomerisation of olefins by hydroboration, p. 10) and involves a 1,2 hydrogen shift whilst mechanism (xiv) involves a 1,3 hydrogen shift.

Tetrabenzylzirconium was an active catalyst for these reactions providing the reaction was done in the light.²¹ This favours mechanism (xviii) since it has been shown that light decomposed tetrabenzylzirconium to give a complex hydride.²¹ It is interesting to note, with respect to this reaction, the organotransition metal compounds act in the reverse direction to the organoboranes, which isomerise olefins to produce the least thermodynamically stable product.

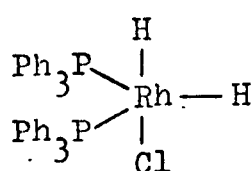
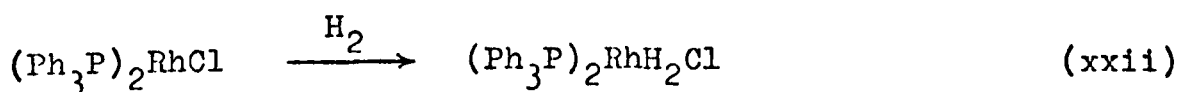
Hydrogenation.

Heterogenous hydrogenations using platinum or palladium black are familiar reactions, but homogenous catalysis using soluble transition metal species is also a convenient method for the reduction of olefins and acetylenes. A variety of transition metal complexes have been used, but the most common were derivatives of the Group VIII metals. Typical reactions include:

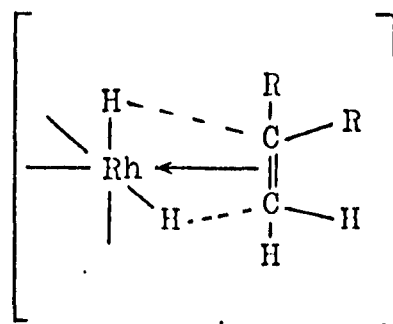
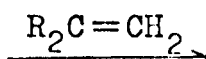


Reaction (xx) proceeded rapidly at room temperature in benzene solution under one atmosphere of hydrogen and was applicable to all olefins except ethylene.⁵² Wilkinson and co-workers suggested that the first step involved the formation of a

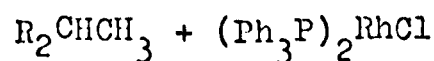
dihydride followed by the addition of an olefin which was reduced, and there was evidence to suggest that the mechanism was:⁵²



(II)



(xxiii)



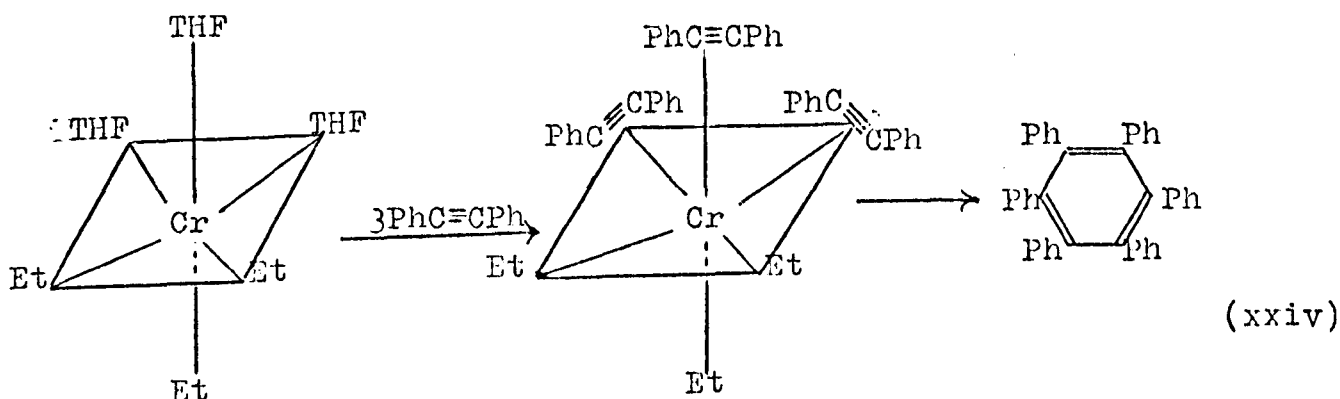
The hydride (II) could be isolated and was a very powerful reducing agent, and reacted with ethylene to give ethane.⁵²

This mechanism is quite similar to reaction scheme (xviii) except that two hydrogens are transferred, and the transfer is irreversible.

Polymerisations.

Dimerisation can be readily achieved; for example, ethylene was converted to butene using an aqueous solution of rhodium trichloride as catalyst.⁵⁴ Acetylenes can be trimerised by a variety of catalysts to give substituted aromatic compounds. Typical was the cyclisation of diphenylacetylene by triethylchromium to hexaphenylbenzene, the triethylchromium

being used as its tetrahydrofuran complex.⁵⁵ The postulated mechanism was:⁵⁶



The acetylenes were believed to enter stepwise since dimerised products were often obtained, as were compounds including an alkyl group transferred from the organometallic compound. Thus in the above example, a minor product was 1,2,3,4-tetraphenylbenzene.⁵⁵

Olefin polymerisations can be achieved by the use of Zeigler-Natta catalysts. These catalysts are made from an organometallic compound from a Group II or III metal and a transition metal halide. Typical examples are titanium tetrachloride-triethylaluminium or ethylaluminium halides, titanium trichloride-triethylborane, and vanadium tetrachloride-triethylaluminium. These are all heterogenous catalysts and they are highly stereospecific.⁵⁷ The mechanism of these reactions is not yet entirely clear, although it does seem probable that the polymerisation involves growth at the metal centre by an insertion reaction:⁵⁷



It is the nature of the intermediate which is not understood, although several suggestions have been made.^{57,58} Giannini et al. investigated the catalytic effectiveness of tetrabenzyltitanium and zirconium and some substituted derivatives.⁵⁹ They found that the tetrabenzyl compounds would polymerise ethylene but the mono- and di-chloro derivatives were more effective, and the addition of tribenzylaluminium had a marked accelerating affect. They concluded that because of the general low catalyst activity and high molecular weight polymers formed, the compounds investigated were only precursors of the true catalyst.

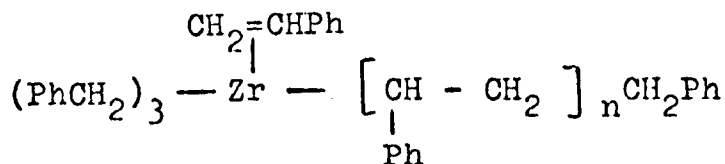
Ballard and Van Lienden made a detailed dilatometric study of the polymersisation of styrene, using a tetrabenzyl zirconium catalyst.⁶⁰ They found that the reaction was photochemically active and that three different processes occurred depending on the wavelength:

(a) $\lambda \geq 600$ n.m. - The rate of polymerisation was unchanged from its value in the dark, and they suggested that the polymerisation involved a co-ordinated - anionic type mechanism.

(b) $\lambda < 450$ n.m. - The rate of polymerisation was much greater than the 'dark rate', and reached a maximum at 317 n.m.. They suggested a radical mechanism since the rate was proportional to the square-root of the light intensity, and also, below 450 n.m. a solution of tetrabenzyl zirconium decomposed to give a range of products consistent with homolytic decomposition.

(c) $600 > \lambda \geq 450$ n.m. - The polymerisation rate was similar

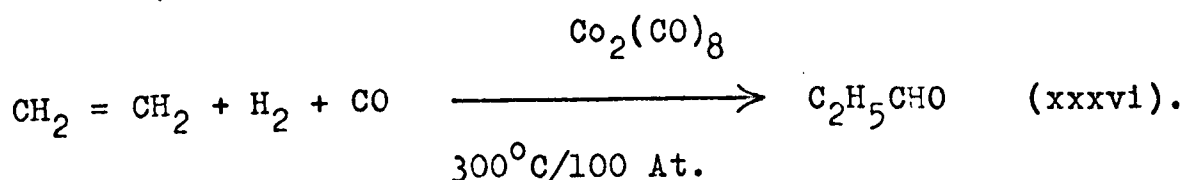
to the 'dark rate' but was photochemically activated. The propagation reaction was suggested as involving attack by monomer on a complexed species of the type:



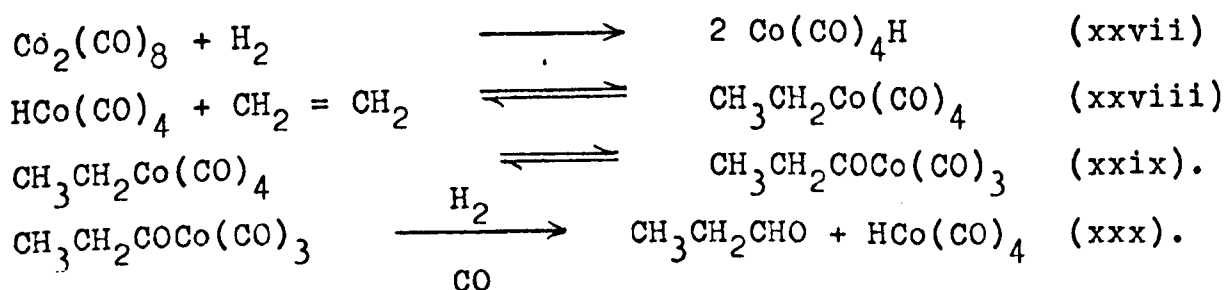
A similar process to reaction (xxv).

Hydroformylation.

This is an important industrial process for the conversion of olefins into aldehydes or ketones by reaction with hydrogen and carbon monoxide. The compound usually added to catalyse the reaction was dicobalt octacarbonyl, but Karapinka and Orchin showed the true catalyst was probably cobalt tetracarbonyl hydride.⁶¹ The process involves treating the olefin, at high temperature, with a mixture of hydrogen and carbon monoxide at 30 to 100 atmospheres in the presence of the catalyst:

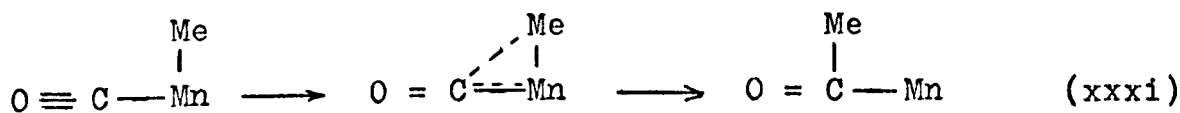


Studies by Heck and co-workers suggested the following mechanism for the process:^{62,63}



Thus, again the mechanism involves the formation of a transient σ -bonded organometallic species. Reaction (xxix) is an

insertion reaction, and the mechanism is probably analogous to that postulated for the carbonylation of pentacarbonylmanganese alkyl compounds:⁶⁴

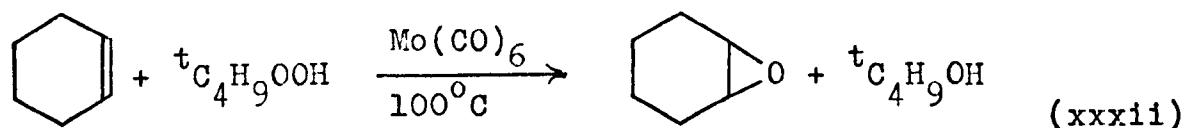


More recently rhodium compounds have been shown to be very effective catalysts for the hydroformylation reaction. Wilkinson et al. investigated various trans - carbonyl tris (triarylphosphine) rhodium chlorides, and in the case of the triphenylphosphine derivative concluded that the active species was dicarbonyl bis (triphenylphosphine) rhodium hydride $((\text{Ph}_3\text{P})_2(\text{CO})_2\text{RhH})$.⁶⁵ Using this compound, alkenes could be hydroformylated at 25°C and 1 atmosphere, giving a far greater ratio of straight chained to branch chained aldehydes than was previously obtained using dicobalt octacarbonyl.

In a later publication, Wilkinson reported that carbonyl tris (triphenylphosphine) rhodium hydride was also an effective catalyst and discussed the mechanism of the reaction.⁶⁶ The mechanism proposed was basically the same as reactions (xxviii) to (xxx) above.

Epoxidation.

The Halcon process is concerned with the production of epoxides from olefins. Although a wide variety of transition metal compounds have a catalytic effect on the reaction of olefins with hydroperoxides, molybdenum compounds have been shown to be the most effective.⁶⁷ A typical reaction was:⁶⁷



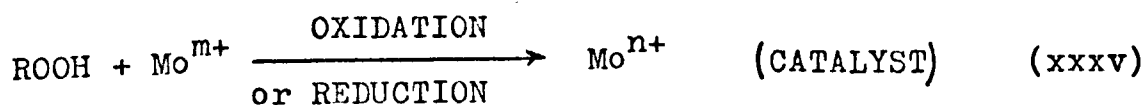
The mechanism for this reaction is not fully understood. Indictor and Brill found that the products were highly stereospecific which suggested an ionic mechanism. However, they also found that oxygen interfered with the reaction and this, together with the rate equation (xxxiii) led them to suggest a possible free-radical process.⁶⁸

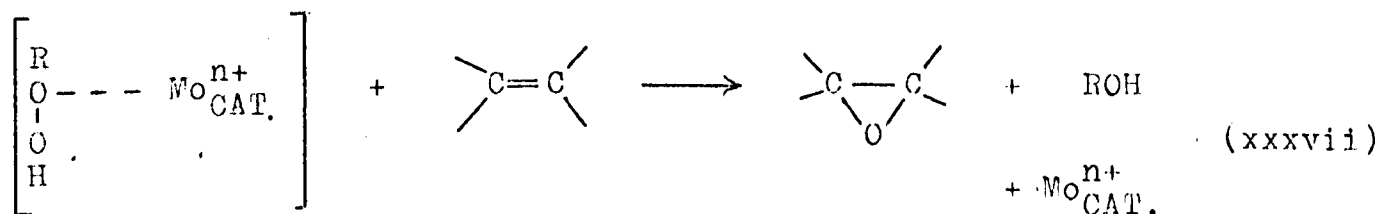
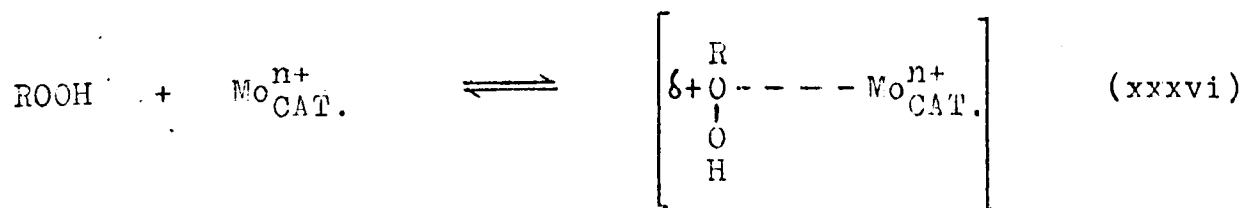
$$-\frac{d[\text{ROOH}]}{dt} = k [\text{ROOH}] [\text{CATALYST}]^{\frac{1}{2}} \quad (\text{xxxiii}).$$

Conflicting evidence was found by Sheng and Zajacek⁶⁷ who also showed the reaction to be highly stereospecific, but found no effect from oxygen and from kinetic studies gave the following rate equation:

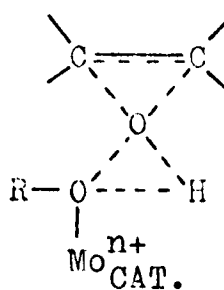
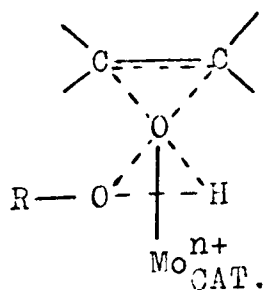
$$\text{RATE} = k [\text{ROOH}] [\text{CATALYST}] [\text{OLEFIN}] \quad (\text{xxxiv}).$$

This together with other evidence, they suggested indicated an ionic mechanism and they proposed the following:





Reaction (xxxvii) was rate determining and they postulated two possible transition states:



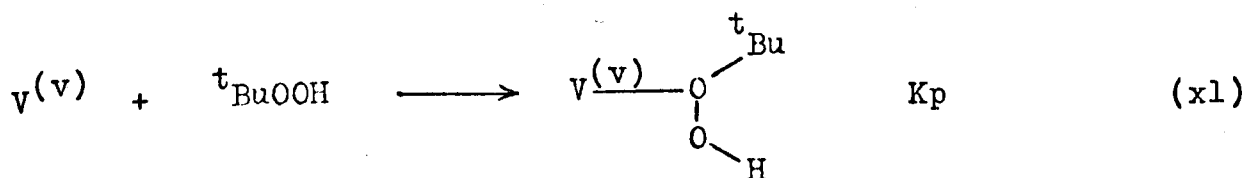
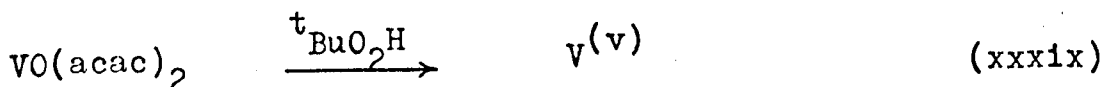
The prior formation of a complex between catalyst and hydroperoxide was also suggested by Japanese workers who reported the effects of metal oxide catalysts and concluded that best results were obtained using molybdenum trioxide.⁶⁹

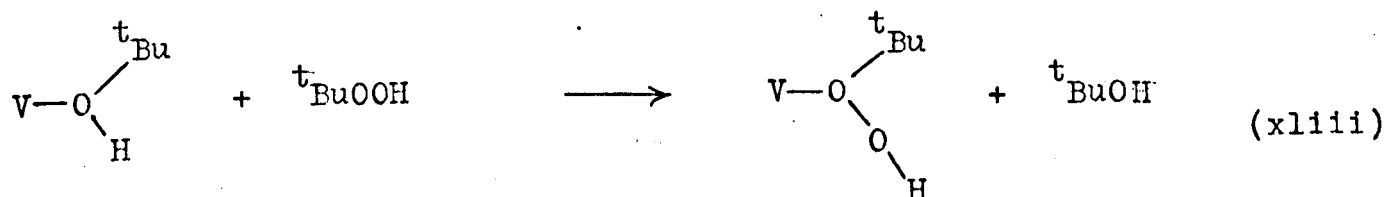
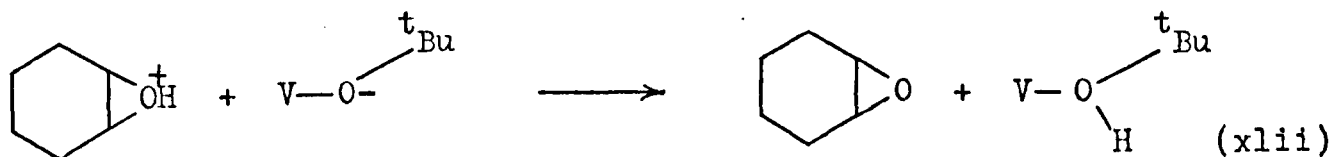
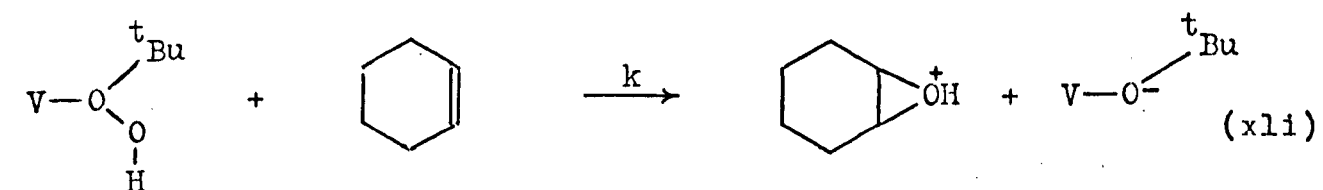
Gould and co-workers made a detailed kinetic study of the epoxidation of cyclohexene by tert-butylhydroperoxide in the presence of vanadium acetylacetonate catalysts.⁷⁰ They found

that cobalt (II) complexes and di-t-butylperoxalate did not catalyse the epoxidation, and this they suggested ruled out a free-radical mechanism. The rate of reaction was proportional to the hydroperoxide concentration at high dilution, but as the concentration was increased the rate approached a limiting value. The following equation applied:

$$\text{Rate} = \frac{k [\text{Vo}]}{\left(\frac{1}{[\text{P}]} K_p \right) + 1} \quad (\text{xxxviii})$$

Where $[\text{Vo}]$ is the concentration of vanadium and $[\text{P}]$ is the concentration of hydroperoxide. The results indicated a reaction, involving the prior formation of a vanadium-hydroperoxide complex with an association constant K_p , with a rate constant of k . The mechanism proposed, involved the reversible formation of the complex followed by a rate determining heterolysis of the oxygen-oxygen bond (xli). Epoxidation was then completed by proton transfer and the catalyst regenerated by ligand exchange:





These workers also suggested the following requirements necessary for a transition metal to have catalytic activity in this type of reaction:⁷⁰

- (a) The ion must have high charge, small size, and low lying d orbitals which are at least partly unoccupied.
- (b) It should not participate in any one-electron redox reactions under strongly oxidising conditions.
- (c) It should form complexes which are not incapable of undergoing substitution reactions.

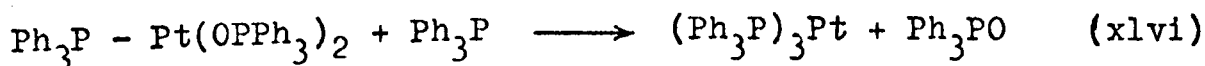
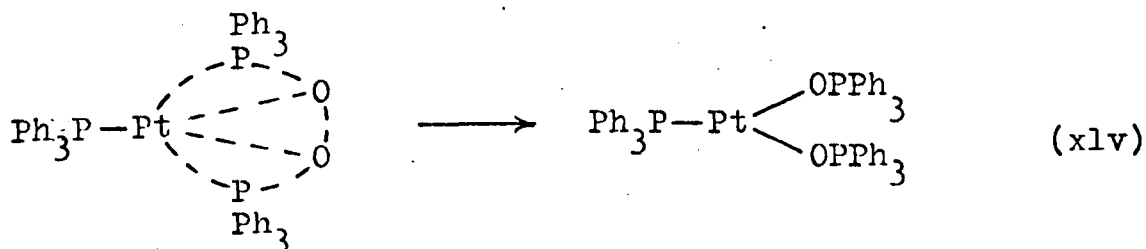
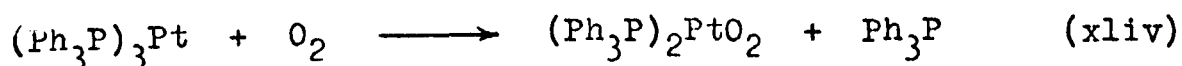
Oxidation.

There are two main mechanisms by which a transition metal may bring about oxidation:

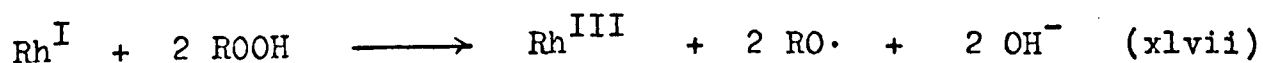
- (a) Activation of molecular oxygen by co-ordination to metal ions.

(b) Metal ion catalysis of free-radical autoxidation.

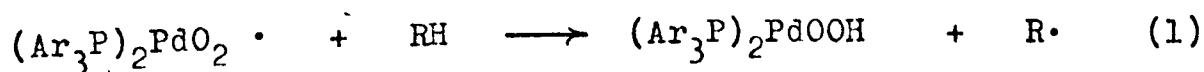
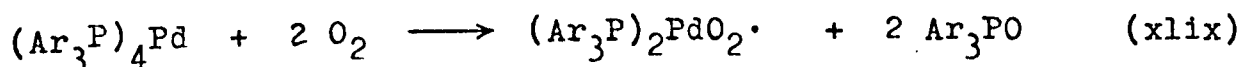
A typical example of a reaction in the first category was provided by the work of Halpern and Pickard.⁷¹ They reported that tris (triphenylphosphine) platinum (0) reacted with oxygen in benzene solution to yield a peroxy complex which then broke down to yield triphenylphosphine oxide:



Examples of category (b) are more common and result from the ability of the transition metal to catalytically decompose hydroperoxides. Typically, carbonyl bis (triphenylphosphine) rhodium chloride catalysed the autoxidation of diphenylmethane to benzophenone and benzhydrol, and the reaction could be inhibited by 2,6 di-t-butyl p-cresol. Further, the addition of tetraphenyl bis (dithiene) nickel, an efficient peroxide destroyer, inhibited the reaction for several hours, and the proposed mechanism for the initiation was:⁷²



Stern investigated the autoxidation of cumene in the presence of palladium (0) complexes and the results appeared to indicate a different mode of catalytic oxidation.⁷³ The cumene was peroxide free and Stern also reported that the tetrakis (triarylphosphine) palladium (0) complexes did not decompose cumene hydroperoxide. However, the oxidation was free radical and he proposed that initiation was brought about by a superoxidic palladium complex capable of hydrogen abstraction:



This mechanism was refuted by Sheldon⁷⁴ on two points:

- (i) The procedure for cumene purification was found to be inefficient, traces of hydroperoxide were still present.
- (ii) Tetrakis (triphenylphosphine) palladium (0) catalytically decomposed t-butyl hydroperoxide by a free radical mechanism.

Sheldon therefore proposed that the oxidation was initiated by catalytic decomposition of traces of cumene hydroperoxide, i.e. a category (b) process.

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PART II

EXPERIMENTAL SECTION

CHAPTER 4

PREPARATION OF SOLVENTS AND REAGENTS AND METHODS OF ANALYSIS.

1. Solvents and Reagents.

(i) Tetrahydrofuran. Tetrahydrofuran was refluxed over, and distilled from potassium hydroxide, the fraction b.p. $66^{\circ}\text{C}/760\text{ mm.}$ being stored over sodium wire, under nitrogen. When required, a sample was freshly distilled from lithium aluminium hydride.

(ii) Benzene. Benzene was stored over sodium wire and distilled immediately prior to use, b.p. $80^{\circ}\text{C}/760\text{ mm.}$

(iii) Ether. Diethyl ether was pre-dried with calcium chloride and stored over sodium wire under nitrogen.

(iv) Iso-Octane and n-Heptane. These solvents were dried with calcium sulphate and stored over activated 4A molecular sieve.

(v) Cyclohexene. Cyclohexene was shaken with dilute acidified ferrous sulphate, washed with water and dried over calcium sulphate. It was then distilled under nitrogen, from a trace of phenothiazine, the fraction b.p. $82^{\circ}\text{C}/760\text{ mm.}$

was stored over 3A molecular sieve, under nitrogen.

(vi) Indene. Indene was washed with successive portions of dilute hydrochloric acid, dilute sodium hydroxide, dilute acidified ferrous sulphate, and dried over sodium sulphate. It was then distilled at reduced pressure, b.p. $104.5^{\circ}\text{C}/98\text{ mm.}$ and stored over 3A molecular sieve under nitrogen.

(vii) Butyl Halides. After drying with molecular sieve, the butyl halides were distilled and stored over 4A molecular sieve, n-butyl bromide b.p. 101°C , sec-butyl bromide b.p. 90.5°C , and tert- butyl chloride b.p. 50°C .

(viii) Benzyl Chloride. After drying with calcium chloride, benzyl chloride was distilled, b.p. 178°C , and stored over 4A molecular sieve.

(ix) Trimethylsilylmethylchloride. Chlorine gas was passed into trimethylsilylchloride (500mls, 4 moles) which was kept at gentle reflux and illuminated by three (60 watt) electric light bulbs. When the reflux temperature reached 80°C , reaction was stopped and excess chlorine removed by purging with a stream of nitrogen. Fractional distillation gave dimethylchloromethylsilylchloride (Yield, 40%), b.p. 116°C .

Dimethylchloromethylsilylchloride (1.1 mole) was added slowly to an ethereal solution of methyl magnesium bromide (1.2 moles) and following acidification, extraction and fractional distillation there was obtained

trimethylsilylmethylchloride (0.65 mole, Yield 60%),
b.p. $99^{\circ}\text{C}/760\text{ mm.}$ (lit² $97.1^{\circ}\text{C}/734\text{ mm.}$). An attempt was
made to prepare this compound directly, by the chlorination
of tetramethylsilane, according to the method of Whitmore
and Somner,² but the yield was found to be poor.

(x) Boron Trifluoride Etherate. Ether (15 mls.) was
added to boron trifluoride etherate (500 mls.), which was
then distilled at reduced pressure. The fraction b.p. $58^{\circ}\text{C}/30\text{ mm.}$
was collected and stored under nitrogen.

(xi) Magnesium. Magnesium turnings were washed with ether,
and dried. They were then stored in a dessicator over
calcium chloride.

(xii) Nitrogen and Argon. White spot nitrogen was further
purified by passage through columns of B.A.S.F. R3-11,
catalyst (finely divided copper on kieselguhr) to remove
oxygen, sodium hydroxide and magnesium perchlorate or
phosphorous pentoxide on dried vermiculite.

Argon was purified in a similar manner.

(xiii) Molecular Sieves. These were activated by heating
at 140°C , under a current of pure nitrogen, for about 6 hours.

(xiv) Degassed Solvents. The dried solvent, in a
suitable vessel, was placed on the vacuum line and frozen down

to -180°C . After reducing the pressure to ca. 10^{-3}mm . the vessel was isolated from the system and the solvent allowed to warm to room temperature. This process was repeated twice more and after filling the vessel with pure nitrogen, it was removed from the vacuum line and securely stoppered.

2. Organoboron Compounds.

(i) Tri-n-butylborane. This was prepared by the method of Hennion, McCusker et al.,³ from n-butyl magnesium bromide (4 moles) and boron trifluoride etherate (1 mole).

Following extraction and distillation at reduced pressure, there was obtained tri-n-butylborane (75% yield, based on boron trifluoride) b.p. $83^{\circ}\text{C}/4\text{ mm.}^4$; (Found: B, 6.0. Calc. for $\text{C}_{12}\text{H}_{27}\text{B}$: B, 5.9%).

(ii) Tri-sec-butylborane. This was prepared as above from sec -butyl magnesium bromide (4 moles) and boron trifluoride etherate (1.0 mole), to yield tri-sec-butylborane (Yield, 60%) b.p. $74^{\circ}\text{C}/9\text{ mm.}^1$ (Found: B, 5.9. Calc. for $\text{C}_{12}\text{H}_{27}\text{B}$: B, 5.9%).

The purity of the above sample was also analysed by oxidation, hydrolysis and gas liquid chromatographic examination of the alcohol produced, and was shown to be at least 98% of the sec-butyl derivative; this value was unchanged after one year at room temperature. Contrary to the report by Henion, McClusker, et al. that isomerisation

occurred at about 200°C over a long period of time,¹ a sample heated at 120°C (12 hours) was found to be 70% tri-n-butylborane

(iii) Tri-iso-butylborane. This was prepared according to the method of Davies, Hare and White,⁵ from tert-butyl magnesium chloride (1 mole) and boron trifluoride etherate (0.25 mole). After extraction, the resultant di-iso-butyl tert-butylborane was isomerised to tri-iso-butylborane by heating at reflux, under nitrogen (3 hrs.). Fractional distillation gave tri-iso-butylborane (Yield, 40%) b.p. 188°C; (Found: B, 5.8. Calc. for C₁₂H₂₇B : B, 5.9%).

(iv) Tri-Cyclohexylborane.⁶ To a solution of cyclohexene (0.1 mole) and sodium borohydride (0.03 mole) in tetrahydrofuran was added boron trifluoride etherate (0.045 mole) at room temperature under nitrogen. After three hours, degassed water (0.4 mole) was added to destroy any residual hydride, and following extraction and crystallisation there was obtained tricyclohexylborane (6.75 m.moles, 20%). The proton magnetic resonance spectrum of this compound, in benzene solution, was consistent with the structure proposed.

(v) Di-n-butyl-n-butylperoxyborane. This compound was prepared by reacting tri-n-butylborane (0.005 mole) in iso-octane (50 mls.) with oxygen at -74°C (15 mins.), in a highly efficient gas liquid mixing apparatus, (Figure 3). The stirrer was rotated by means of a magnetic coupling at speeds of up to 4000 r.p.m.. Gas was drawn in through

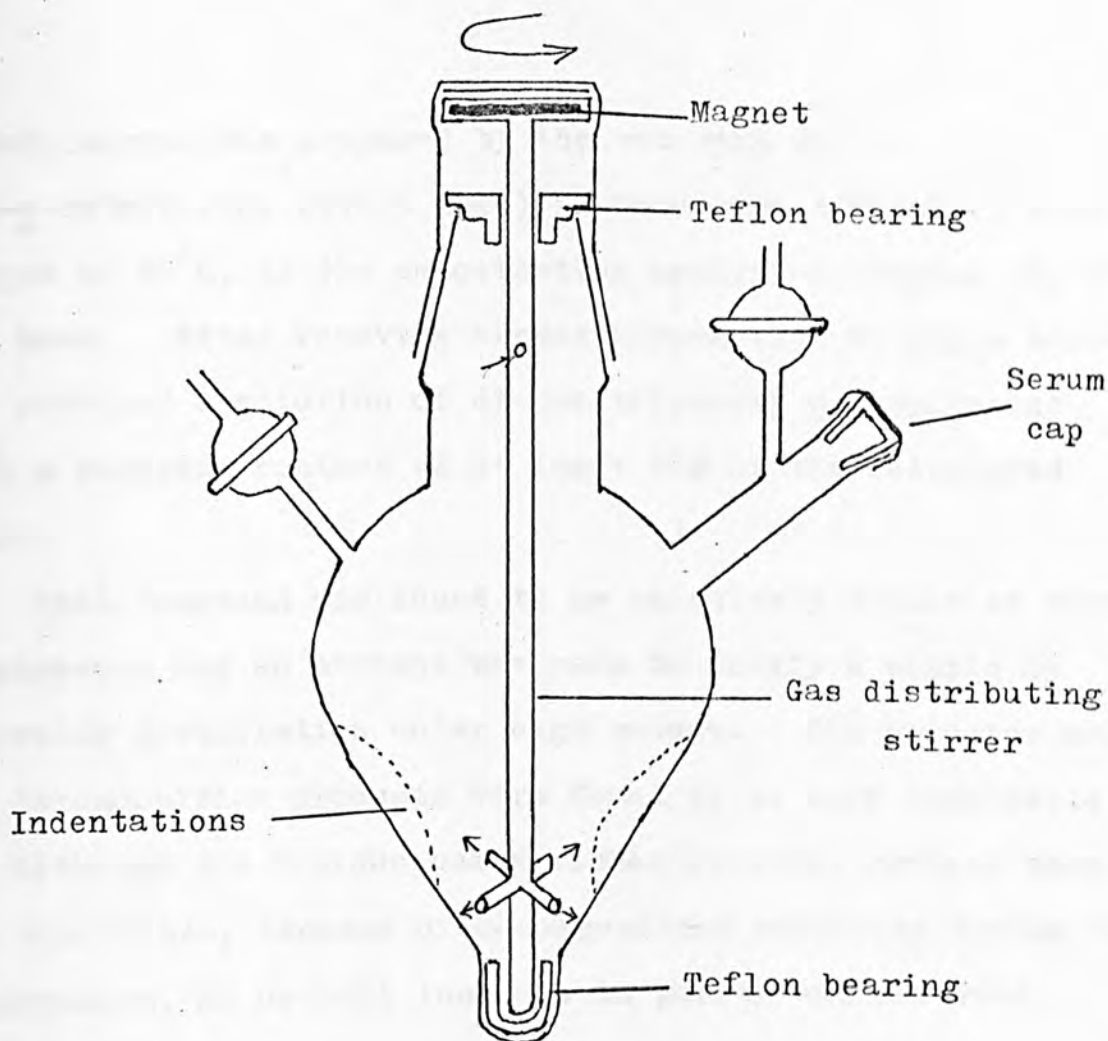


Figure 3. Autoxidation Apparatus.

the upper hole and distributed into the liquid via four lower outlets. Mixing was increased by means of indentations in the sides of the vessel. At the end of the reaction, it was purged with nitrogen, to leave a solution of di-n-butyl n-butylperoxyborane with a peroxide content of not less than 95% of the theoretical maximum. Because of the unstable nature of this compound, at room temperature, it was never isolated, and all experiments were carried out on freshly prepared solutions.

(vi) Di-n-butylperoxy n-butylborane.

Di-n-butylperoxy

n-butylborane was prepared by the reaction of tri-n-butylborane (0.005 mole) in iso-octane (50 mls.) with oxygen at 20°C, in the autoxidation apparatus (Figure 3), for one hour. After removing excess oxygen with nitrogen there was obtained a solution of di-n-butylperoxy n-butylborane with a peroxide content of at least 95% of the calculated value.

This compound was found to be relatively stable at room temperature and an attempt was made to purify a sample by molecular distillation under high vacuum. The peroxide and its decomposition products were found to be very involatile and although the residue had a richer peroxide content than the distillate, because of decomposition occurring during the evaporation, no overall increase in purity was achieved.

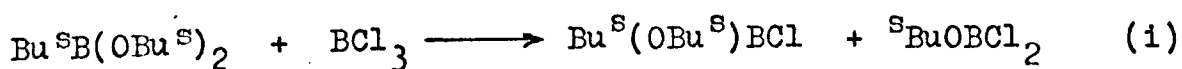
(vii) Di-sec-butylperoxy sec-butylborane. This was prepared in an analogous manner to di-n-butylperoxy n-butylborane, to leave a solution with a peroxide content of not less than 97% of the theoretical value.

(viii) sec-Butylperoxy sec-butylalkoxy sec-butylborane.

(a) Di-sec-butyl sec-butylboronate was prepared by the method of Brindley, Gerrard, and Lappert⁷ by the slow addition of an ether solution of sec-butyl magnesium bromide (1.42 mole) to tri-sec-butylborate (1.4 mole) in ether at -70°C. Subsequent acidification, extraction, and fractional distillation at reduced pressure yielded the boronate in

high yield, b.p. 54°C/1 mm.; n_D^{20} 1.4045 (Found: C, 67.5; H, 12.6; B, 4.9. $C_{12}H_{27}O_2B$ requires C, 67.4; H, 12.6; B, 5.1%).

(b) sec-butylchloroboronate was prepared by the slow addition of redistilled boron trichloride (0.11 mole) in pentane to di-sec-butyl sec-butylboronate (0.11 mole) in pentane at -70°C.⁸ The solution was allowed to warm to 0°C over one hour and the solvent and low boiling products, viz. sec-butylchloride, removed at 10°C/40 mm.. The mixture was distilled at low temperature into a trap at -180°C at 0.05 mm. to leave a small brown residue. This condensate was distilled three times, the middle fraction being used in each following distillation. The sec-butyl dichloroboronite, which was formed according to the equation,

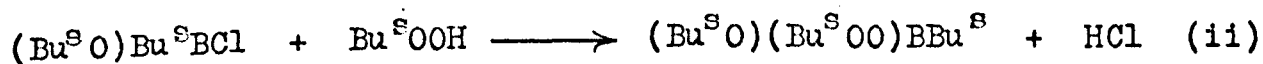


decomposed during distillation,⁸ and was obtained as an impure lower boiling point fraction.

Thus there was obtained impure sec-butyl sec-butoxy chloroborane in 80% yield, b.p. 58-62°C/15 mm., n_D^{20} 1.4077 (Found: B, 6.7; Cl, 21.3. $C_8H_{18}OBCl$ requires B, 6.2; Cl, 20.1%). Further attempts to purify by distillation were unsuccessful, so the compound was stored at -80°C and flash distilled before use. An experiment using the reverse addition of reagents gave a much poorer quality product.

(c) sec-Butyl hydroperoxide was prepared by the method of Brown and Midland.⁹ Di-sec-butylperoxy sec-butylborane

(0.15 mole) in tetrahydrofuran (150 ml.) was treated with hydrogen peroxide (50 mls. of a 30% aqueous solution) at 0°C. This was followed by extraction with hexane and 40% aqueous potassium hydroxide, neutralisation and drying. Further purification was achieved by distillation at 0°C/10 mm. to yield sec-butyl hydroperoxide in high yield. The hydroperoxide was stored as a 70% solution in pentane in a refrigerator until required. The preparation of sec-butylperoxy sec-butylalkoxy sec-butylborane was achieved by adding dropwise sec-butyl hydroperoxide (3.3 mls. of a 70% solution in pentane) to sec-butoxy sec-butylchloroboronate (0.02 mole) in pentane at 0°C while a slow current of argon was passed through the mixture. The exit gases were passed through a tube containing moistened sodium hydroxide pellets. After fifteen minutes the mixture was allowed to warm to 20°C during which time hydrogen chloride gas was evolved and absorbed by the sodium hydroxide (total hydrogen chloride recovered, 103%) according to the equation,



The residue was stripped of solvent under vacuum to leave a residue (4.9g.). (Found: Peroxide 0.015 mole, 75% yield). Further evaporation at 20°C under high vacuum into a trap at -180°C gave a condensate (2.9g., Found: Peroxide, 0.005 moles) and a residue (2.0g., Found: Peroxide, 0.009 Moles), which was used for all subsequent experiments.

3. Organotransition Metal Compounds.

(i) Tetrakis (trimethylsilylmethyl) Titanium.¹ To an ethereal solution of trimethylsilylmethyl magnesium chloride (0.1 mole) in ether was added dry, degassed dioxan (0.1 mole). The precipitated magnesium chloride, dioxan complex was filtered off under nitrogen to leave an ethereal solution of bis (trimethylsilylmethyl) magnesium. The ether was removed under reduced pressure and the organometallic suspended in dry, degassed n-heptane. To the bis (trimethylsilylmethyl) magnesium (0.04 moles) was added titanium tetrachloride (0.018 moles) in n-heptane at -10°C . This was stirred for twelve hours at this temperature under nitrogen. The mixture was then filtered under nitrogen to yield a pale amber solution of tetrakis (trimethylsilylmethyl) titanium. This solution was stored at 0°C under nitrogen and was used without purification for all subsequent experiments. The proton magnetic resonance spectrum of this solution showed two singlets at $9.7\tau(\text{CH}_3)$ and $7.6\tau(\text{CH}_2)$ in agreement with the values given by Lappert et al.¹

(ii) Tetrakis (trimethylsilylmethyl) Zirconium.¹ This was prepared as above from zirconium tetrachloride and bis (trimethylsilylmethyl) magnesium. The light brown solution obtained after filtration was again stored at 0°C under nitrogen and used without further purification.

(iii) Hexakis (trimethylsilylmethyl) bimolybdenum. An

analogous method was used to prepare this compound from bis (trimethylsilylmethyl) magnesium and molybdenum trichloride. After filtration there was obtained a brown solution.

Removal of the solvent at low pressure left a brown residue from which yellow crystals sublimed out at $110^{\circ}\text{C}/10^{-3}\text{mm.}$. These yellow crystals had m.p. $96-99^{\circ}\text{C.}$ (hexakis (trimethylsilylmethyl) bimolybdenum sublimes $100^{\circ}\text{C}/10^{-4}\text{mm.}$; m.p. 99°C^{10}). The proton magnetic resonance spectrum of this compound in benzene solution was consistent with that given by Wilkinson et al.,¹¹ i.e. singlets at $9.60\tau(\text{CH}_3)$ and $7.8\tau(\text{CH}_2)$, using the benzene singlet (2.73τ) as the reference peak.

All experiments were performed on the above solutions (i) to (iii) within one week of preparation.

(iv) Tetrabenzyl Zirconium. This was prepared by the method of Zucchini et al.¹² by the reaction of benzyl magnesium chloride with zirconium tetrachloride in ether; precautions were taken to exclude light and oxygen. After filtration and removal of the ether, the yellow-brown residue was extracted with dry, degassed toluene to yield an amber solution from which yellow platelets of tetrabenzyl zirconium crystallized on cooling to -20°C. Experiments were conducted using this toluene solution which was stored at 0°C under nitrogen, and shielded from light.

(v) Hexabenzyl Bitungsten.¹³ Hexabenzyl bitungsten was

prepared from the reaction of benzyl magnesium chloride and tungsten *hex*achloride in ether. After filtration under nitrogen, removal of the solvent and extraction with dry, degassed n-heptane, an orange solution of this compound was obtained.

(vi) Hexa-neo-pentyl Bimolybdenum. An attempt to prepare this compound from the Grignard reagent and molybdenum tetrachloride produced a rather impure sample as shown by proton magnetic resonance spectroscopy. Therefore, the lithium reagent was used according to the method of Wilkinson et al. (private communication).

To lithium chippings (0.2 mole) (obtained by grating lithium sticks on a "surform" blade in an argon filled dry-box) in ether, under argon, was added dry, degassed neopentyl chloride (0.1 mole). Reaction started after the addition of a few drops of 1,2 dibromoethane and gentle warming. It was completed after six hours. The bulk of the ether was replaced by benzene and the mixture filtered under argon to yield a benzene solution of neopentyl lithium (0.38 mole, 38% yield). To the whole of this was added molybdenum tetrachloride (0.13 mole) under nitrogen with stirring (12 hrs.). After filtration, the bulk of the solvent was removed at reduced pressure to leave a dark brown residue. This was purified by column chromatography using alumina (neutral, Hopkin and Williams 'M.F.C. grade') as the solid phase, and a mixture of degassed petroleum spirit-ether (1:1) as the eluent. The preparation of the column, free from oxygen

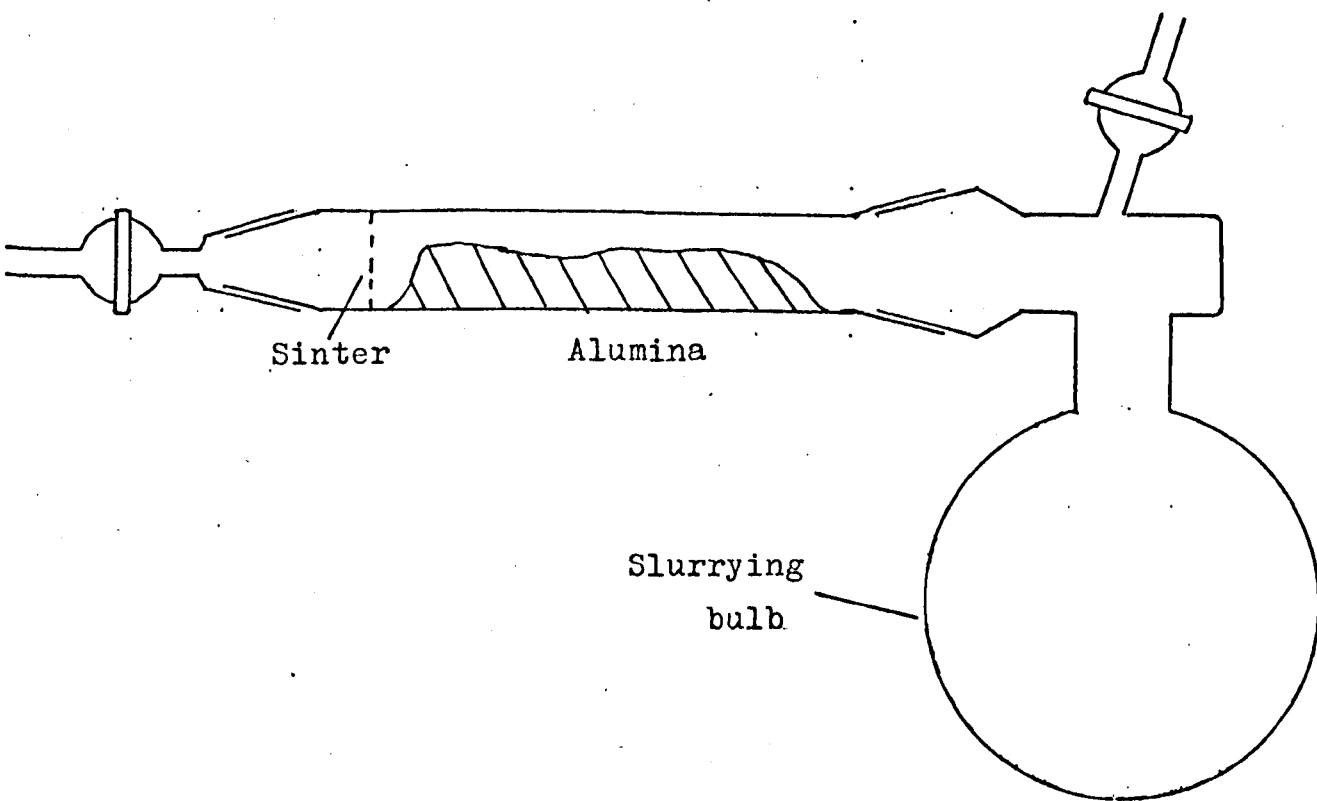


Figure 4. Preparation of Chromatography Column under Nitrogen.

was achieved using the apparatus shown in Figure 4. The alumina which had been degassed under vacuum and stored under nitrogen was placed in the column and heated to ca. 120°C by a heating coil for 12 hours under a stream of nitrogen. Degassed solvent was poured in when the alumina had cooled, and a slurry was made in the bulb. The slurry was returned to the column and after removing the bulb, the column was placed between a separating funnel and a collecting flask. All manipulations were carried out under nitrogen. The impure product was placed on the column, and on elution resolved into mauve and yellow bands, the yellow band being collected. After removal of the solvent there was obtained a yellow oily solid and the proton magnetic resonance spectrum was recorded in benzene solution. This showed singlets at $8.65\tau(\text{CH}_3)$ and $7.75\tau(\text{CH}_2)$ and a complex at 9.2 to 9.4τ due

to impurity.

4. Inhibitors

(i) Galvinoxyl. Crude galvinoxyl was twice recrystallized from benzene under nitrogen to yield dark blue needles, m.p. 151-152°C, (lit. m.p. 153.2-153.6°C¹⁴). This was stored under nitrogen at 0°C, and was shown iodometrically to be 99% pure.

(ii) 2,2,6,6, Tetramethyl piperid-4-one nitroxide (Triacetoneamine nitroxide). The crude material was recrystallized from n-heptane to yield light orange crystals, m.p. 44-47°C, (lit. m.p. 36°C¹⁵).

(iii) Azagalvinoxyl. This compound was prepared according to the method of Coppinger,¹⁶ with the modification that the reduction of 2,6 di-t-butyl 4-nitrophenol was done by refluxing with hydrazine hydrate and 10% palladium on charcoal, in ethanol. Following the work up of the 2,3',5',6 tetra-t-butyl indophenol, dark green crystals of azagalvinoxyl were obtained, m.p. 149-151°C (lit. m.p. 155-156°C¹⁶). A large scale preparation gave poor yields.

(iv) Other Inhibitors. Phenothiazine was recrystallized from petroleum ether. Copper (II) NN dibutyl dithiocarbamate and all other inhibitors were used as supplied without

further purification.

5. Methods of Analysis.

(i) Peroxide. The peroxide was heated under reflux in propan-2-ol (50 mls.) with sodium iodide (lg.) and glacial acetic acid (1 ml.), under nitrogen for ten minutes. The mixture was cooled, and the liberated iodine titrated with standard sodium thiosulphate solution.

This method was checked for accuracy and reproducibility with standard solutions of peroxide, and was found to be satisfactory.

(ii) Free Radicals. The sample was shaken with sodium iodide (lg.) in benzene (25 mls.) and glacial acetic acid (25 mls.) under nitrogen. The mixture was then poured into water (100 mls.) and the liberated iodine titrated with standard sodium thiosulphate solution.

(iii) Boron. Weighed samples of the organoboron compound, containing ca. 5 mg. of boron, were treated with 30% hydrogen peroxide (10 ml.) at 60°C for one hour. After the addition of mannitol, the solutions were titrated with 0.05N sodium hydroxide, using bromothymol blue indicator. Blanks were run with each analysis.¹⁷

(iv) Transition Metals. Following oxidation and hydrolysis

of a weighed sample, the metal was estimated using standard methods.¹⁸

Molybdenum and tungsten samples were taken up in concentrated hydrochloric acid and oxidised with a few drops of nitric acid. The acids were then boiled off and the residue ignited in a nickel crucible to a constant weight of the respective trioxide.

Titanium solutions were acidified with dilute sulphuric acid and treated with potassium permanganate until a pink colour persisted. This solution was then passed through a Jones reductor, the resultant titanium (III) solution being collected in an acidified ferric alum solution. The ferrous ions produced were titrated with standard potassium permanganate solution.

Zirconium solutions were adjusted to pH 3.6 with sulphuric acid and treated with metaphosphoric acid (5 g.). After standing overnight the solution was boiled and the precipitate filtered off and washed with ammonium nitrate solution. This precipitate was then ignited in a nickel crucible and weighed as zirconium pyrophosphate.

(v) Carbon, Hydrogen. These micro-analyses were performed by Beller, W. Germany.

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CHAPTER 5.

ORGANOBORANES - THEIR AUTOXIDATION AND DECOMPOSITION OF THE
PEROXIDIC PRODUCTS.

1. Rates of Initiation of Autoxidation of Trialkylboranes.

The measurement of the absorption of small quantities of oxygen by organoboranes whilst undergoing autoxidation in the presence of galvinoxyl, was carried out.

Standard solutions of the organoboranes were prepared by adding, with a syringe, borane to a weighed quantity of dry, degassed benzene in a nitrogen filled flask fitted with a serum cap. The concentration of borane was accurately determined by a boron estimation and was usually designed to be ca. 0.3 M.

Galvinoxyl solutions in degassed benzene were prepared at a concentration of ca. 0.01 M, and a small quantity of hydrogalvinoxyl (up to 5%) added to stabilize the solution.

Varying oxygen partial pressures were obtained by pre-mixing nitrogen and oxygen in the required ratio, in a gas mixing apparatus, Figure 5, before passing them through calcium chloride drying tubes and into the oxidation apparatus.

The autoxidation apparatus, Figure 6, was based on the design used by Carlsson and Robb for their studies on hydrocarbon autoxidations.¹ The oxidation chamber was similar to the autoxidation apparatus previously mentioned (Figure 3) , in that a baffled flask and gas circulating

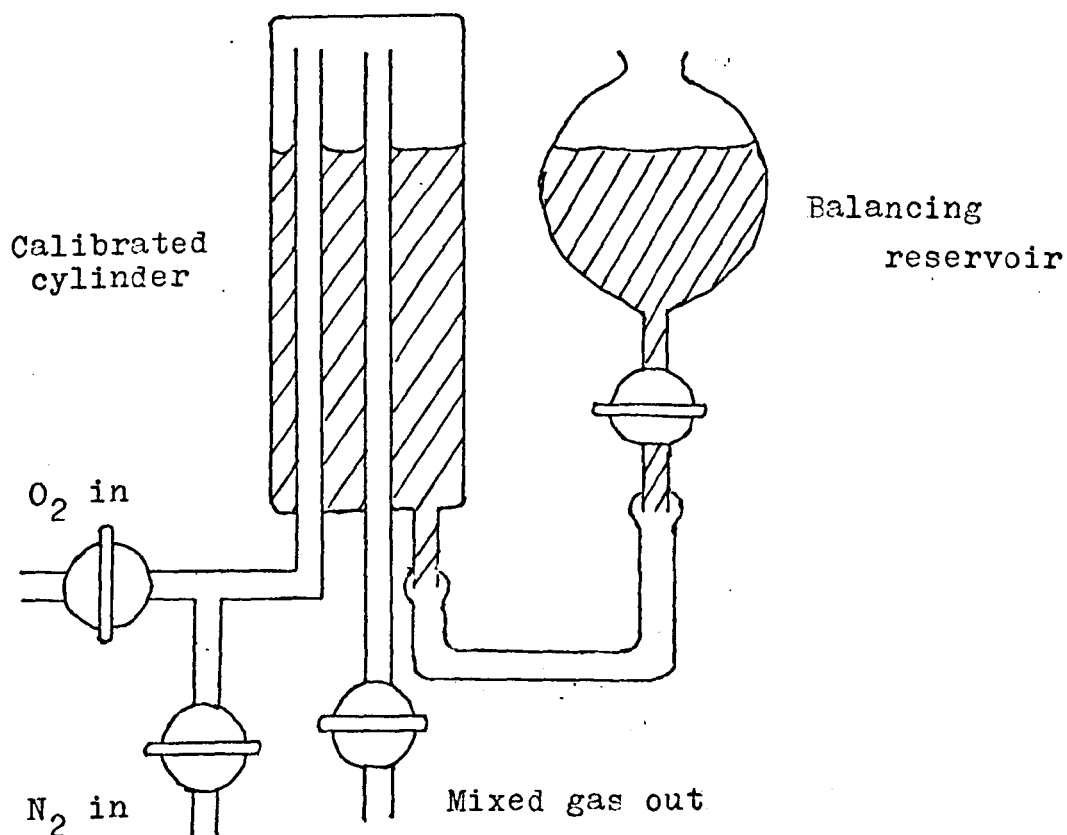
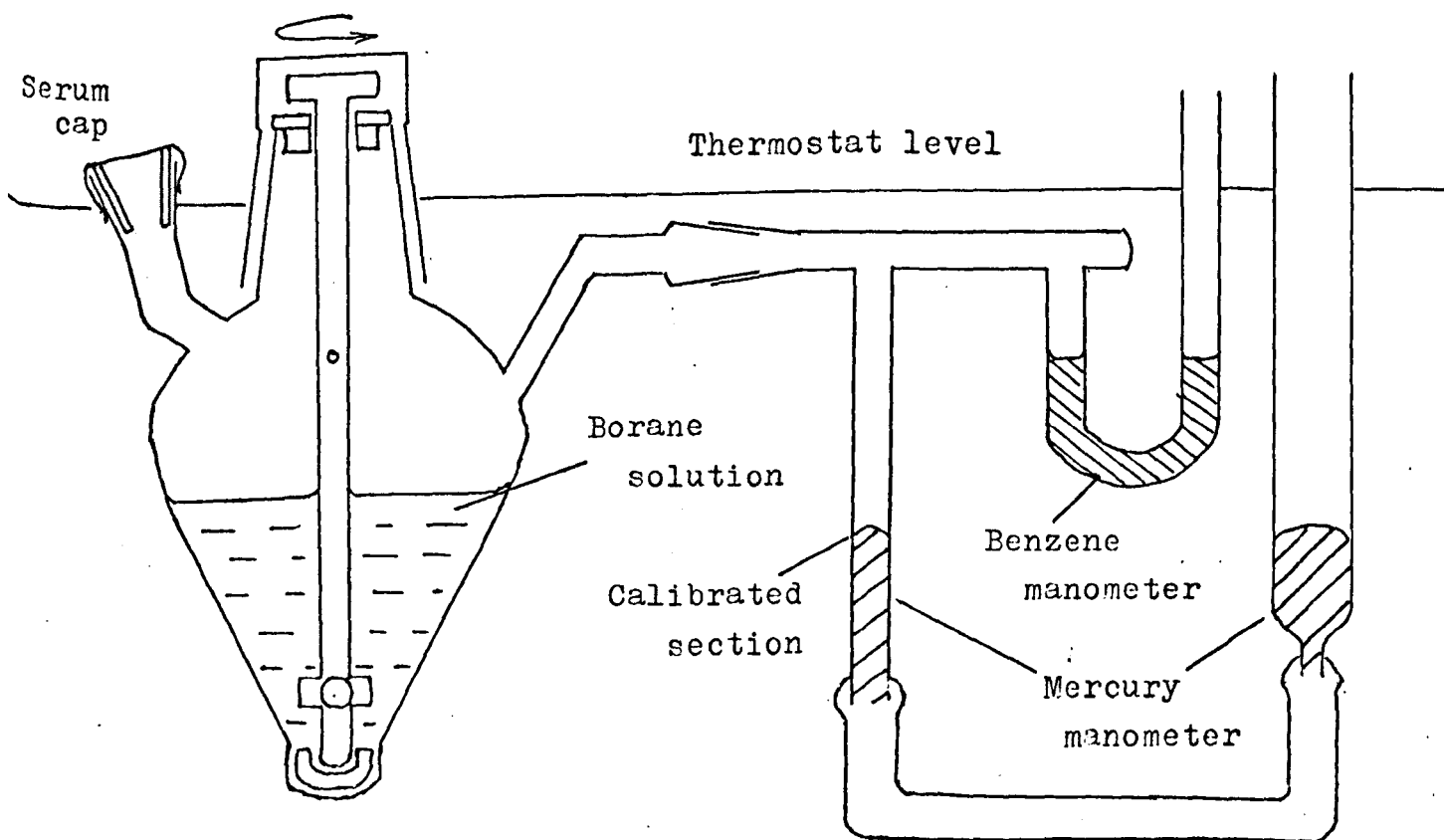


Figure 5. Gas Mixing Apparatus.

Figure 6. Gas Burette-Autoxidation Apparatus.



stirrer was used. The benzene manometer indicated changes of volume (at constant pressure) within the closed system, and was kept in balance by raising or lowering the mercury manometer reservoir. The change in volume could be read off the calibrated section of the mercury manometer which had a capacity of 0.5 ml., graduated in 0.02 ml. divisions.

Method of Operation. The whole of the apparatus was filled with oxygen at the required partial pressure. Benzene (50 mls.) was then introduced and the apparatus placed in the thermostat at 25°C. Stirring was commenced and the apparatus allowed to reach equilibrium. The required amounts of galvinoxyl solution, quickly followed by the borane solution (at 25°C), were injected through the serum cap using calibrated syringes. After about three minutes, equilibrium was re-established and meaningful readings were taken. Because of the limited volume of the calibrated section, readings could not be taken right up to the point where inhibition ceased, and therefore the length of induction periods were estimated by the change in colour of the solution.

The results obtained are summarised in Table 4, typical runs in Figure 9, and the variations of the rate of oxygen absorption with changing concentration of borane and oxygen shown in Figures 7 and 8. The results are the average of at least three experiments.

2. The Decomposition of Organoperoxyboron Compounds.

The samples of peroxide in iso-octane and under nitrogen

were allowed to reach equilibrium in a thermostat. Samples were then removed at fixed times for analysis. Two methods were used.

(i) Di-n-butyl n-butylperoxyborane. Because of its unstable nature at room temperature, all manipulations and transferences were kept to a minimum. Consequently, the autoxidation vessel used in its preparation was also used for the decomposition studies. Samples of the thermostatted peroxide solution (0.08 M.) were withdrawn through a side-arm, under a purging stream of nitrogen, using a nitrogen filled dry pipette.

Inhibitors were added prior to placing the solution in the thermostat.

(ii) Other Peroxyboranes. Di-n-butylperoxy n-butylborane, di-sec-butylperoxy sec-butylborane, and sec-butylperoxy sec-butylalkoxy sec-butylborane were found to be relatively stable at room temperature. The previous technique was modified to reduce possible solvent losses and to generally improve accuracy. Aliquots of peroxide solution (0.08 M. in iso-octane) were placed in stoppered, nitrogen filled, dry test-tubes. The stoppers were spring-loaded and the samples placed in the thermostat. At the required time, a tube was withdrawn, cooled and its contents washed out thoroughly with solvent and analysed for peroxide.

Varying peroxide concentrations were achieved by adding quantities of dry, degassed iso-octane to the individual peroxide samples.

(iii) Results. In all cases except s-butylperoxy s-butylalkoxy s-butylborane, good plots of $\log_e a/a-x$ against time were obtained over about 40% reaction (Figure 10a), where

a = initial peroxide concentration.

$a-x$ = final peroxide concentration.

Rate constants were evaluated by a computer program (see appendix) designed to calculate the slope of the least squares line drawn through the points of these first order plots. The rate constants so determined are listed in Table 5, each the results of at least two experiments.

To distinguish clearly from possible second order kinetics, the first order nature of the decompositions was confirmed by the change in the initial rate of reaction with varying peroxide concentrations, Figure 10.

The Arrhenius plots of the variation of the rate constants with temperature are shown in Figure 11. From the slopes of these graphs activation energies were determined, and thus the first order rate constants may be expressed in terms of the full Arrhenius equations. For

(a) Di-n-butyl n-butylperoxyborane,

$$k = 6.0 \times 10^3 e^{-11,100 \pm 530/RT} \text{ s.}^{-1}$$

(b) Di-n-butylperoxy n-butylborane,

$$k = 4.55 \times 10^4 e^{-14,300 \pm 1,070/RT} \text{ s.}^{-1}$$

(c) Di-s-butylperoxy s-butylborane,

$$k = 6.46 \times 10^5 e^{-15,900 \pm 400/RT} \text{ s.}^{-1}$$

The mixed alkoxy-peroxy compound, s-butylperoxy s-butylalkoxy s-butylborane was only studied briefly; it was found to have decomposed by 10% after 24 hours at 50°C.

Assuming this to be a first order process, by analogy with those compounds above, the rate constant is ca. $1 \times 10^{-6} \text{ s.}^{-1}$.

3. The Reaction Between Organoboranes and Organoperoxyboranes.

(i) Iodometric Studies. Samples of peroxide in iso-octane were placed in dry, nitrogen filled test-tubes, fitted with serum caps. These were put in a thermostat and the required amount of tri-n-butylborane added to each. Samples were analysed for peroxide periodically, and the results are shown in Figure 12. The time for the end of reaction was taken as being when the sample was placed in the analysing mixture, and the shortest manipulation time was ca 30 secs..

(ii) Disappearance of Inhibitors. Triacetoneamine nitroxide has an absorption maximum at 455nm. due to the unpaired electron, and it was possible to study the reaction of it with free radicals by the disappearance of this band. Consequently, to a solution of di-n-butylperoxy n-butylborane (2×10^{-4} mole) and triacetoneamine nitroxide (4×10^{-5} mole) in n-heptane, in a nitrogen filled ultra-violet (u.v.) cell fitted with a serum cap, was added tri-n-butylborane (2×10^{-4} mole). There was an almost immediate 70% reduction in the optical density of this sample at 455nm. compared to a sample without tri-n-butylborane. Similar results were obtained using n-butylperoxy di-n-butylborane in place of the diperoxide, or galvinoxyl instead of triacetoneamine nitroxide. Although the reaction could not be followed satisfactorily, it appeared as though it was virtually complete within 15 secs.. The addition of a n-heptane solution of

n-butylperoxy di-n-butylborane (2×10^{-4} mole) to a n-heptane solution of galvinoxyl (1×10^{-6} mole) in a nitrogen filled u.v. cell resulted in a 60% reduction of the optical density after five mins., measured at 430nm.. In a similar experiment, the addition a n-heptane solution of tri-n-butylborane (2×10^{-4} mole) to galvinoxyl (1×10^{-6} mole), resulted in a 30% reduction in the optical density after six mins..

4. The Polymerisation of Vinyl Acetate.

The rate of polymerisation of vinyl acetate, initiated by peroxyboranes, was studied by dilatometry.

A blank experiment was performed to ensure that the acetate grouping did not induce the decomposition of the peroxides. Ethyl acetate was chosen as a model compound. A degassed solution of di-s-butylperoxy s-butylborane (5 m.mole) in iso-octane was prepared and to this was added dry, degassed ethyl acetate (0.5 mole). The rate constant for the decomposition of the peroxide was determined in the usual way, and was found to be unchanged from the value obtained for the decomposition in pure iso-octane.

Apparatus² and Technique³. The dilatometer used in these experiments is shown in Figure 13.

Operations on the vacuum line were carried out at 10^{-3} mm. pressure. A sample of peroxide solution, containing about 1×10^{-4} moles of peroxide, was pipetted into bulb A. The dilatometer was then attached to the vacuum line and the solvent removed. Vinyl acetate² (10 mls.), which had been degassed three times, was distilled into bulb A, and after freezing down the mixture in this bulb, the dilatometer was sealed off at C. The contents were allowed to warm to room temperature, thoroughly mixed, and sufficient poured into bulb B so that at the temperature of the experiment the liquid level would be some way up the precision bore tubing. Bulbs A and B were then frozen down simultaneously (to avoid

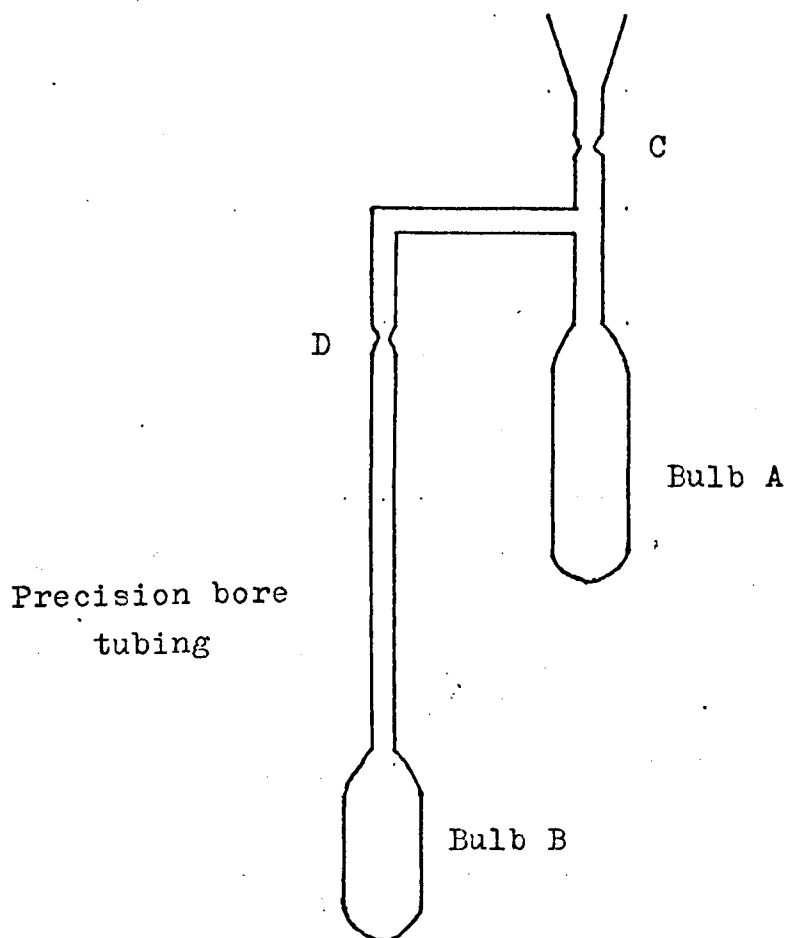


Figure 13. Vacuum Dilatometer.

"distillation"), and the apparatus sealed off at D. The dilatometer was immersed in a thermostat and the meniscus level followed using a cathetometer, readings being noted at regular intervals.

The volume of the dilatometer bulb B up to the calibration mark, was determined by weighing a liquid of known density. Thus, the volume of vinyl acetate used in each polymerisation was easily determined.

Results. Typical plots are shown in Figure 14, the extent of polymerisation being calculated from:

$$C_t = \frac{D_t \pi r^2 100 \rho_p}{V (\rho_p - \rho_M)} \quad (1)$$

and polymerisation rates from:

$$R_p = \frac{R_c \pi r^2 [M]}{V 60} \left(\frac{\rho_p}{\rho_p - \rho_M} \right) \quad (ii)$$

Where D_t = Distance travelled by meniscus (cm.)

R_p = Initial rate of polymerisation (MS^{-1})

R_c = Initial rate of decrease of meniscus level ($cm. min.^{-1}$)

V = Volume of solution at reaction temperature (mls.)

r = radius of precision bore tubing (cm.)

M = Initial concentration of monomer at $20^\circ C$ (M)

ρ_p = density of polymer at $20^\circ C$ ($g. ml.^{-1}$)

ρ_M = density of monomer at $20^\circ C$ ($g. ml.^{-1}$)

For vinyl acetate at $20^\circ C$:

$$[M] = 10.85 M.$$

$$\rho_p = 1.19 g. ml.^{-1} \quad 5$$

$$\rho_M = 0.9338 g. ml.^{-1} \quad 4$$

The rates of polymerisation of vinyl acetate, initiated by organoperoxyboranes, were:

using (a) di-sec-butylperoxy sec-butylborane (9.0 mM.) at $49.9^\circ C$, $R_p = 1.66 \times 10^{-5} M.S.^{-1}$

(b) di-sec-butylperoxy sec-butylborane (8.5 mM.) at $60.5^\circ C$, $R_p = 7.52 \times 10^{-5} M.S.^{-1}$

(c) di-n-butylperoxy n-butylborane (8.5 mM.) at $60.5^\circ C$, $R_p = 5.73 \times 10^{-5} M.S.^{-1}$

The use of n-butylperoxy di-n-butylborane at $25^\circ C$ as the initiator yielded a curve (Figure 14) and therefore it was not possible to determine a meaningful polymerisation rate.

5. 'Halcon Type' Reactions Using Organoperoxyboron Compounds.

(i) Attempted Epoxidation of Cyclohexene with Di-n-butylperoxy n-butylborane. To a solution of the peroxide (10 m.mole) in n-heptane, was added cyclohexene (100 m.mole) and molybdenum hexacarbonyl (0.4 m.mole) as catalyst. After one week at 25°C, the volatile components were removed at reduced pressure and examined by gas liquid chromatography. They were shown to consist of solvent and unreacted cyclohexene. The residue was treated with water and ether extracted to rid any organic components of boric acid. After removal of the solvent, the residue was shown to consist of n-butyl alcohol which was produced by hydrolysis of the boron compounds.

(ii) Attempted Epoxidation of Indene with Di-n-butylperoxy n-butylborane. To a n-heptane solution of the peroxide (10 m.mole) was added indene (100 m.mole) and the catalyst molybdenum hexacarbonyl (0.4 m.mole). After 18 hours at 40°C, the solvent was removed at reduced pressure, and the residue treated with water and extracted with ether. Gas liquid chromatographic analysis showed there to be indene, n-butyl alcohol and a minor product (ca. 1%) present. By comparing retention volumes with an authentic sample, this was shown to be indan-2-one, and this was supported by infra-red spectroscopy, band at 1740 cm.⁻¹ (C=O stretch.).

(iii) Reaction of Cyclohexene with Di-n-butylperoxy n-butylborane in the Presence of Excess Molybdenum Hexacarbonyl. The peroxide (8.0 m.mole) in n-heptane was reacted with cyclohexene (250 m.mole) and molybdenum hexacarbonyl (4 m.mole)

at 60°C. for 6 hours. The volatile components were removed at reduced pressure and shown to consist of solvent, cyclohexene, and a minor product (ca. 1%). No products could be isolated from the residue. After one week a precipitate was found in the distillate and this was shown to contain molybdenum but no boron. Its infra-red spectrum is shown in Figure 15. This compound decomposed at 170°C. to yield a white sublimate and a black residue. The white sublimate is suggested as being trans cyclohexene-1,2-diol by virtue of its infra-red spectrum (Figure 16), bands at 3350 cm.⁻¹ (O-H stretch); 1420 cm.⁻¹ (O-H deformation), and 1060 cm.⁻¹ (C-O stretch). Its mass spectrum gave a value for the parent ion of 116, (C₆H₁₂O₂ requires, M = 116). The black residue was probably a hydrated molybdenum oxide (found: Mo, 40. Calc. for MoO₂ : Mo, 75; MoO₃ : Mo, 66.6%).

(iv) Reaction of Di-n-butylperoxy n-butylborane with Molybdenum Hexacarbonyl. A sample of di-n-butylperoxy n-butylborane (20 m.mole), free of volatile organic impurities, was added to an n-heptane solution of molybdenum hexacarbonyl (0.2 m.mole). After one hour at 25°C., 85% of the peroxide had decomposed, and when no peroxide remained (24 hrs.) the volatile components were removed and analysed by gas liquid chromatography. Only solvent was detected. The residue was distilled under reduced pressure and a fraction collected, b.p. 40°C./0.2mm.. (Found: B, 4.74; C, 65.20; H, 11.98. Calc. for C₁₂H₂₇O₃B: B, 4.68; C, 62.6; H, 11.85. Calc. for C₁₂H₂₇O₂B: B, 5.05; C, 67.2; H, 12.72%).

Table 4. Initiation of Borane Autoxidations in the Presence
of Galvinoxyl at 25°C in Benzene.

$[R_3B] \times 10^2$ (M)	$[O_2] \times 10^2$ (M) (a)	$[Galvinoxyl]$ $\times 10^2$ (M)	$\frac{-d[O_2]}{dt} \times 10^8$ M.s. ⁻¹	$r'i \times 10^8$ (b) M.s. ⁻¹
<u>Tri-s-butylborane.</u>				
0.76	0.75	0.015	20.34	14.0
0.76	0.37	0.015	9.10	11.7
0.76	0.16	0.015	3.14	7.7
0.76	0.16	0.029	2.72	12.9
0.36	0.16	0.029	1.12	10.6
1.48	0.16	0.029	4.60	22.8
2.10	0.16	0.029	8.98	46.7
0.76	0.16	0.073	2.40	13.9
<u>Tri-iso-butylborane.</u>				
1.44	0.75	0.015	20.28	12.9
1.44	0.16	0.015	3.34	8.7
0.75	0.16	0.015	1.96	5.4
2.10	0.16	0.015	5.52	12.9
1.44	0.16	0.059	3.32	9.3
2.80	0.16	0.015	9.20	15.3
<u>Tri-cyclohexylborane.</u>				
0.13	0.37	0.029	11.4	24.79
0.13	0.16	0.029	4.70	19.33
0.19	0.16	0.029	5.93	24.17
0.078	0.16	0.029	2.82	-

(a) Calculated from partial pressures and solubility coefficients.

(b) Calculated from $[G]/\gamma$ where γ = induction period.

Table 5. First Order Rate Constants for the Decomposition
of Organoperoxyboranes in Iso-Octane.

1. Di-n-butyl n butylperoxyborane.

Temperature ($^{\circ}\text{K}$).	Rate Constant $\times 10^5$ (s^{-1}).
273.3	0.86
280.1	1.44
285.1	1.91
291.2	2.65
294.3	3.37
298.1	4.68
300.1	5.58
303.1	5.96

2. Di-n-butylperoxy n-butylborane.

Temperature ($^{\circ}\text{K}$).	Rate Constant $\times 10^5$ (s^{-1}).
322.4	0.86
332.6	2.00
343 .6	3.78
349.7	4.87

3.. Di-s-butylperoxy s-butylborane.

Temperature ($^{\circ}\text{K}$).	Rate Constant $\times 10^5$ (s^{-1}).
321.4	0.99
332.6	2.13
343.6	4.80
349.7	7.46

Figure 7. Effect of Borane Concentration on the Rate of Initiation of Tributylborane autoxidations at 25°C, in Benzene.

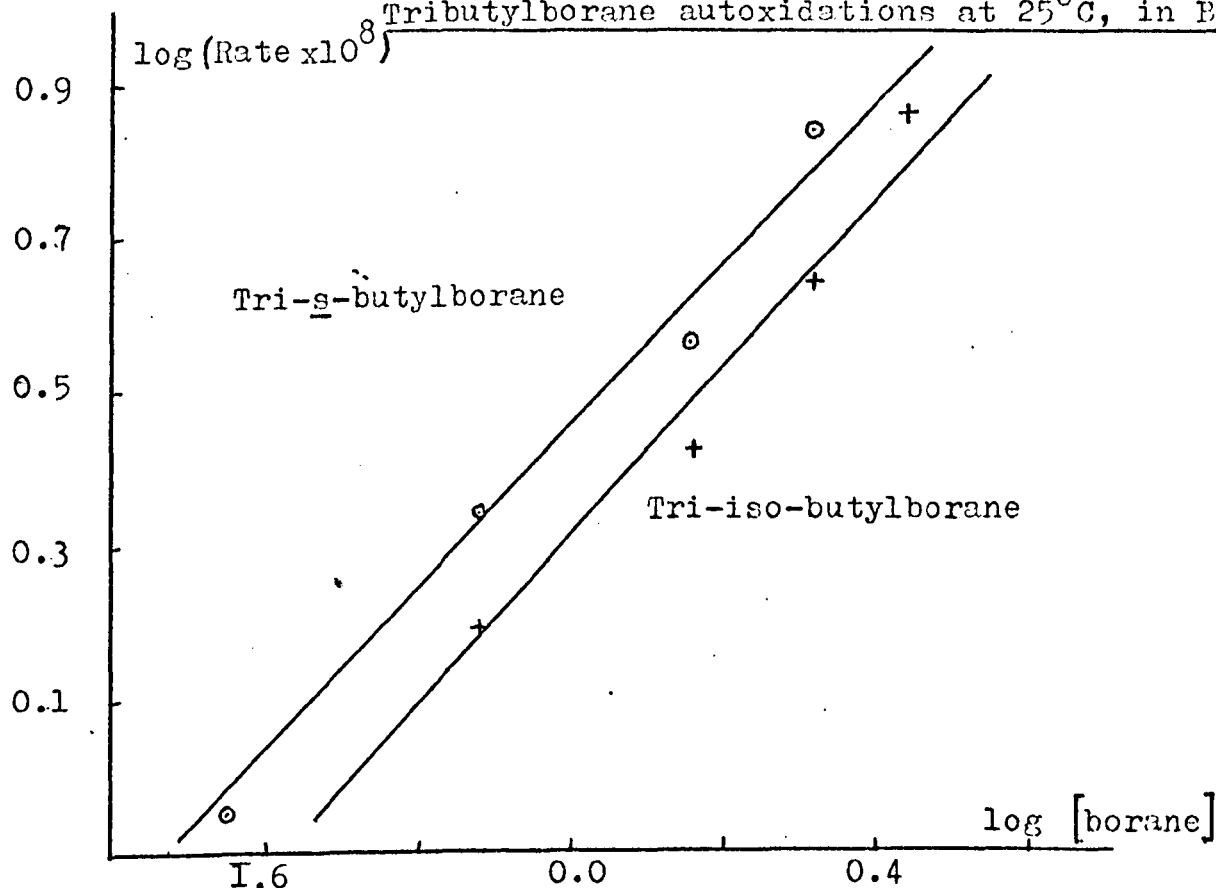


Figure 8. Effect of Oxygen Concentration on the Rate of Initiation of Tributylborane Autoxidations at 25°C, in Benzene.

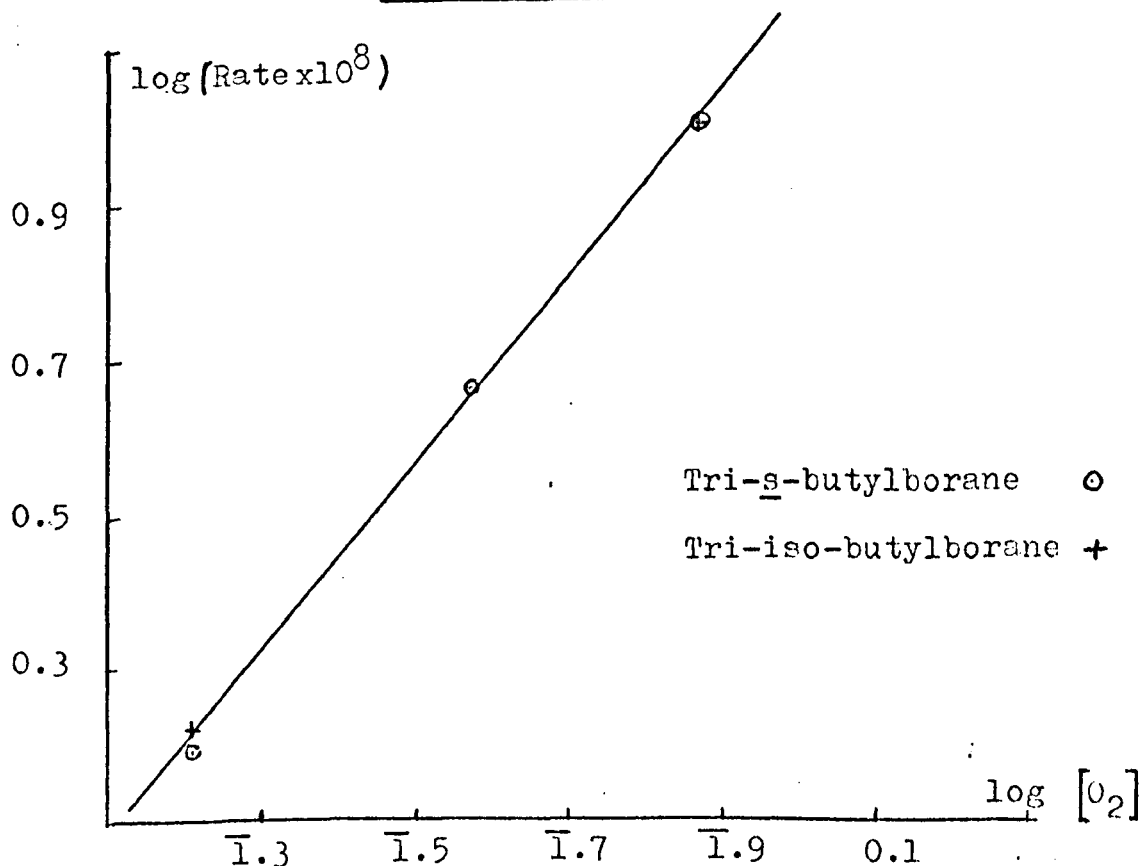
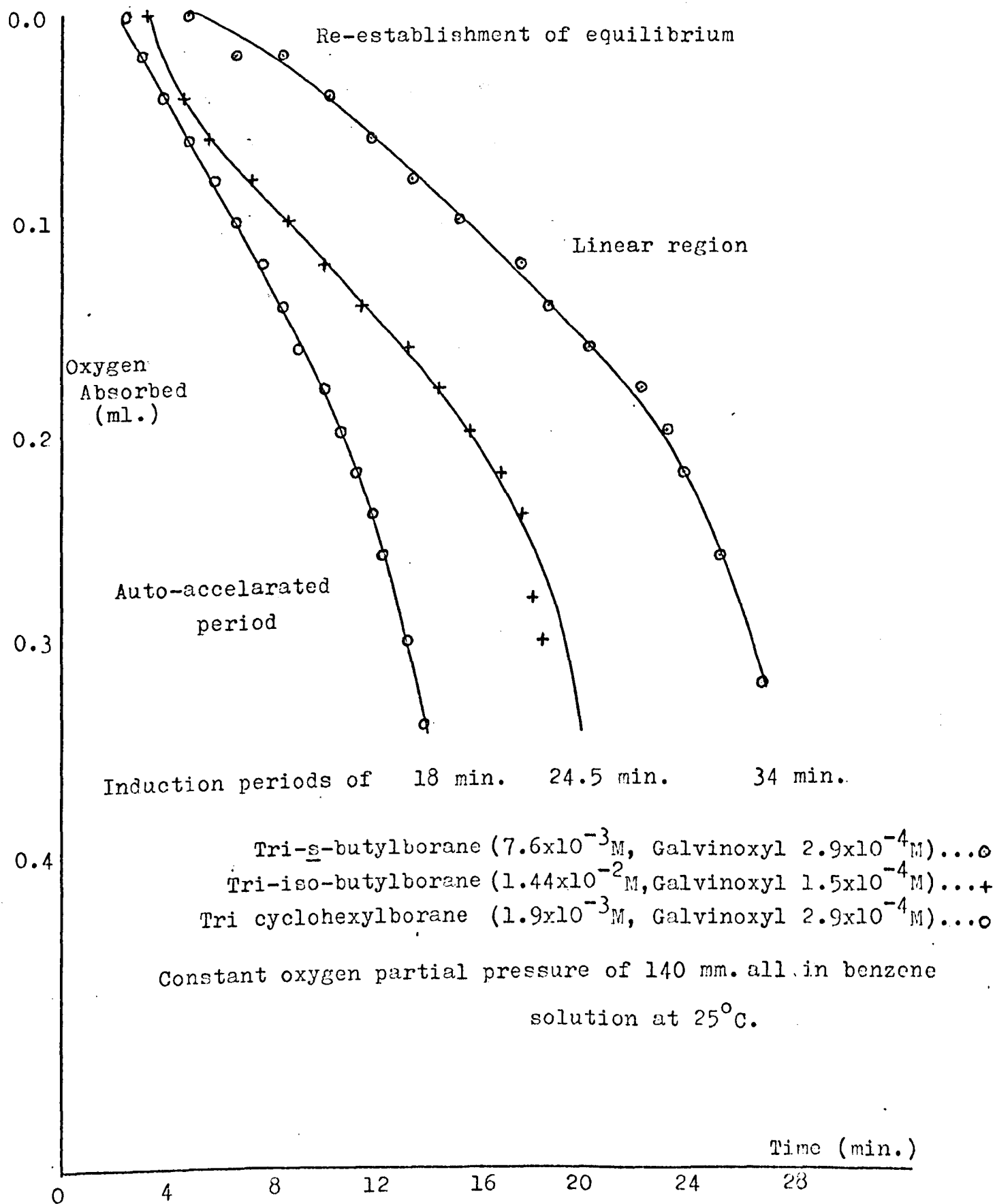


Figure 9. Absorption of Oxygen by Borane Solutions in the Presence of Galvinoxyl.



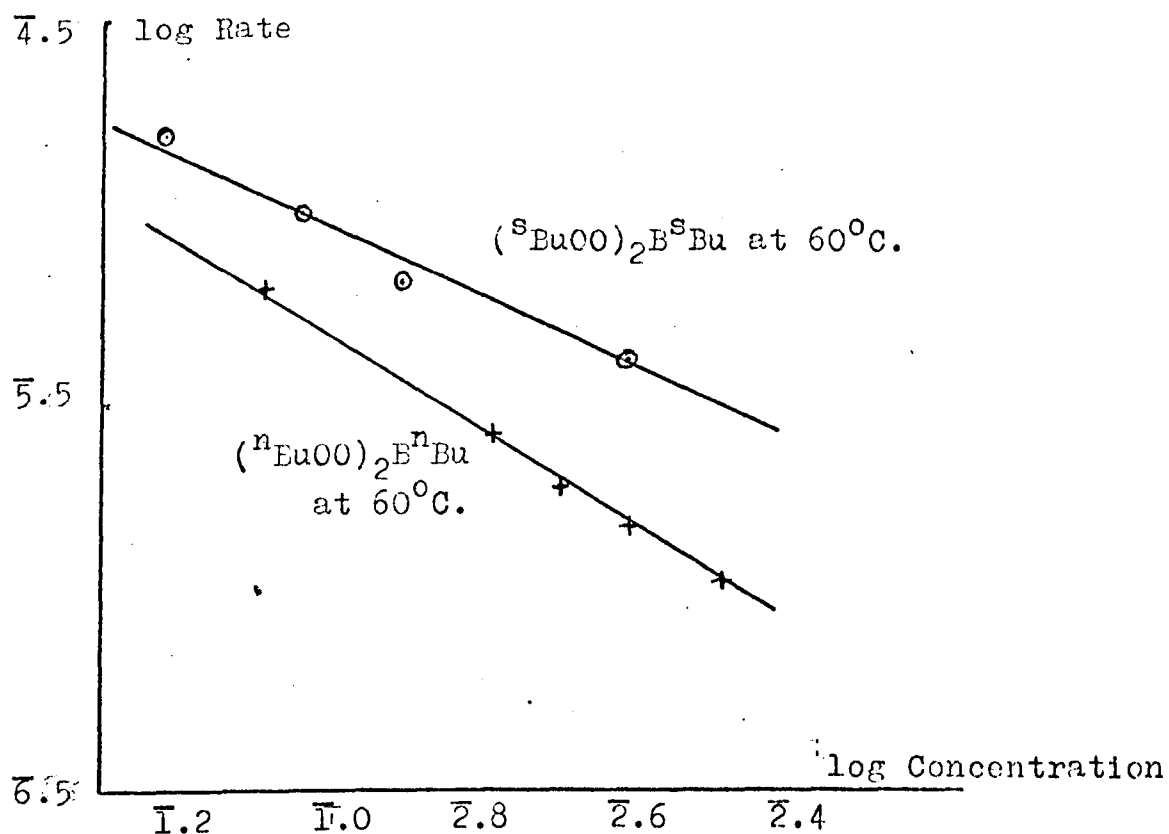


Figure 10. Variation of Decomposition Rate with Changing Organoperoxyborane Concentration.

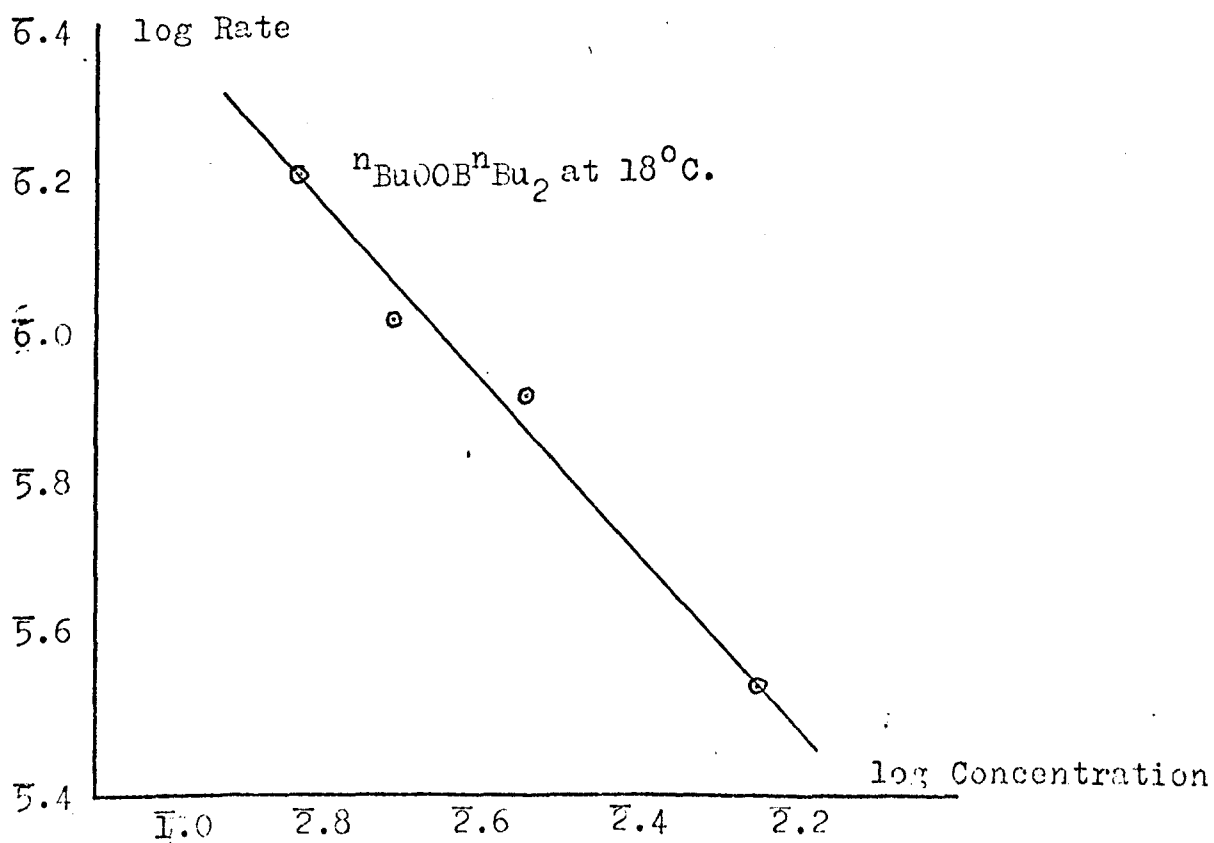


Figure 10a. Graphs of $\log \frac{a}{a-x}$ against Time for
Organoperoxyboranes in Iso-Octane Solution.

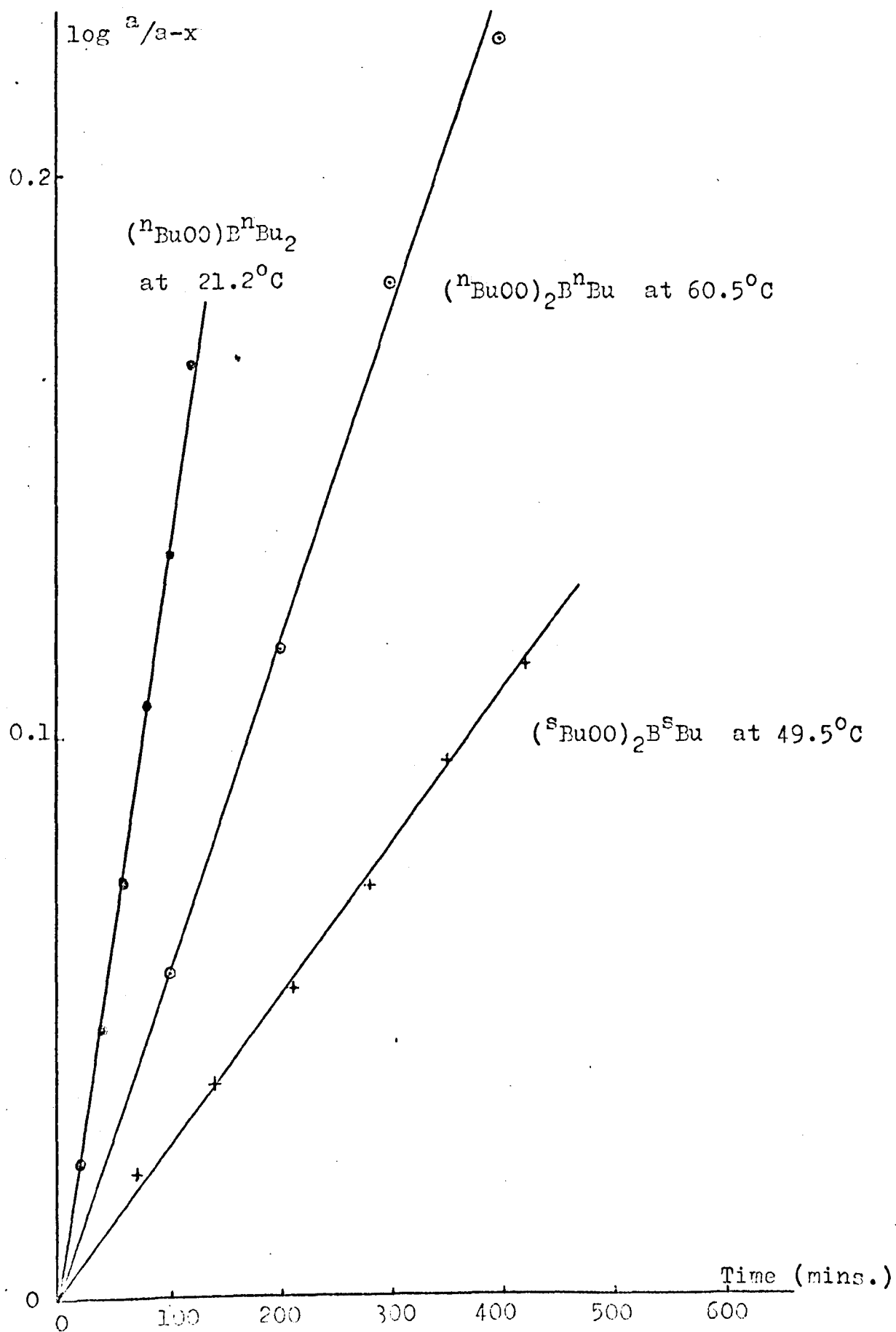


Figure 11. Arrhenius Graphs for the Decomposition
of Organoperoxyboranes in Iso-octane Solution.

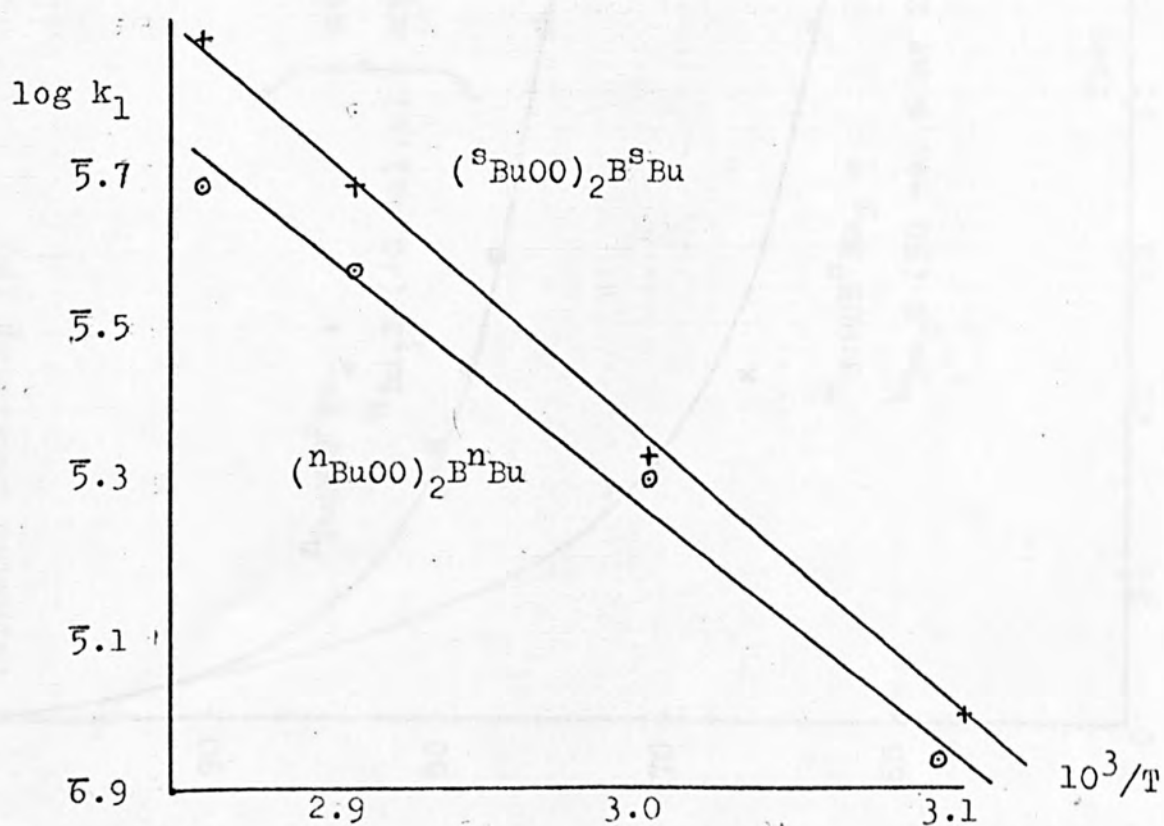
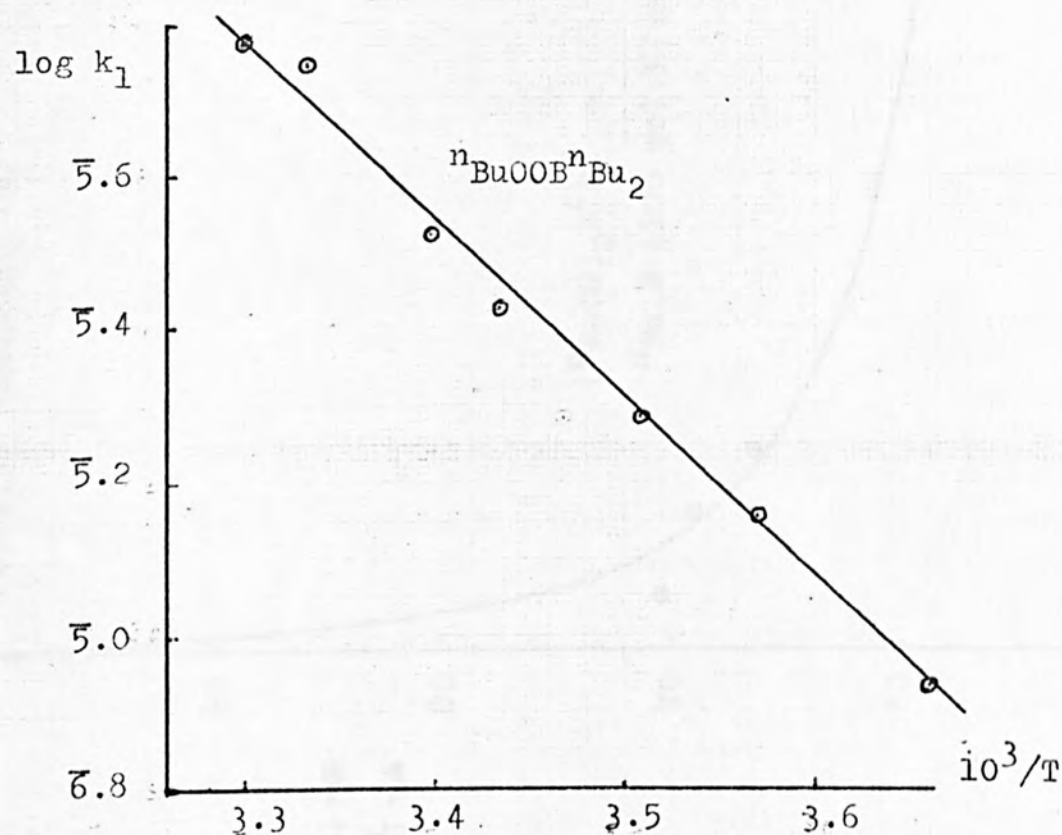


Figure 12. Reaction Between Organoboranes and Organoperoxyboranes, in n-Heptane.

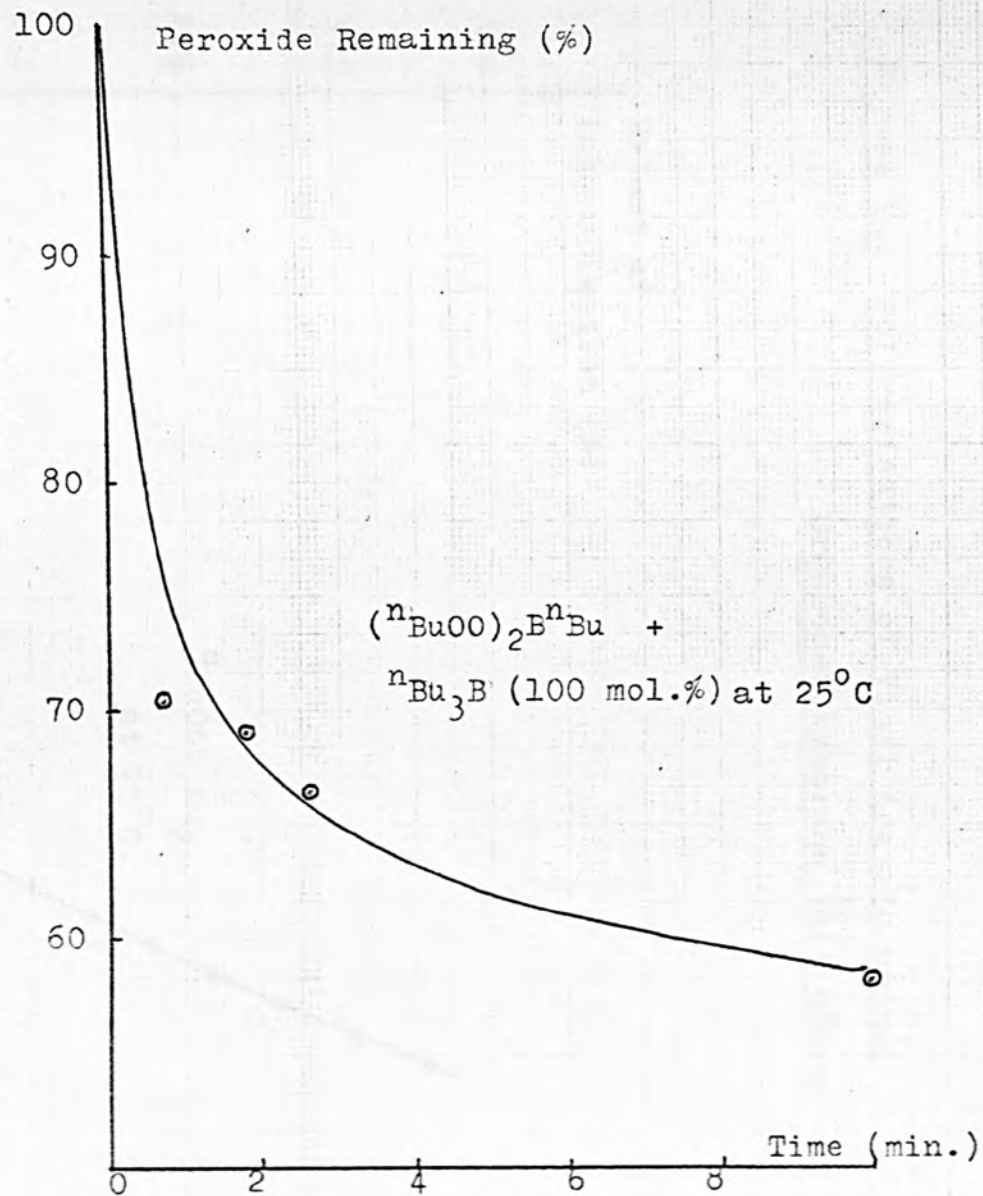
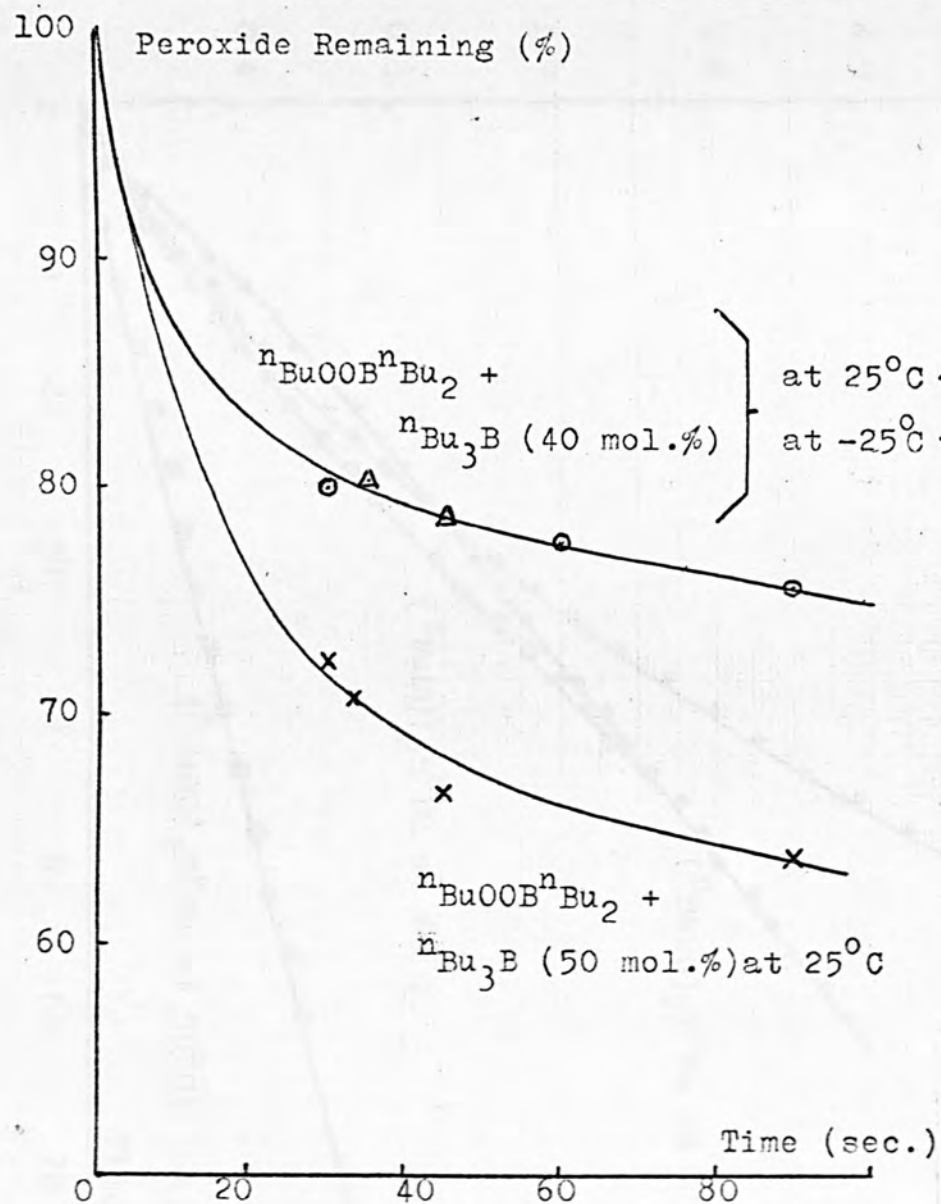


Figure 14. Polymerisations of Vinyl Acetate using
Organoperoxyborane Initiators.

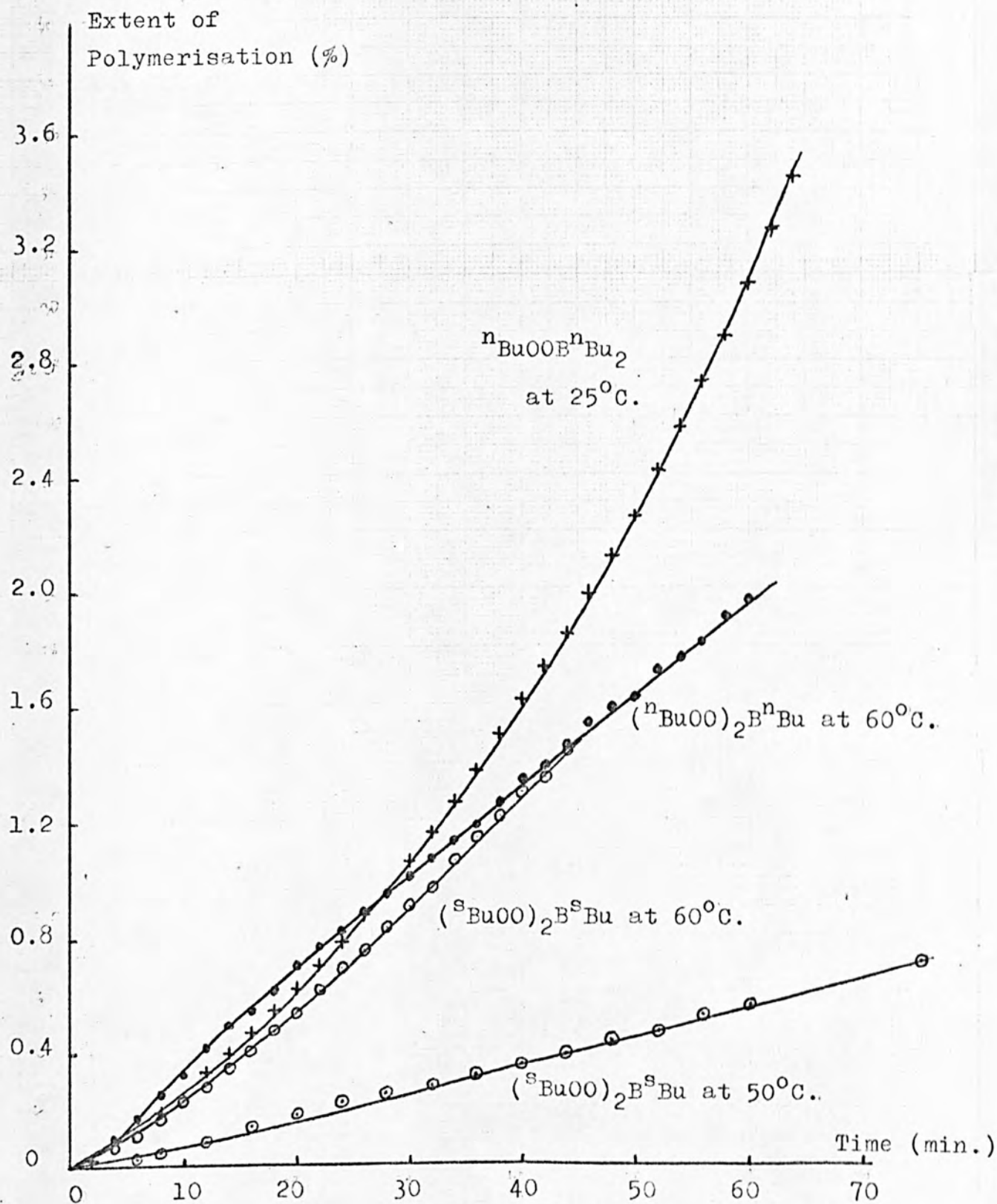


Figure 16. Infra-red Spectrum of Sublimed Solid.

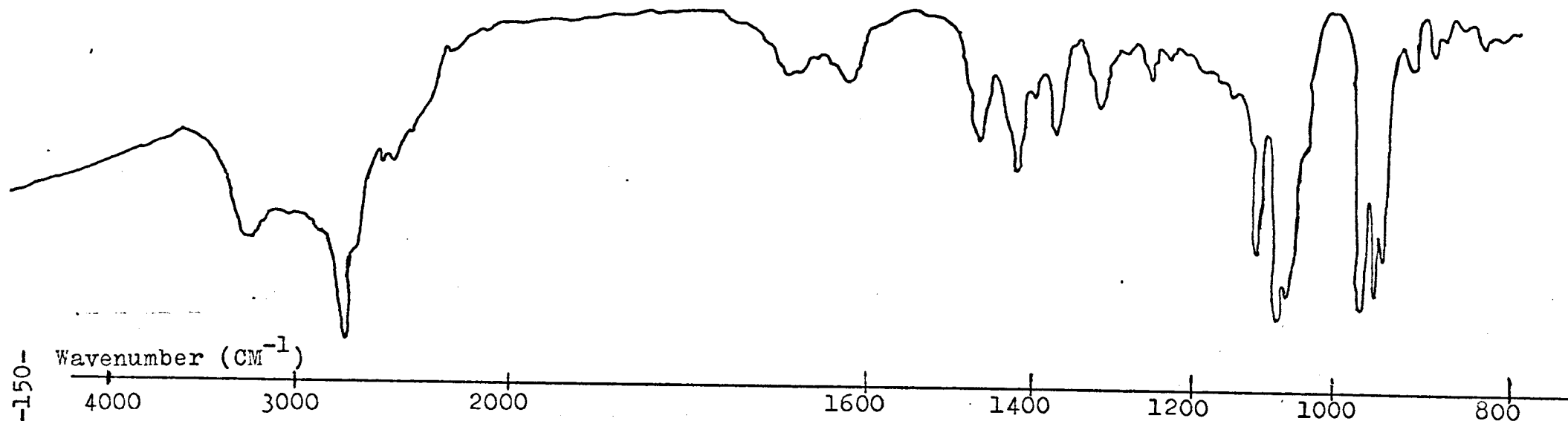


Figure 15. Infra-red Spectrum of Solid Distilled from Reaction of $(^n\text{BuOO})_2\text{B}^n\text{Bu}$, Cyclohexene and Mo(CO)_6 at 60°C.

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CHAPTER 6.

The Autoxidation of Organotransition Metal Compounds.

1. Autoxidation Experiments.

Autoxidations were carried out in an apparatus based on that used by Davies, Ingold, et al. for their studies on the autoxidation of organoboranes¹, and is shown in Figure 17.

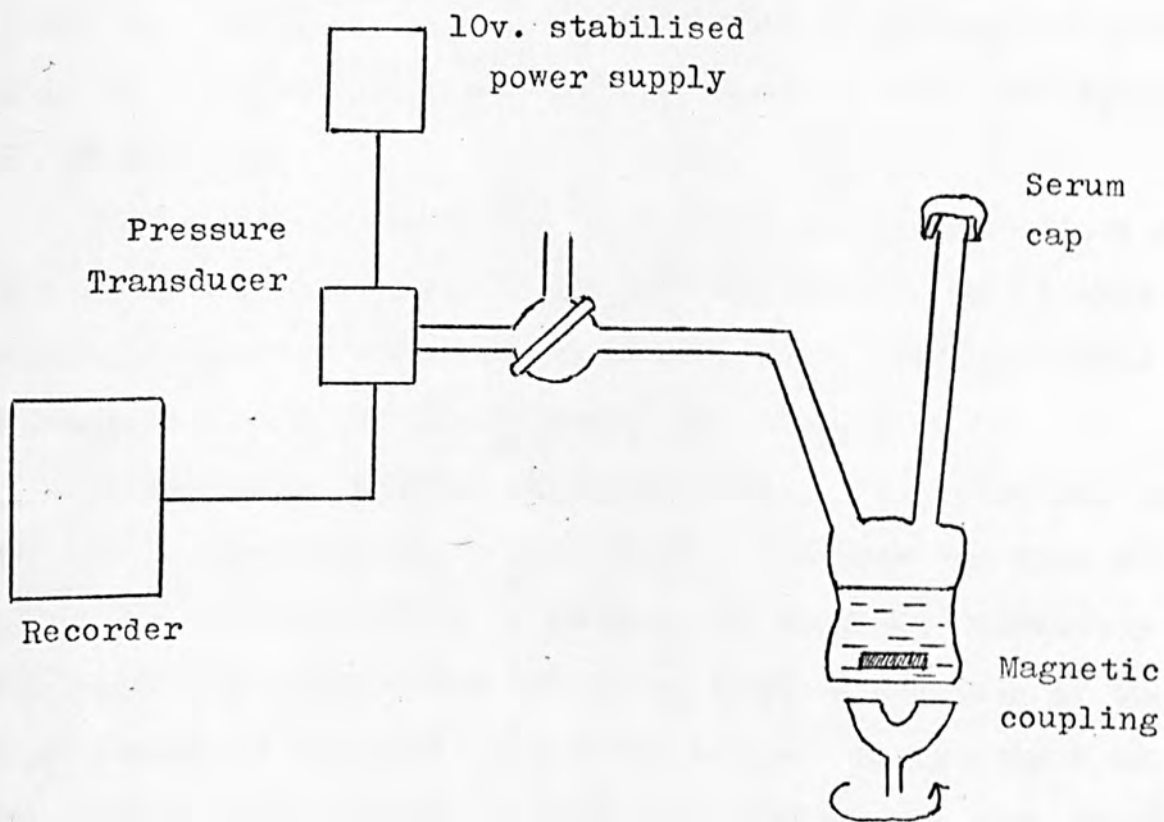


Figure 17. Schematic Diagram of Small Scale Oxidation Apparatus.

This consisted of a small reaction vessel, about 5ml. in volume, with a side arm fitted with a serum cap through which samples could be introduced with a syringe. Stirring was achieved by means of a glass covered bar magnet and a magnetic stirrer; the vessel could be thermostatted. Autoxidations were carried out at 20°C or -74°C, in the latter case the whole of the reaction flask was immersed in powdered solid carbon dioxide. The reaction flask was attached to a Bell and Howell pressure transducer (type 4-326-L261-0120) by means of a glass to metal seal. The pressure transducer operated in the range 0 to 15 p.s.i., and was fed by a stabilized 10 v. power supply unit (Farnell, type MSU). The output signal was fed into a Honeywell potentiometric recorder (1 mv., 1 sec. full scale). In order that recorder readings could be translated into volume changes, a calibration plot was made by withdrawing volumes of gas from the apparatus with a gas tight syringe.

Experiments were always done under one atmosphere of oxygen, and the sample size of the organometallic adjusted so that ca. 5×10^{-5} mole of oxygen would be absorbed. The gas space volume was constant for all experiments (ca. 5 ml.).

A typical experiment was performed in the following manner. The whole apparatus was filled with dry oxygen and then was added the solvent, using a syringe, if required, inhibitor solution. The volume of solvent was varied so that on addition of the organometallic solution, the total volume was exactly 2 ml.. The system was isolated, stirring commenced, and when equilibrium was obtained, the organometallic solution was introduced as a ca. 0.1M. solution in hydrocarbon solvent (n-heptane, toluene

or benzene, Tables 6 and 7) via the serum cap using a gas tight syringe. After absorption was completed, the apparatus was flushed with nitrogen and the solution analysed for peroxide by iodometric titration.

Typical experiments are shown in Figures 18-20 (tri-n-butylborane is included in Figure 18 as a reference) and the results obtained are summarised in Tables 6 and 7.

Autoxidation in the Presence of Inhibitors. In those cases where galvinoxyl was used it was noticed, for all the compounds studied, that a magenta colour was produced immediately the organometallic was added to the solution. This same colour was produced in the total absence of oxygen and it appears therefore, that there is a direct reaction between galvinoxyl and the transition metal organometallic.

The use of the phenols "Ethyl 702" and "Ethyl 720" resulted in the gradual production of wine red or mauve colours during the course of the autoxidation.

The effects of the inhibitors are given in Table 6 and 7 and shown in Figures 19 and 20.

2. Experiments in the Presence of Donors.

(i) Autoxidation of Tetrabenzyl Zirconium in the Presence of Pyridine and piperidine. A toluene solution of tetrabenzyl-zirconium (2.5×10^{-5} mole) was injected into a solution of pyridine in toluene, in the autoxidation apparatus. The pyridine content was varied from 5×10^{-3} mole to 2×10^{-2} mole. There was found to be no change in either the speed or extent of the autoxidation. Analogous results were obtained on treating the

tetrabenzyl zirconium with pyridine prior to injecting it into the autoxidation flask.

The use of piperidine similarly had no effect on the course of autoxidation.

(ii) The Reaction of Pyridine with Hexakis (trimethylsilylmethyl)

Bimolybdenum. This reaction was investigated using proton magnetic resonance (^1H n.m.r.) spectroscopy. Two solutions containing hexakis (trimethylsilylmethyl) bimolybdenum (1×10^{-4} mole) were prepared in dry, degassed benzene, and in a dry, degassed solution of pyridine (5×10^{-3} mole) in benzene. Samples were then placed in dry, nitrogen filled ^1H n.m.r. tubes, sealed with tightly fitting serum caps. The spectra were recorded and the peaks at 7.8τ (CH_2) and 9.6τ (CH_3) were found unchanged in position or intensity in the presence of pyridine. This indicated that there was no complex formation.

Hexa neopentyl bimolybdenum behaved similarly.

3. The Autoxidation of Tetrabenzyl Zirconium in the Presence of Iodine.

To a solution of iodine (8×10^{-6} mole) in toluene in the autoxidation apparatus was added tetrabenzyl zirconium (2.5×10^{-5} mole) in toluene. The colour of the iodine was gradually discharged during the course of the autoxidation, and although the rate of autoxidation was unaffected, the amount of oxygen absorbed (4.3×10^{-5} mole) was a 15% reduction in the normal value. After purging with nitrogen, the solution was

analysed by gas liquid chromatography (10% carbowax column at 140°C) and benzyl iodide was identified by comparison with an authentic sample.

An identical experiment was performed in the absence of oxygen. The colour of the solution remained unchanged during 15 minutes and no benzyl iodide could be detected.

4. Products of Autoxidation.

(i) General Technique. Following autoxidation, the samples were analysed for peroxide by iodometric titration and the results are summarised in Tables 6 and 7. Only the autoxidations of tetrabenzyl zirconium and hexabenzyl bitungsten at -74°C were found to produce significant quantities of peroxidic material. The peroxide obtained from tetrabenzyl zirconium was found to be very unstable, having a half life of ca. 50 minutes at 20°C. The stability of the peroxide produced from the low temperature autoxidation of hexabenzyl bitungsten was not examined.

After being analysed for peroxide the samples were hydrolysed by pouring in to water, and the organic components were extracted with ether. The residue obtained after removal of solvent was analysed by gas liquid chromatography (g.l.c.) and ¹H n.m.r. spectroscopy.

(ii) Trimethylsilylmethyl Derivatives. The hydrolysis products of all of these transition metal derivatives were found to be extremely complex and only trimethylsilylmethanol, the major product, was positively identified (g.l.c. on 10% carbowax column at 140°C, comparison with authentic sample). The

hydrolysis products of an ethereal solution of trimethylsilylmethyl magnesium chloride were examined in a similar manner following autoxidation at 0°C . As well as the expected trimethylsilylmethanol there were many minor products, as had been reported by Eisch and Husk², but no attempt was made to indentify them.

The ^1H n.m.r. spectrum of tetrakis (trimethylsilylmethyl) titanium was recorded before and after autoxidation. Prior to autoxidation two peaks were apparent at $9.7 \text{ } \tau$ (CH_3) and $7.6 \text{ } \tau$ ($-\text{CH}_2-$). After autoxidation the singlet at $7.6 \text{ } \tau$ had disappeared, and was replaced by a new singlet at $5.4 \text{ } \tau$.

(iii) Tetrabenzyl Zirconium. The autoxidation in toluene at 20°C and subsequent hydrolysis of tetrabenzyl zirconium (8×10^{-5} mole) produced two major products, benzyl alcohol (1.7×10^{-4} mole, 53% of benzyl groups originally present) and benzaldehyde (2.4×10^{-5} mole, 7.5%). These were indentified and estimated (g.l.c. on 10% carbowax column at 140°C) by comparison of peak areas with standard solutions. A small amount of an unknown product (ca. 5% of the total) was also present and the hydrolysis products had a small peroxide content (3.1×10^{-6} mole, 0.95%).

The autoxidation of a similar sample at -74°C produced, after hydrolysis, benzyl alcohol (1×10^{-4} mole, 32%), benzaldehyde (3.1×10^{-5} mole, 9.7%), and peroxide (1.01×10^{-5} mole, 3.2%).

The peroxide was extracted with dilute sodium hydroxide from the toluene extracts of the hydrolysis products of tetrabenzyl zirconium (5×10^{-4} mole), autoxidised at -74°C in toluene. The aqueous solution was neutralized with dilute hydrochloric acid at 5°C and gave, after extraction with ether and removal of the solvent, a yellow peroxidic oil. Examination by ^1H n.m.r.

spectroscopy showed the sample to be contaminated with benzaldehyde, probably due to the instability of the sodium salt³, and benzyl alcohol, presumably due to its solubility in water. The benzyl hydroperoxide was purified by thin layer chromatography, using a silica stationary phase and a mixture of benzene, methanol and acetic acid (10:1:1) as the eluent. The peroxide could be detected by ultra-violet light or by spraying with p-aminophenol hydrochloride in methanol⁴. It was then extracted from the silica with ether, and after washing the extracts with water to remove acetic acid and removal of the solvent, there remained a highly peroxidic oil. The benzyl hydroperoxide was taken up in carbon tetrachloride and its ¹H n.m.r. spectrum recorded, which consisted of a singlet, 2.74 τ , a shoulder, 2.78 τ , and a singlet, 5.10 τ , in good agreement with literature values.^{5,6}

(iv) Hexabenzyl Bitungsten. The autoxidation, at both 20°C and -74°C, and hydrolysis of hexabenzyl bitungsten (4×10^{-5} mole) gave identical products to those from tetrabenzyl zirconium. No quantitative estimates were made.

Table 6. Autoxidation of Organotransition Metal Compounds at 20°C.

Compound(Mx10 ³) (Solvent)	Inhibitor ^a (mol.%)	Effect ^b	O ₂ uptake (Mx10 ³)	O ₂ uptake (mol.)	Peroxide(mol.% per alkyl group)
[(CH ₃) ₃ SiCH ₂] ₄ Ti (9.5)(<u>n</u> -heptane)	None	-	19.5	2.07	None
	Pheno (11)	R.	19.0	2.00	"
	Galv. (5)	-	19.5	2.07	"
	Top. (12)	-	18.0	1.90	"
[(CH ₃) ₃ SiCH ₂] ₄ Zr (9.5)(<u>n</u> -heptane)	None	-	20.1	2.11	None
	Galv. (10)	-	16.5	1.74	"
[(CH ₃) ₃ SiCH ₂] ₆ Mo ₂ (7.0)(<u>n</u> -heptane)	None	-	21.0	3.00	None
	Galv. (5)	-	22.6	3.23	"
	Pheno. (10)	-	21.2	3.03	"
	E.720 (5)	-	21.5	3.07	"
	Top. (12)	-	23.0	3.29	"
[(CH ₃) ₃ CCH ₂] ₆ Mo (6.5)(benzene)	None	-	19.7	3.03	Trace
	Galv. (8)	-	17.5	2.70	
	Pheno. (12)	R	17.5	2.70	
	Top. (12)	S.R	19.8	3.05	
	T.A.N.	-	17.5	2.70	
(PhCH ₂) ₄ Zr (12.0)(toluene)	None	-	25.0	2.08	<u>ca.</u> 4
	Galv. (3)	-	23.9	1.99	"
	Pheno. (9)	-	22.8	1.90	"
	Top. (8)	-	24.0	2.00	"
	E.702 (4)	-	23.0	1.99	"
	T.A.N. (10)	-	24.6	2.05	"
(PhCH ₂) ₆ W ₂ (4.1)(<u>n</u> -heptane)	None	-	12.8	3.12	<u>ca.</u> 5
	Galv. (6)	-	11.3	2.76	"
	Pheno. (12)	-	11.1	2.71	"
	E.702 (6)	-	13.5	3.29	"
	T.A.N. (12)	-	12.7	3.09	"

Table 6 cont.

Key:

- (a) Top. = Topanol 354 - 2,6 di-t-butyl-4-methoxy phenol.
Pheno. = Phenothiazine -
Galv. = Galvinoxyl
E.720 = Ethyl 720 - bis-(4-hydroxy-3-methyl-5-t-butyl-
phenyl) methane.
E.702 = Ethyl 702 - bis-(4-hydroxy-3,5-di-t-butylphenyl)
methane
T.A.N. = tri-acetonamine nitroxide.
- (b) R = Retardation
S.R. = Slight retardation.

Table 7. Autoxidation of Organotransition Metal Compounds at -74°C .

Compound($\text{Mx}10^3$) (Solvent)	Inhibitor ^a (mol.%)	Effect ^b	O_2 uptake ($\text{Mx}10^3$)	O_2 uptake (mol.)	Peroxide(mol.% per alkyl group
$[(\text{CH}_3)_3\text{SiCH}_2]_4\text{Ti}$ (9.5)(<u>n</u> -heptane)	None	-	21.0	2.21	None
	Galv. (5)	-	17.7	1.87	"
$[(\text{CH}_3)_3\text{SiCH}_2]_4\text{Zr}$ (9.5)(<u>n</u> -heptane)	None	-	21.0	2.21	Trace
	Galv. (5)	-	18.5	2.21	None
	Pheno. (10)	S.R..	17.5	1.85	"
$[(\text{CH}_3)_3\text{SiCH}_2]_6\text{Mo}_2$ (7.0)(<u>n</u> -heptane)	None	-	24.0	3.43	<u>ca.</u> 3
	Galv. (5)	-	23.9	3.41	
	Pheno. (10)	-	23.5	3.36	
	E.720 (8)	-	22.5	3.21	
$(\text{PhCH}_2)_4\text{Zr}$ (8.2)(toluene)	None	-	22.5	2.74	14.5
	Galv. (5)	-	22.1	2.70	15.0
	Pheno. (12)	S.R.	21.2	2.58	11.0
	Top. (12)	S.R	21.9	2.67	12.0
	E.720 (6)	S.R.	20.8	2.54	14.0
$(\text{PhCH}_2)_6\text{W}_2$ (2.4)(<u>n</u> -heptane)	None	-	8.0	3.34	13.0
	Galv. (10)	-	7.5	3.13	13.5
	Pheno. (12)	-	7.0	2.92	9.0
	Top. (10)	-	7.5	3.13	13.0

Key as for Table 6.

Figure 18. Autoxidation of Organotransition Metal Compounds
at 20°C.

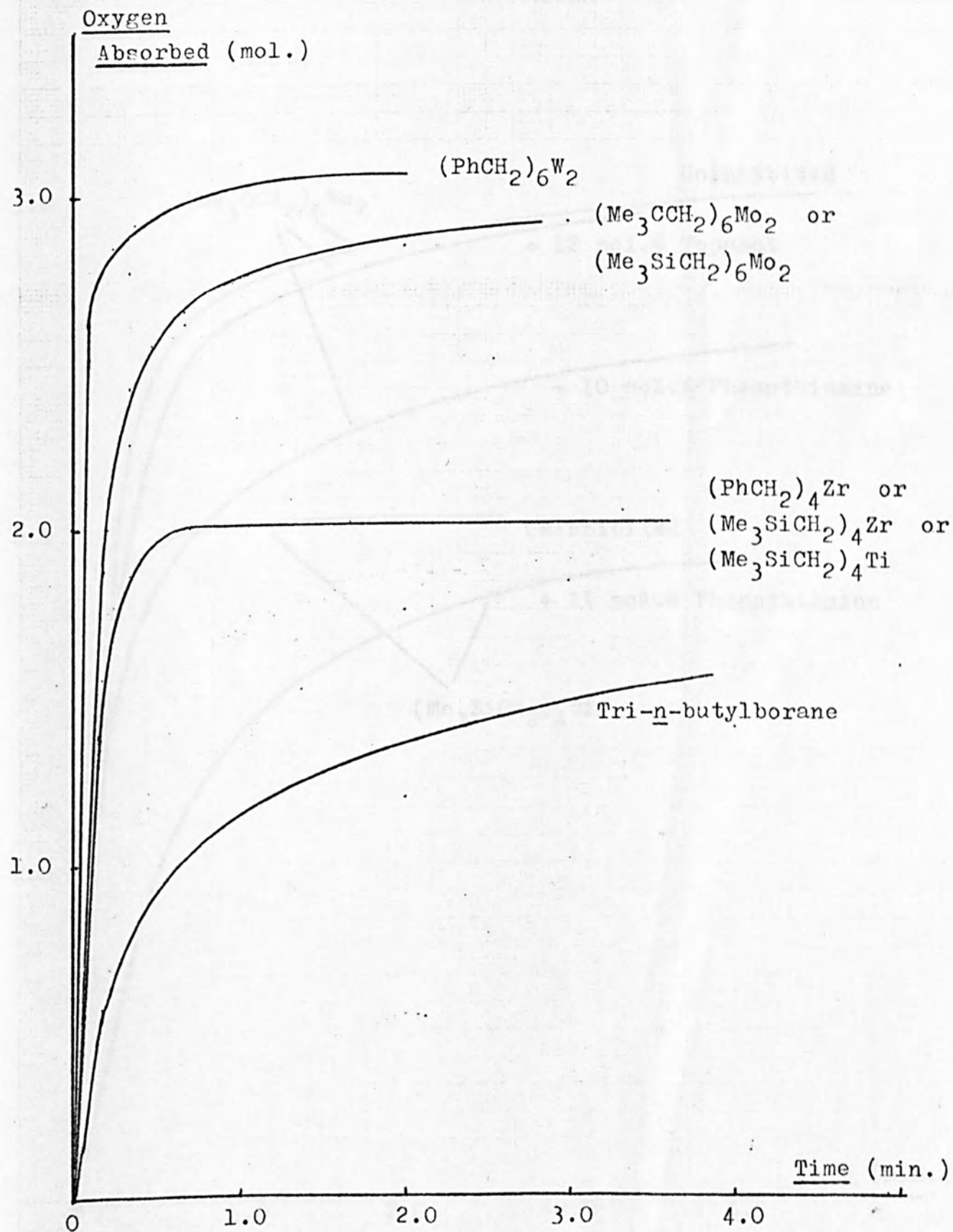


Figure 19. Autoxidation of Organotransition Metal Compounds
in the Presence of Inhibitors at 20°C.

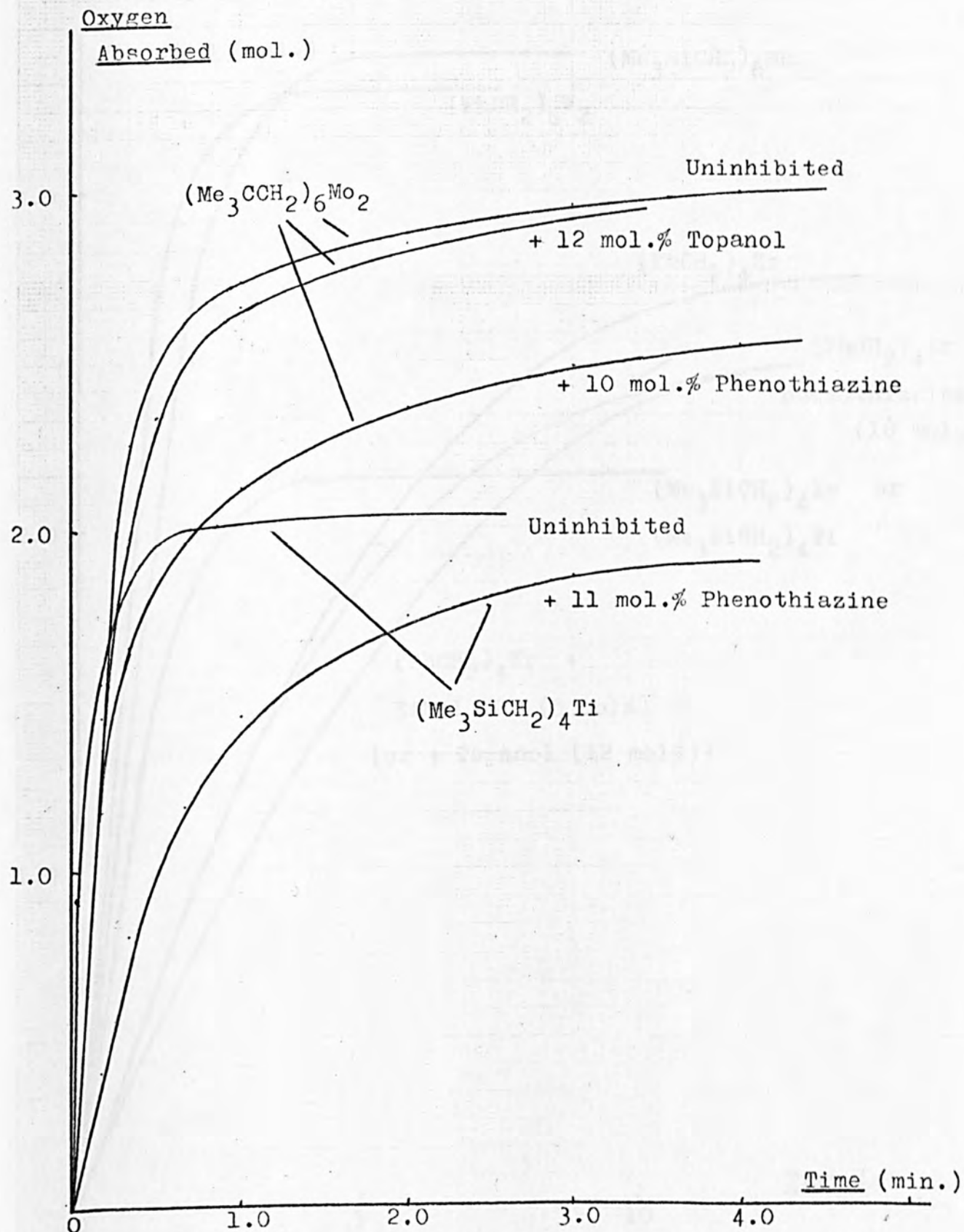
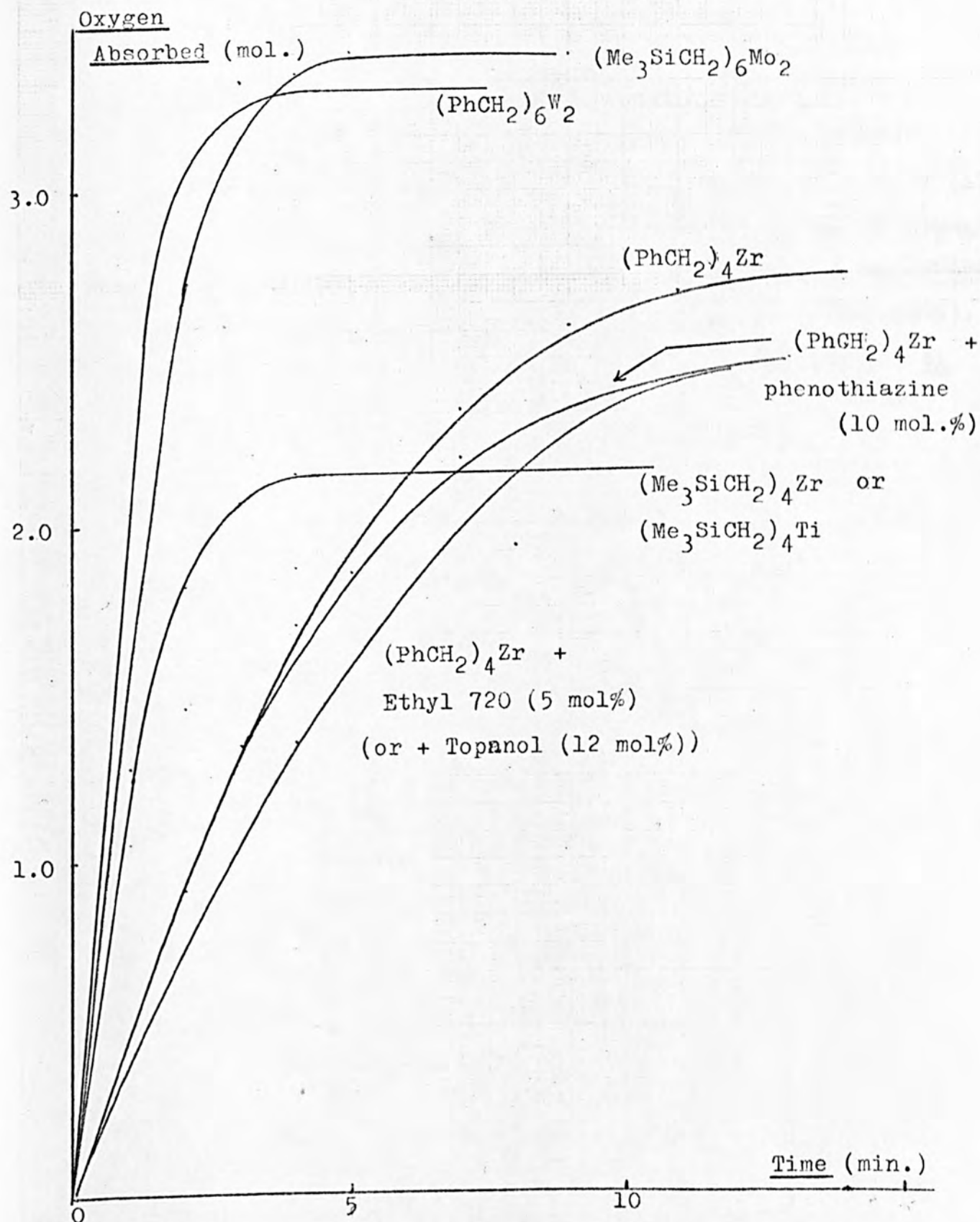


Figure 20. Autoxidation of Organotransition Metal Compounds
at -74°C .



References.

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J. Chem. Soc., (B) 698 (1971).
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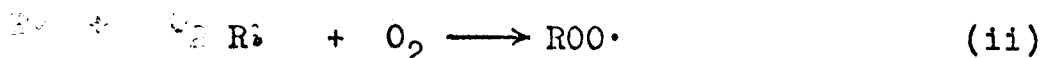
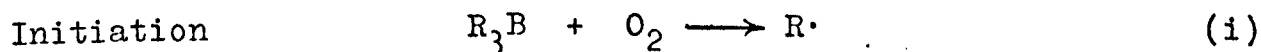
PART III

DISCUSSION OF RESULTS

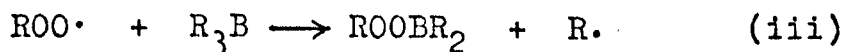
CHAPTER 7.

THE PRIMARY INITIATION OF TRIALKYLBORANE AUTOXIDATIONS.

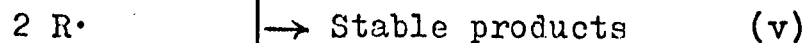
It is now well established that trialkylboranes autoxidise with a free-radical chain mechanism^{1,2}:



Propagation



Termination



The termination reactions do not involve borane and also occur in hydrocarbon autoxidations, and rate constants for these termination reactions involving many radicals are now available³. Reaction (ii) similarly is well known from hydrocarbon autoxidations, but rate constants for this process are rather inaccessible. Van den Berg and Callear have determined a value for the reaction of methyl radicals with oxygen as $10^{12} M^{-1} s^{-1}$ in the vapour phase⁴.

Reactions (i) and (iii) are pertinent to organoborane chemistry, but it is only recently that either has received any critical attention. The propagating S_H^2 reaction has been studied for a number of boranes by Ingold and Davies⁵ and Ingold et al.⁶ and rate constants determined. These values had been previously inaccessible because of the extreme vigour of the reaction which resulted in a diffusion controlled autoxidation. These workers eliminated this problem by studying the autoxidations in the presence of pyridine which, because of complex formation, resulted in a very low concentration of free borane thus providing a reaction of measurable speed.

Although values for the rates of initiation of trialkylborane autoxidations had been determined by several workers, there were no data concerning either the mechanism or the rate constants of the primary initiation reaction. Two main methods for the determination of initiation rates had been used in previous studies:

(a) Calculated from the length of the induction period using known concentrations of inhibitor:

$$R_i = \frac{n [A]}{\gamma} \quad (\text{vii})$$

where n = number of radicals removed by one molecule of inhibitor, and is unity in the case of galvinoxyl⁷.

$[A]$ = initial concentration of inhibitor.

γ = inhibition period.

The inhibitor most frequently used in such determinations has been galvinoxyl^{5,6,7}, although Ingold and Davies have also used 2,6-di-t-butyl 4-methoxyphenol⁵.

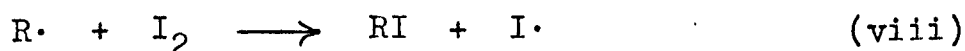
Galvinoxyl inhibits the reaction by removing the alkyl and alkylperoxy radicals produced by initiation thus suppressing the S_H^2 propagating step of alkylperoxy radicals attacking borane (reaction (iii)).

This method for the determination of primary initiation rates is an indirect method and is subject to errors through the removal of galvinoxyl by alternative reactions. Firstly galvinoxyl is itself susceptible to autoxidation although only slowly, and most galvinoxyl samples are contaminated with hydrogalvinoxyl which considerably stabilises galvinoxyl solutions towards oxygen⁸. Significant errors from this source will therefore only be apparent if the inhibition period is particularly long - Allies found that his galvinoxyl solutions were resistant to autoxidation for 180 minutes⁹. As the concentration of galvinoxyl is reduced during inhibited autoxidations by the trapping of radicals, its ability to completely suppress the S_H^2 propagation step (reaction (iii)) will be lowered, and the probability of peroxide formation is increased. The production of peroxide gives rise to the major errors. Galvinoxyl reacted slowly with organoperoxyborane (page 135) but the reaction between organoperoxyborane and organoborane results in the rapid removal of galvinoxyl (page 135).

These errors will produce a rate of initiation in excess of the true value.

(b) Recently it has been demonstrated that iodine could act

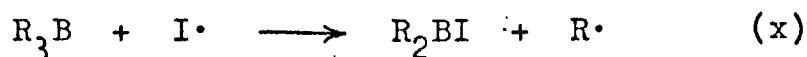
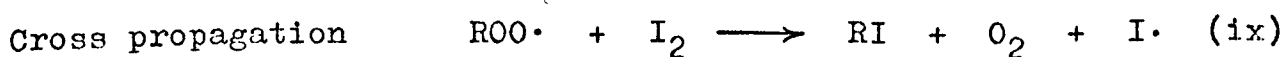
as a successful inhibitor of organoborane autoxidations^{10,11} and Brown suggested that it functioned by removing the alkyl radicals produced by initiation:



Brown and Midland¹¹, although giving inhibition period data, did not convert these figure into rates of initiation by use of the formula (vii). In a later publication,¹² these workers reported the determination of initiation rates by estimating the rate of production of alkyl iodide, presumably formed as a result of reaction (viii).

As in the case of galvinoxyl above, other reactions can be proposed to account both for the removal of iodine and for the formation of alkyl iodide. If the iodine does not remove free radicals efficiently, organoperoxyborane will be produced, and Grotewold has shown that the reaction between organoperoxyborane and organoborane rapidly removed iodine.¹⁰

The following reactions could also contribute to the removal of iodine and the formation of alkyl iodide:

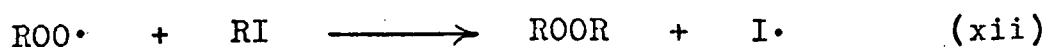


Iodine chain propagation



Reactions of this type were dismissed by Brown but without supporting evidence, and this may well be an oversimplification.

It has also been pointed out by Ingold⁶ that the induction period does not vary linearly with increasing iodine concentration and Brown's data¹¹ showed that doubling the iodine concentration caused an almost fourfold increase in the inhibition period. Brown and Midland ascribed this to the fact that at low iodine concentrations a relatively large proportion of radicals were not trapped but followed the chain pathway, but this proportion was reduced as the iodine concentration was increased. This argument is not convincing and there was no evidence to support it. The suggestion by Ingold⁶ that iodine is regenerated after the initial inhibition step, by analogy with the suggested mechanism of iodine inhibited hydrocarbon autoxidations, appears more reasonable.

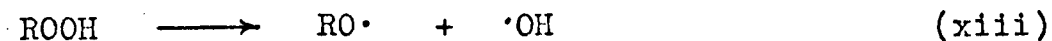


In view of the uncertainties associated with the inhibition of organoborane autoxidations by iodine, rates of initiation determined from such reactions should be treated with caution.

Because of the shortcomings of the methods outlined above, it was decided to study the primary initiation reaction directly by measuring the slow rate of oxygen absorption by an organoborane solution while under inhibition by galvinoxyl.¹³

Hydrocarbon autoxidations are often initiated by the homolytic decomposition of traces of peroxide in the hydrocarbon

sample¹⁴:



Thus, in order to study the spontaneous initiation process for hydrocarbon autoxidations, it has been necessary to rigorously purify the hydrocarbon.¹⁵ Ingold and Davies have suggested an analogous homolytic decomposition for organoperoxyboranes under oxygen⁶. However, it is concluded in the next chapter that such a reaction is extremely slow at ambient temperature when conducted in vacuo (dilatometry measurements). Ingold and Davies,⁶ and Grotewold et al.¹⁰ have also proposed that the reaction between borane and organoperoxyborane could be responsible for self-initiation of the autoxidation. However, the extreme vigour of this reaction ($t_{\frac{1}{2}}$ ca. 10 sec., Ch. 8) precludes the existence of traces of peroxide in a borane sample, and consequently, provided the galvinoxyl removes radicals efficiently, there will be no peroxide present to cause initiation by such mechanisms, and only the direct reaction between oxygen and borane can be responsible for the production of radicals and the absorption of oxygen.

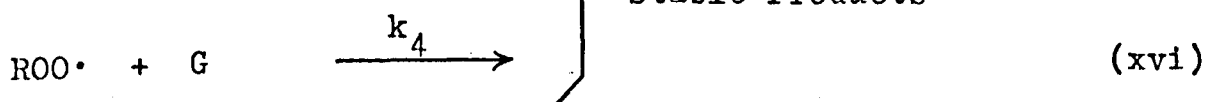
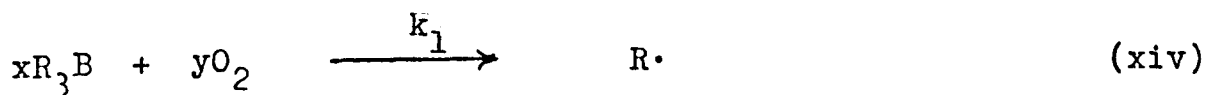
The oxygen absorption - time graphs (Figure 9) showed three distinct regions:

(a) Re-establishment of equilibrium. The injection of the borane solution temporarily displaced the liquid - vapour equilibrium, but this was usually restored within two or three minutes.

(b) Linear region. Oxygen was steadily absorbed during this period and it is assumed that galvinoxyl was effectively removing the radicals produced by initiation, thus suppressing the S_H^2 reaction between alkylperoxy radicals and borane (reaction (iii)).

(c) Auto-accelerated period. The rate of absorption of oxygen gradually increased and the onset of this period presumably occurred when the galvinoxyl concentration was reduced to a level at which it no longer completely suppressed the S_H^2 propagation reaction. This results in the formation of organoperoxyborane which provides additional initiating processes and auto-catalysis.

The rates of oxygen absorption (Table 4) from the linear region can be related to the rates and rate constants for the primary initiation step. The following reactions are relevant:



where G = Galvinoxyl.

The rate of absorption of oxygen will be given by

$$\frac{-d [O_2]}{dt} = k_1 [R_3B]^x [O_2]^y + k_2 [O_2] [R\cdot] \quad (xvii)$$

Assuming a steady state concentration of alkyl radicals:

$$\frac{d[R\cdot]}{dt} = 0 = k_1 [R_3B]^x [O_2]^y - k_2 [R\cdot] [O_2] - k_3 [R\cdot] [G] \quad (xviii)$$

$$\text{and therefore } [R\cdot] = \frac{k_1 [R_3B]^x [O_2]^y}{k_2 [O_2] + k_3 [G]} \quad (xix)$$

Substituting for $[R\cdot]$ in equation (xvii) and rearranging:

$$\frac{-d[O_2]}{dt} = k_1 [R_3B]^x [O_2]^y \left(1 + \frac{k_2 [O_2]}{k_2 [O_2] + k_3 [G]} \right) \quad (xx)$$

There are two limiting cases to this equation. Firstly, if

$$k_2 [O_2] > k_3 [G] \quad \text{then,}$$

$$\frac{-d[O_2]}{dt} = 2 k_1 [R_3B]^x [O_2]^y \quad (xxi)$$

and secondly if $k_3 [G] > k_2 [O_2]$

$$\frac{-d[O_2]}{dt} = k_1 [R_3B]^x [O_2]^y \quad (xxii)$$

Thus rate constants calculated from either expression cannot be more than a factor of two from the true value.

1. Order of Reaction. At constant oxygen and galvinoxyl concentrations, equation (xx) simplifies to,

$$\frac{-d[O_2]}{dt} = k' [R_3B]^x \cdot (1 + C) \quad (xxiii)$$

$$\text{where } k' = k_1 [O_2]^y$$

$$C = \frac{k_2 [O_2]}{k_2 [O_2] + k_3 [G]} = \text{Constant}$$

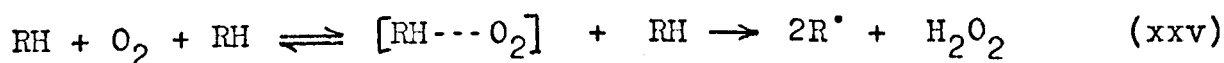
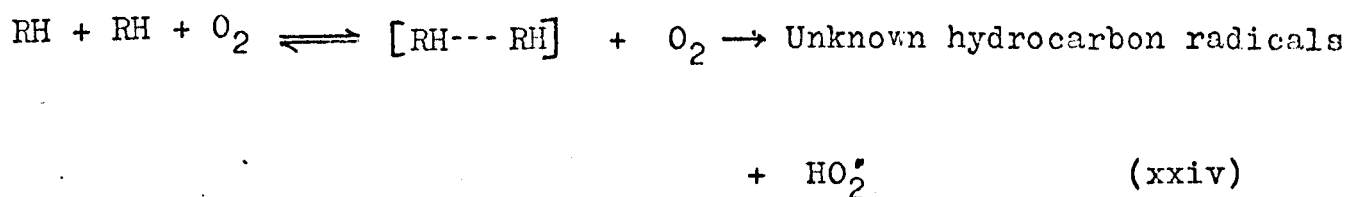
Thus a plot of $-\log \frac{d[O_2]}{dt}$ against $\log [R_3B]$ should

give a straight line of slope x . These graphs are shown for tri-s-butylborane and tri-isobutylborane in Figure 7, and the slopes were found to be 1.05 and 1.09 respectively; for tricyclohexylborane this value was 0.85. For all three boranes investigated, the reaction is therefore assumed to be first order with respect to borane.

It was not possible to derive a simple equation, analogous to equation (xxiii), for the variation of the rate with changing oxygen concentration. It was therefore necessary to assume that either of the limiting equations (xxi) or (xxii) were sufficiently accurate such that a plot of $-\log \frac{d[O_2]}{dt}$ against $\log [O_2]$ would yield a straight line of slope y . That this assumption was justifiable is shown by the fact that reasonable straight lines were obtained for tri-s-butylborane and tri-isobutylborane (Figure 8), and the slopes were 1.2 for both boranes. The greater reactivity of tricyclohexylborane meant that the measurement of the rate of initiation was only possible within a relatively small range of oxygen concentrations. Nevertheless, the limited data indicated a value for y of 1.1.

It therefore seems that the primary initiation reaction of organoborane autoxidations is first order with respect to oxygen,

and second order overall. This is in contrast to hydrocarbon autoxidations^{15,16} where the initiation step was second order in hydrocarbon, first order in oxygen and hence third order overall. Carlsson and Robb suggested two possible mechanisms for the primary initiation of indene and tetralin autoxidations:¹⁵



Both mechanisms involved complex formation followed by a rate determining reaction with a third molecule. Since there was some spectroscopic evidence for the formation of an oxygen-hydrocarbon complex, they favoured the second mechanism. In a later publication Robb and Betts¹⁷ suggested that the spectra were "collisional" in origin rather than due to charge-transfer complex formation, in agreement with the work of Tsubomura and Mulliken.¹⁸ Robb and Betts therefore proposed that the third order kinetics could be attributable to a direct three body collision.

2. Determination of Rate Constants.

Rate constants calculated from either expression (xxi) or (xxii) were found to be not strictly constant, particularly for tri-*s*-butylborane, varying from $0.97 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ to $1.78 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, and tri-isobutylborane, $0.72 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ to $1.03 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ (Table 8). This indicates that the assumption that

$k_2[O_2]$ and $k_3[G]$ are widely different, is not completely valid. Further, the rate of oxygen absorption was not wholly independent of the galvinoxyl concentration, there being a slight inverse dependence (Table 4). These two facts show that accurate rate constants can only be calculated from expression (xx). However, this expression contains two unknowns, k_2 and k_3 , but it was possible, using the method of successive approximations to calculate the value of k_3/k_2 , initial values of k_1 being calculated from equation (xxi). The values of k_3/k_2 so determined were 13.5 for tri-s-butylborane, 2.84 for tri-isobutylborane, and sufficiently large (>100) for tricyclohexylborane to allow values of k_1 to be determined from equation (xxii). These values of k_3/k_2 , when substituted in equation (xx), gave values for the primary initiation rate constant which were sensibly constant, irrespective of oxygen, galvinoxyl, or borane concentration. The rate constants so determined are given in Table 8 and mean values are:

- | | | |
|---------------------------------|---|-------------------------|
| (a) Tri- <u>s</u> -butylborane, | $1.84 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ | at 25°C . |
| (b) Tri-isobutylborane, | $0.94 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ | at 25°C . |
| (c) Tricyclohexylborane, | $2.28 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$ | at 25°C . |

Table 8. Rate Constants for the Primary Initiation of
Trialkylborane Autoxidations at 25°C, in Benzene.

$R_3B \times 10^2$ (M)	$O_2 \times 10^2$ (M)	Galvinoxyl $\times 10^2$ (M)	$k_1 \times 10^3$ (M ⁻¹ s ⁻¹)	$k_{1c} \times 10^3$ (M ⁻¹ s ⁻¹)
<u>Tri-s-butylborane</u>			(a)	(c)
0.76	0.75	0.015	1.78	2.01
0.76	0.36	0.015	1.62	1.96
0.76	0.16	0.015	1.29	1.86
0.76	0.16	0.029	1.12	1.81
0.36	0.16	0.029	0.97	1.56
1.48	0.16	0.029	0.97	1.57
2.10	0.16	0.029	1.34	2.15
0.76	0.16	0.073	0.99	1.80
<u>Tri-isobutylborane</u>			(a)	(c)
1.44	0.75	0.015	0.94	0.97
1.44	0.16	0.015	0.72	0.84
0.75	0.16	0.015	0.82	0.95
2.10	0.16	0.015	0.82	0.95
1.44	0.16	0.059	0.72	1.01
2.80	0.16	0.015	1.03	1.19
<u>Tricyclohexylborane</u>			(b)	
0.13	0.37	0.029	23.70	-
0.13	0.16	0.029	22.60	-
0.19	0.16	0.029	19.51	-
0.078	0.16	0.029	22.60	-

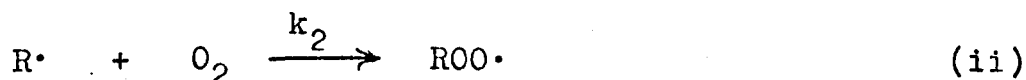
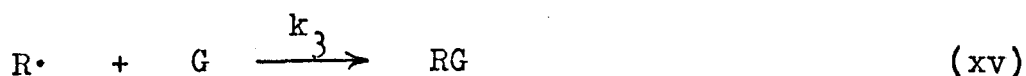
(a) - Calculated from $-d[O_2]/dt = 2 k_1 [R_3B][O_2]$

(b) - Calculated from $-d[O_2]/dt = k_1 [R_3B][O_2]$

(c) - Calculated from $-d[O_2]/dt = k_1 [R_3B][O_2] \left(1 + \frac{k_2 [O_2]}{k_2 [O_2] + k_3 [G]} \right)$

3. Mechanism of Initiation and Implications of Results.

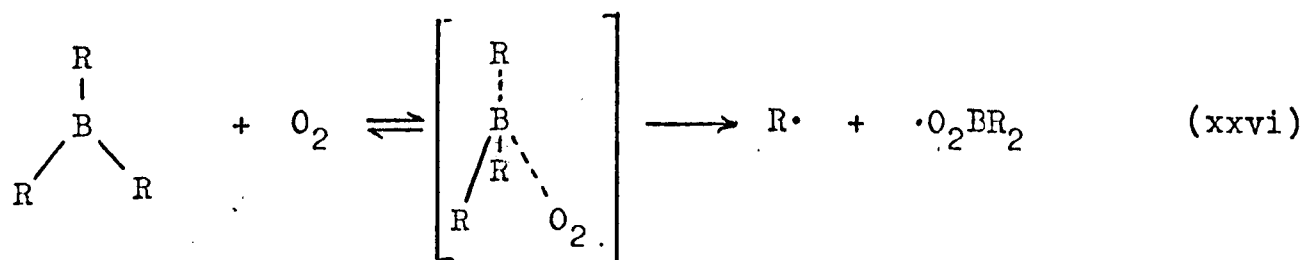
One point of interest, which can be considered as a "by-product" of this work, is that for the first time it has been possible to assess the relative reactivity of galvinoxyl towards alkyl radicals compared to the reaction between oxygen and alkyl radicals.



i.e. the ratio k_3/k_2 is a measure of the relative rates of these two processes. It should be borne in mind that, because of the method of determination of this ratio, the values will in part be dependent upon the errors in the evaluation of the primary initiation rate constants. Nevertheless, it seems beyond doubt that the reaction of galvinoxyl with s-butyl, isobutyl and cyclohexyl radicals is a reaction at least of comparable speed to the reaction of these radicals with oxygen. The unexpectedly high value of k_3/k_2 for tricyclohexylborane (> 100), implying that cyclohexyl radicals reacted almost exclusively with galvinoxyl, is difficult to explain in the absence of further information. It could be that galvinoxyl in some way assists in the primary initiation step, removing the cyclohexyl radicals, whereas the s-butyl and isobutyl radicals are kinetically free when trapped by galvinoxyl.

The propagation reaction between alkylperoxy radicals and

borane (reaction (iii)) is now generally considered as involving the attack by the peroxy radical on the central boron atom via its vacant p orbital^{5,19}. Oxygen is a diradical and since the primary initiation reaction was second order it does not seem unreasonable to suggest a similar mechanism:



The recombination of the alkyl and dialkylboronperoxy radicals is, as Lissi et al. have pointed out¹⁰, spin forbidden and thus the displaced alkyl radical is free to react with oxygen to give a peroxy radical, which, in the absence of inhibitor can initiate chains.

The rates of primary initiation of organoborane autoxidations will be dependent on several factors, including

- (a) Steric hindrance to the incoming oxygen molecule.
- (b) Steric strain in the transition state.
- (c) Stability of the displaced radical.

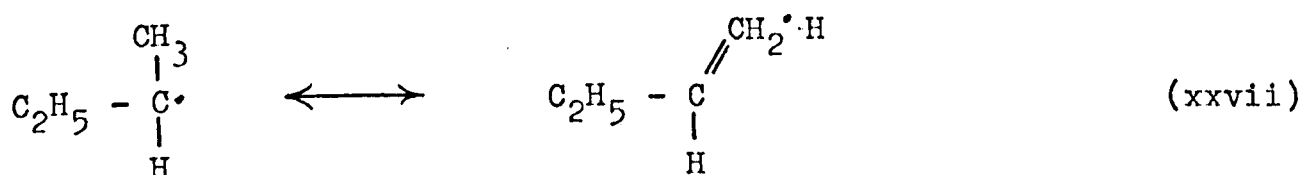
An increase in steric hindrance around the trigonal central boron atom makes the approach of the oxygen molecule more difficult.

Although somewhat subjective, framework molecular models suggested that steric hindrance to an incoming oxygen molecule increased in the order $^i\text{Bu}_3\text{B} < ^s\text{Bu}_3\text{B} \simeq (\text{cyclo-C}_6\text{H}_{11})_3\text{B}$.

The effect of steric strain in the transition state, (b), is difficult to predict, although there will be steric relief in passing from the transition state (or metastable intermediate)

to the products.

If the displaced alkyl radical is particularly stable, it is likely to provide the reaction with a considerable "thermodynamic drive". Ingold et al. have suggested that radical stability was the reason for the increased propagation rate constant for the autoxidation of tribenzylborane compared to those for the autoxidation of trialkylboranes.⁶ Of the compounds studied in this investigation, the displaced s-butyl radical will be the most stable because of the contribution of resonance structures such as:



Such hyperconjugative stabilisation is not possible either with the secondary cyclohexyl radical or the primary isobutyl radical, and the difference in stability between these two species is unlikely to be significant. In the absence of other factors therefore, factor (c), the stability of the displaced radical, would predict an order of reactivity of $^s\text{Bu}_3\text{B} > ^i\text{Bu}_3\text{B} \approx (\text{cyclo-C}_5\text{H}_{11})_3\text{B}$.

Brown and Midland¹² suggested that the factor of major importance was steric hindrance to the approach of the oxygen atom, but the observed order of the rate constants, $(\text{cyclo-C}_6\text{H}_{11})_3 > ^s\text{Bu}_3\text{B} > ^i\text{Bu}_3\text{B}$, indicates that it does not operate to the exclusion of other influences. The increased stability of the s-butyl radical compared to the isobutyl radical could account for the observed reactivity of these two boranes.

The factors (a), (b) and (c) do not account for the unexpectedly high rate constant determined for tricyclohexylborane, which is difficult to explain and must be related to its high

value of k_3/k_2 . Possible participation of galvinoxyl in the initiation step would provide not only an explanation for the high value of k_3/k_2 (> 100) but also for this relatively large initiation rate constant. The primary initiation of tricyclohexylborane autoxidations certainly warrants further investigation, and knowledge of the effect of galvinoxyl concentration on the rate of reaction, and also of the value of the rate constant determined by the rate of oxygen absorption whilst under inhibition by other inhibitors, azagalvinoxyl or 2,6-di-t-butyl 4-methoxyphenol, would be worthwhile.

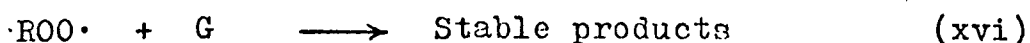
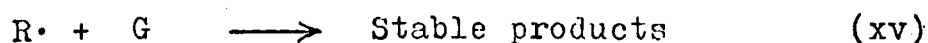
It was not possible to study the rate of primary initiation for the autoxidation of tri-n-butylborane, since galvinoxyl does not inhibit but only retards this reaction.⁷ This is presumably a reflection of the very fast propagation reaction, Ingold and Davies give $k_p = 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$,⁵ and this fact can be rationalised on the basis of the low degree of steric crowding around the central boron atom and the high reactivity of the primary alkyl radical.

4. Comparisons of Rate Constant Data.

As a result of this work the order of the primary initiation reaction in borane and oxygen is now known and it is possible to convert other workers rate measurements into specific rate constants and in this way comparisons can be made between the results.

(i) Galvinoxyl Inhibition Period Data. From a consideration of the following reactions it is clear that the rate of

disappearance of galvinoxyl is equal to the rate of primary initiation, provided that no autocatalytic reactions are occurring:



Estimations of initiation rates from the total length of the induction period are therefore liable to errors because of the shortening of this time due to the removal of galvinoxyl by the alternative reactions occurring, once peroxide has been formed (page 168).

The rate of disappearance of galvinoxyl is therefore given by:

$$\frac{-d[G]}{dt} = k_1 [R_3B] [O_2] + Z \quad (xxviii)$$

where Z is a term dependent upon the rate of removal of galvinoxyl by all reactions except the primary initiation step. It is not possible to estimate the contribution of Z and rate constants were therefore calculated from the approximation:

$$\frac{[G]}{\tau} = k_1 [R_3B] [O_2] \quad (xxix)$$

where τ = induction period.

Rate constants calculated from the inhibition periods measured

in this investigation are given in Table 9. The results are not consistent, there being a general increase in the "rate constants" as either the borane or oxygen concentrations are lowered or the galvinoxyl concentration increased. (Typically, the values for tri-s-butylborane vary from $2.47 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ to $18.78 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$). These factors all bring about an increase in the length of the inhibition period. Thus the contribution of Z increases as the induction period increases, a fact which has been observed previously⁹ and is presumably due to the increasing probability of peroxide formation under the conditions resulting in a long inhibition period.

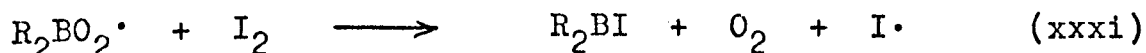
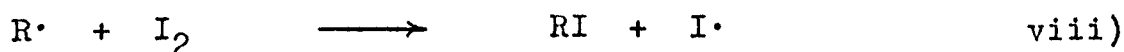
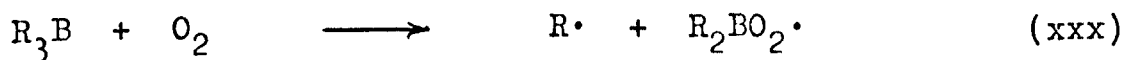
A comparison of these results with the mean rate constants determined by the rate of absorption of oxygen, tri-s-butylborane $1.84 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$, tri-isobutylborane $0.94 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$, tricyclohexylborane $22.8 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$, shows that agreement is quite good, especially under concentration conditions resulting in short inhibition periods. The best values for the three boranes are, tri-s-butylborane $2.47 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$, tri-isobutylborane $1.20 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$, and tricyclohexylborane $51.54 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$.

The rates of initiation determined by Allies and Brindley⁷ were also converted into rate constants and details are given in Table 9. Their values of $1.05 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ for tri-s-butylborane and $2.10 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ for tri-isobutylborane at 25°C again show good agreement with values determined by the rate of oxygen absorption.

The rates of initiation determined by Ingold and Davies⁵, Ingold et al.⁶ cannot be converted into primary rate constants

because their estimations were made in the course of the autoxidation when considerable quantities of peroxide were present. Thus the contribution of Z in equation (xxviii) will be considerable and rate constants calculated from equation (xxix) would be meaningless.

(ii) Iodine Inhibition Period Data. Brown and Midland proposed that iodine inhibited borane autoxidations by removing the alkyl and dialkylboronperoxy radicals produced in the primary initiation step¹¹:



Other routes for the removal of iodine have already been discussed (page 169), autocatalytic reaction resulting from peroxide formation, an oxygen initiated borane-iodine chain etc., and the rate of removal of iodine can be expressed as:

$$\frac{-d[I_2]}{dt} = 2 k_1 [R_3B] [O_2] + Y \quad (xxxii)$$

where Y is a summation of all additional reactions removing iodine. As in the case of galvinoxyl, it is not possible to assess the contribution of Y and rate constants were therefore calculated from:

$$n \frac{[I_2]}{\gamma} = 2 k_1 [k_3 B] [O_2] \quad (xxxiii)$$

n is assumed to be unity since the fate of the iodine atom is unknown.

Unfortunately Brown gave no data concerning the concentration of oxygen in solution and there appears to be no data for the solubility coefficient of oxygen in tetrahydrofuran. Oxygen concentrations were therefore estimated from the solubility coefficient of oxygen in diethyl ether, a not dissimilar solvent. Errors from this assumption are unlikely to produce more than a three-fold change in the value of the rate constant. The high concentrations of borane and inhibitor used by Brown and Midland, however, make it unlikely that the solutions can correctly be assumed as ideal, and the calculated values are most probably an overestimation. Nevertheless these assumptions should not produce a rate constant deviating from the true value by more than a five-fold error.

The rate constants calculated from equation (xxxiii) are given in Table 9 and the values of $1 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ for tri-s-butylborane and $1.3 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ for tricyclohexylborane at 0°C are much smaller than those calculated from either the length of the galvinoxyl inhibition period ($2.47 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and $51.54 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ respectively) or from the rate of oxygen absorption ($1.84 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and $22.8 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ respectively) and the divergence becomes greater with increasing iodine concentration. The uncertainties concerning this method of inhibition have been mentioned (page 169) but these factors would all predict a spuriously high rate constant and thus it is

necessary to propose new reasons to account for the low values:

(a) The work of Brown and Midland¹¹ was carried out at 0°C in contrast both to this study and the work of Allies and Brindley⁷, where rates were determined at 25°C. If the initiation step had an appreciable activation energy, differences of ten to twenty-fold might be satisfactorily explained. Evidence against this is the observation of Allies and Brindley⁷ that even at -78°C trialkylboranes autoxidised at a diffusion controlled rate, without an induction period which would imply a low activation energy.

(b) Since tetrahydrofuran was used as the solvent there could have possibly been some slight complex formation with the organoboranes. Brown stated that they obtained similar results in n-hexane but these results were not reported.

(c) Perhaps the most plausible explanation of these low rate constants is that the iodine was regenerated from the alkyl iodide, as suggested by Ingold et al.⁶. Aleksandrov et al.²⁰ have reported that, during the iodine inhibited autoxidation of cumene, iodine was regenerated by the reaction between peroxy radicals (or oxygen) and the alkyl iodide:

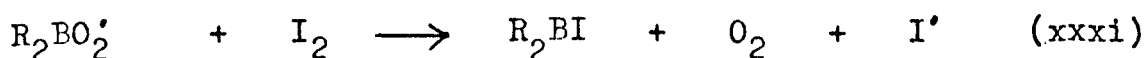
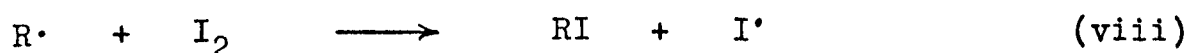
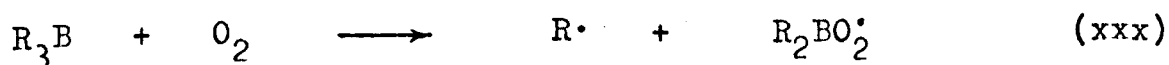


Since this reaction does not involve the substrate, Ingold's suggestion that a similar step might occur in iodine inhibited organoborane autoxidations seems entirely justified. Thus one molecule of iodine is capable of removing the radicals produced by more than one primary initiation reaction and therefore the

rate of removal of iodine will be much slower than the rate of primary initiation. Further, this effect will have a greater influence on the calculated rate of reaction as the iodine concentration is increased.

Until the magnitude of these effects and those alternative reactions for the removal of iodine suggested earlier is clearly understood, rates of primary initiation determined from the length of inhibition periods produced by iodine, should be viewed with extreme caution. Bearing this in mind, it is still interesting to note that at comparable iodine concentrations, the primary initiation rate constant for the autoxidation of tricyclohexylborane was only slightly in excess of that for tri-s-butylborane. This can be contrasted with the large difference between the rate constants for these two boranes determined in the presence of galvinoxyl.

(iii) Rate of Production of Alkyl Iodide from Iodine Inhibited Autoxidations. This method used by Brown and Midland¹² relied on the assumption that iodine, in very high concentration (40 mol. %), trapped the alkyl radicals produced in the primary initiation step to quantitatively yield alkyl iodide:



Based on these reactions it is clear that the rate of

production of alkyl iodide would be equal to the rate of primary initiation:

$$\frac{d [RI]}{dt} = k_1 [R_3B] [O_2] \quad (xxxiv)$$

However, considering the limitations concerning iodine inhibited autoxidations already expressed (page 169 and page 186) this equation must be a gross oversimplification. Oxygen concentrations were estimated as on page 185 and the rate constants calculated from equation (xxxiv) were, at 0°C, $6 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ for tri-s-butylborane (0.5M. in tetrahydrofuran) and $3 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ for tri-isobutylborane (0.5M. in tetrahydrofuran).

These very low values are not entirely unexpected in view of the high iodine concentrations used, since errors from the suggested regeneration of iodine from alkyl iodide would be very large.

It is concluded that the rates of initiation calculated from oxygen absorption in the presence of galvinoxyl and the rates calculated from the relationship $n \frac{[G]}{[I]}$ are in good agreement, whereas the inhibition using iodine does not give comparable results and this probably arises from a number of alternative reactions involving the iodine.

Table 9. Primary Initiation Rate Constants Calculated from
the Relationship $\frac{n [A]}{\gamma}$

$[R_3B] \times 10^2$ (a) (M)	$[O_2] \times 10^2$ (M)	[Inhibitor] $\times 10^4$ (c) (M.)	Temp. °C.	$R_i \times 10^8$ (M.s. ⁻¹)	$k_i \times 10^3$ (M. ⁻¹ s. ⁻¹)	Ref.
<u>Tri-s-butylborane</u>						
0.76	0.75	G, 1.5	25	14.0	2.47	This work
0.76	0.36	" 1.5	"	11.7	4.17	"
0.76	0.16	" 1.5	"	7.7	6.54	"
0.76	0.16	" 2.9	"	12.9	10.98	"
0.36	0.16	" 2.9	"	10.6	18.78	"
1.48	0.16	" 2.9	"	22.8	9.94	"
2.10	0.16	" 2.9	"	46.7	14.35	"
0.76	0.16	" 7.3	"	13.9	11.83	"
0.575	0.75	" 0.29	"	5.0	1.05	7
50	1.84 ^(b)	I, 50	0	87.5	0.10	11
50	1.84 ^(b)	" 100	0	55.5	0.06	11
<u>Tri-isobutylborane</u>						
1.44	0.75	G, 1.5	25	12.9	1.20	This work
1.44	0.16	" 1.5	"	8.7	3.92	"
0.75	0.16	" 1.5	"	5.4	4.70	"
2.10	0.16	" 1.5	"	12.9	3.96	"
1.44	0.16	" 5.9	"	9.3	4.18	"
2.80	0.16	" 1.5	"	15.3	3.52	"
0.75	0.75	" 3.75	"	11.7	2.10	7
<u>Tricyclohexylborane</u>						
0.13	0.37	G, 2.9	25	24.79	51.54	This work
0.13	0.16	" 2.9	"	19.33	92.93	"
0.19	0.16	" 2.9	"	24.17	79.51	"
50	1.84 ^(b)	I 50	0	122	0.13	11

(a) In benzene solution except for experiments in the presence of iodine when tetrahydrofuran was the solvent.

(b) Estimated.

(c) G = Galvinoxyl. I = Iodine

References

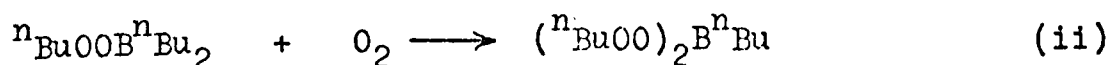
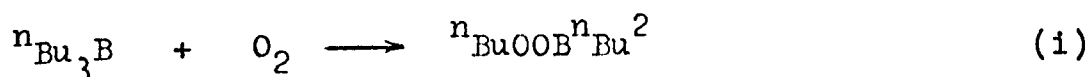
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CHAPTER 8

ORGANOPEROXYBORON COMPOUNDS

It is now well established that the autoxidation of a dilute solution of an organoboron compound results in the formation of an organoperoxyborane^{1,2,3}. Typically, the autoxidation of tributylboranes at 25°C, with efficient gas-liquid mixing gave and almost quantitative yield of the corresponding dibutylperoxy butylborane.³ The alternative route of preparation, nucleophilic substitution, has proven useful for the synthesis of many peroxyborate compounds.^{4,5,6} Both methods have been used in this investigation.

The preparation of the monoperoxide, n-butylperoxy di-n-butylborane, took advantage of the fact that there is an activation energy difference between the autoxidation stages borane to monoperoxide (i), and monoperoxide to diperoxide (ii):



This has been demonstrated by Allies and Brindley who reported that at -74°C the autoxidation of tri-n-butylborane ceased after the absorption of 1 mol. of oxygen³. Unfortunately the autoxidation of tri-s-butylborane did not stop completely after

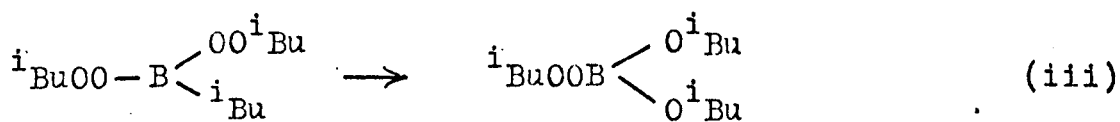
the first step³, and it was thought unlikely that a solution of s-butylperoxy di-s-butylborane so prepared would be of sufficient purity to validate a kinetic study.

All of the peroxides studied were used "as prepared" since an attempt to purify even the relatively more stable di-n-butylperoxy n-butylborane by high vacuum distillation was unsuccessful because distillation time could not be made sufficiently small compared with its rate of decomposition. Nevertheless, the purity of the peroxide solutions was always in excess of 95%.

The study on these compounds was carried out in order to obtain a greater understanding of their possible role in organoborane autoxidations and also to evaluate their potential use as possible free-radical polymerisation initiators. Although there was a considerable quantity of literature concerning these compounds as polymerisation initiators much of it is subject to ambiguity largely through an ignorance of the nature of organoborane autoxidations and stabilities of organoperoxyboron compounds.

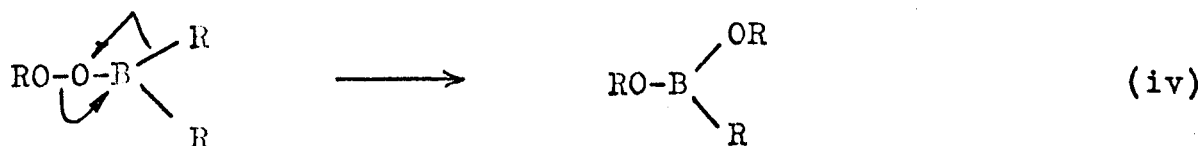
1. Thermal Decomposition.

Previous studies on the thermal decomposition of organoperoxyboron compounds indicated that, with respect to this property, it was necessary to divide the peroxides into two distinct catagories. Those organoperoxyboranes containing boron-alkyl bonds were considerably less stable than those without such bonds (organoperoxyborates). Davies et al. reported that di- isobutylperoxy isobutylborane had decomposed by 30% in 2½ hours at room temperature to give di-isobutoxy isobutylperoxyborane.

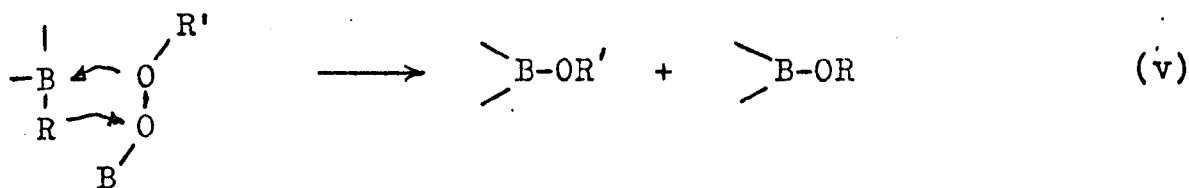


More recently, Russian workers have studied the decomposition of many organoperoxyborates, and these compounds were found to decompose at a measurable rate only at temperatures in excess of 120°C ,^{5,8} and therefore resemble dialkyl peroxides in this respect.

These differences in behaviour would appear to indicate different modes of decomposition. The organoperoxyborates decomposed by a homolytic chain mechanism,^{5,8} and although the organoperoxyboranes containing boron-alkyl bonds have not been investigated in such detail, Davies has suggested that such compounds decomposed primarily by a nucleophilic 1,2 rearrangement:⁷



This intramolecular mechanism can be contrasted with the intermolecular rearrangement suggested by Murviss:⁹



In the present investigation, two methods were used to study the decomposition. Firstly, by iodometric titration, which showed the total loss of peroxide, and secondly, by the initiation of vinyl acetate polymerisations which indicated the contribution of any radical pathways to the total loss of peroxide.

(i) Iodometric Study. Iodometric titrations as a method of

estimating organoperoxyboron compounds has been criticised by Grotewold et al.¹⁰. They reported that, during the autoxidations of triethylborane in solution, at relatively low oxygen consumptions the peroxide titration was far below the value expected from the amount of oxygen absorbed, but at high oxygen consumptions agreement was good. A simple explanation for this is at relatively low oxygen consumptions a substantial amount of unreacted borane would be present and this would react with organoperoxyborane by reactions such as (v), to yield non-peroxidic products, hence giving rise to a lower peroxide titration than was expected.

The iodometric method of analysis used in this study was found to be both accurate and reproducible.

The order of the decomposition process was determined from the variation of the initial rate of reaction with changing concentration. A consideration of the rate equation:

$$\text{Rate} = k_1 [\text{Peroxide}_o]^n \quad (\text{vi})$$

where k_1 = rate constant.

n = order of reaction.

$[\text{Peroxide}_o]$ = initial concentration of organoperoxyborane compound.

shows that

$$\log \text{Rate} = \log k_1 + n \log [\text{Peroxide}_o] \quad (\text{vii})$$

and hence a graph of $\log \text{Rate}$ against $\log [\text{Peroxide}_o]$ should yield a straight line of slope n . These graphs are shown in Figure 10,

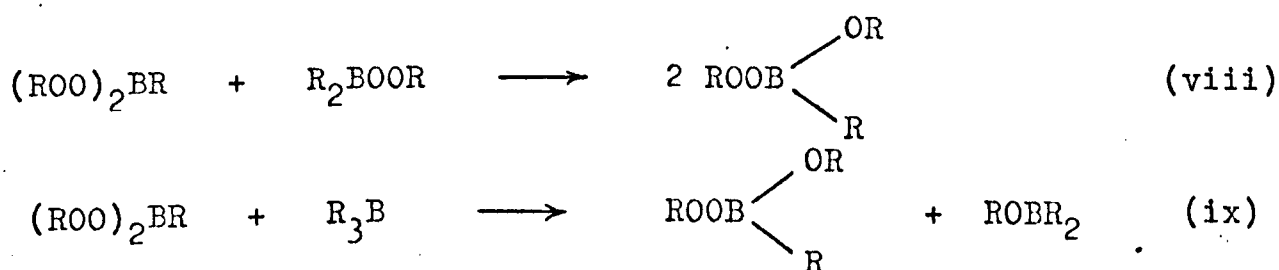
and n for di-n-butylperoxy n-butylborane is 1.2 at 60°C, for di-s-butylperoxy s-butylborane 1.0 at 60°C, and for di-n-butyl n-butylperoxyborane 1.1 at 18°C, all in iso-octane solvent. These values substantiated the first order kinetics suggested by the good straight lines obtained from plots of $\ln \frac{[\text{Peroxide}]_0}{[\text{Peroxide}]_t}$ against time over about 40% reaction (Figure 10a). These graphs and the resultant first order rate constants, were calculated and plotted by a computer program (see appendix). The first order rate constants are given in Table 5, each being the mean of at least two experiments, and the Arrhenius graphs of the variation of $\log k_1$ with temperature in iso-octane solvent are shown in Figure 11. The activation energies calculated by the least squares method had values of 14.3 ± 1.07 kcal. mole⁻¹ for di-n-butylperoxy n-butylborane, 15.9 ± 0.40 kcal. mole⁻¹ for di-s-butylperoxy s-butylborane, and 11.1 ± 0.53 kcal. mole⁻¹ for di-n-butyl n-butylperoxyborane.

These activation energies are considerably smaller than those determined for the homolytic decomposition of the butylperoxyborates which were usually in the range 30-35 kcal. mole⁻¹.^{5,8} This would tend to confirm the earlier suggestion that those compounds containing boron-alkyl bonds decompose by a different mechanism to those without such bonds and consequently these bonds must be responsible for providing a decomposition route of relatively low energy. This, together with the first order kinetics concur with the intramolecular 1,2 alkyl rearrangement suggested by Davies⁷.

The relatively low activation energies also indicate a synchronous process, the energy required for bond breaking being partly compensated by the energy released from bond formation.

Ta-Hsun Lee et al.¹¹ have studied the decomposition of diethyl ethylperoxyborane and found it to decompose with first order kinetics, and determined an activation energy of 12 kcal. mole⁻¹. This shows good agreement with the results of this investigation for di-n-butyl n-butylperoxyborane. These workers also studied the decomposition of a mixture of diethylperoxy ethylborane and ethylperoxy ethoxy ethylborane and they reported that this decomposed with second order kinetics and an activation energy of 21 kcal. mole⁻¹.

Since compounds of the type alkoxy-alkyl-peroxyboranes might be expected as intermediates arising from peroxide decomposition on the lines of equation (v), e.g.:



s-butylperoxy s-butoxy s-butylborane had been synthesised and was found to be more stable than di-s-butylperoxy s-butylborane. The s-butylperoxy s-butoxy s-butylborane was only decomposed by 10% after 24 hours at 50°C, whilst the di-s-butylperoxy s-butylborane decomposed by 10% after 3½ hours at the same temperature. The result of Ta-Hsun Lee et al. for the mixture of peroxides cannot, therefore, be compared to the results obtained from the decomposition of pure dibutylperoxy butylboranes.

One thermodynamic quantity which is particularly useful for providing information concerning the nature of the activated

complex is the entropy of activation. The rate constant of a reaction is related to the entropy and enthalpy of activation:

$$k_1 = \frac{kT}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT} \quad (x)$$

where

k = Boltzmann constant.

T = temperature in degrees Kelvin.

h = Plank's constant.

ΔS^* = entropy of activation.

R = gas constant.

ΔH^* = enthalpy of activation.

This expression was originally derived by Wynne-Jones and Eyring¹².

ΔH^* is related to the experimentally determined activation energy, E_{exp} , by the expression:

$$E_{exp} = \Delta H^* + RT - P\Delta V^* \quad (xi)$$

where P is the pressure and ΔV^* the change in volume in going from reactants to the activated complex. For a unimolecular reaction in solution ΔV^* is zero and hence:

$$E_{exp} = \Delta H^* + RT \quad (xii)$$

Substitution of E_{exp} for ΔH^* in equation (x) gives:

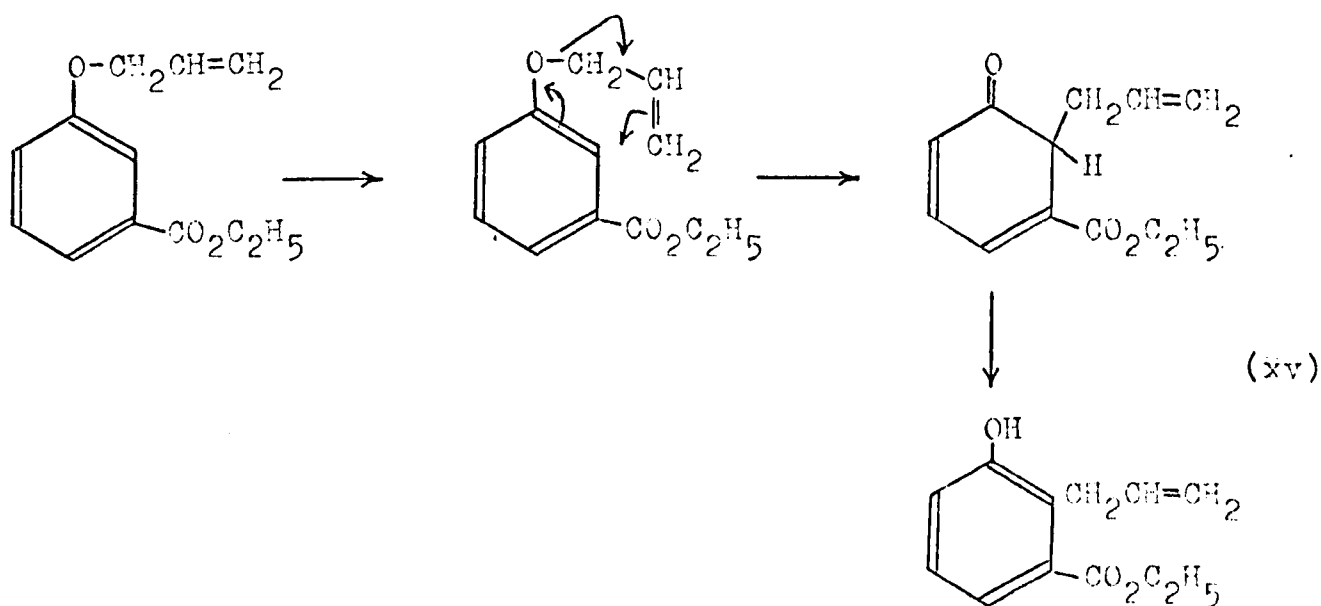
$$k_1 = \frac{kT}{h} e^{\Delta S^*/R} e^{-(E_{exp}-RT)/RT} \quad (xiii)$$

$$\text{or } k_1 = \frac{kT}{h} e^{\Delta S^*/R} e^{-E_{exp}/RT} \quad (xiv)$$

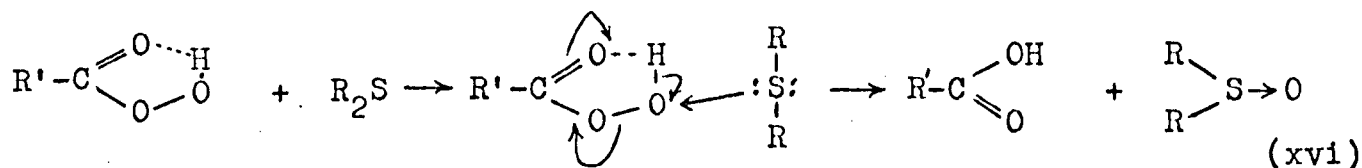
Entropies of activation determined from expression (xiv) were $-43.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ for di-n-butyl n-butylperoxyborane at 298.1°K , $-39.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ for di-n-butylperoxy n-butylborane at 343.6°K , and $-34.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ for di-s-butylperoxy s-butylborane at 343.6°K . In all cases therefore, there is a large decrease in the randomness of the system on passing from reactant to the activated complex.

Since the solvent, iso-octane, is not particularly polar, this large decrease in entropy cannot be attributed to an increase in solvation on passing from a non-polar reactant to a partially charged activated complex. A more reasonable explanation is that the rearrangement involves a cyclic activated complex with a reduced entropy due to the loss of internal rotations. Analogies can be drawn from organic chemistry:

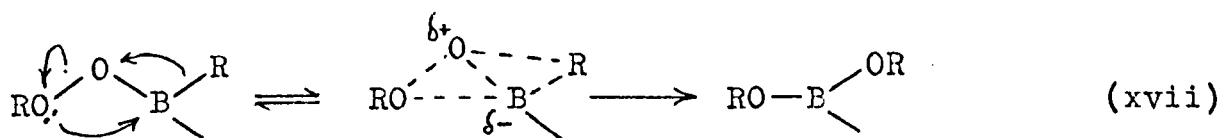
(a) The Claisen rearrangement undergone by m-acetylphenyl allyl ether at 184°C in diphenyl ether solution involves a cyclic intermediate and has an entropy of activation of $-16 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$:



(b) The oxidation of p,p'-dichlorobenzyl sulphide by p-methoxyperbenzoic acid to the sulphoxide in toluene involved an entropy of activation of $-29.5 \text{ cal. deg.}^{-1} \text{ mole.}^{-1}$ at -35°C , and a highly restricted transition state was suggested¹⁴:



To summarize, therefore, the primary route of decomposition of organoboranes is a first order synchronous process involving a highly restricted activated complex and a possible mechanism is:



The mechanism shown has, as its first step, the donation of a lone pair of electrons from the β -oxygen into the vacant boron p orbital. On this assumption the increased activation energy for di-n-butylperoxy n-butylborane and di-s-butylperoxy s-butylborane compared to di-n-butyl n-butylperoxyborane is readily explained. The electron density at the boron atom will be higher in the case of the diperoxides because of the presence of two α -oxygens both of which will be involved in $p\pi$ - $p\pi$ interactions with the boron atom via its vacant p orbital.

The increased stability of s-butylperoxy s-butoxy s-butylborane

relative to di-s-butylperoxy s-butylborane (10% decomposition in 24 hours compared to 10% decomposition in $3\frac{1}{2}$ hours at 50°C in iso-octane solution), is subject to the same argument of increased electron density on the boron atom. An alkoxy α -oxygen atom should be a more powerful $p\pi$ donor than peroxy α -oxygen atom, since in a peroxy grouping electrons are drawn away towards the alkoxy function, an effect manifested in the increased acidity of a hydroperoxide compared to the corresponding alcohol.

(ii) Polymerisation Studies. The monomer vinyl acetate, was chosen for this study because it almost exclusively polymerises by a free-radical mechanism. The reactivity ratios for the anionic copolymerisation of vinyl acetate (M_1) and acrylonitrile (M_2) at 40°C were $r_1 : r_2$, 0.03 : 5.6, whilst for the cationic copolymerisation of vinyl acetate (M_1) and styrene (M_2) $r_1 : r_2$ was $0.18 \pm 0.08 : 6.1$ ¹⁵. Further, vinyl acetate occurs towards the middle of a "polarity series" of the vinyl monomers (it has a small negative e value) and this also implies only a slight tendency to undergo ionic polymerisation.¹⁶ All of the organoperoxyboranes investigated were found to initiate the polymerisation of vinyl acetate and the graphs of the extent of polymerisation against time are shown in Figure 14.

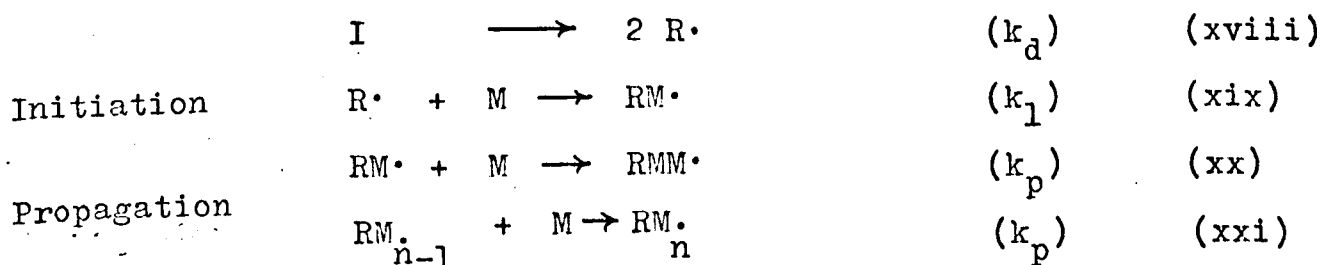
The polymerisation initiated by di-n-butylperoxy n-butylborane was unusual in that the rate was initially rapid and then slowed after ca. twenty minutes to a constant value. It is the reverse of a "typical plot", such as shown by the polymerisation initiated by di-s-butylperoxy s-butylborane where the rate gradually increases to a constant value, and this was presumably due to the presence of traces of the less stable di-n-butyl n-butylperoxyborane in the

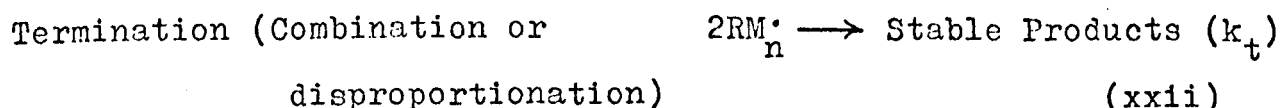
di-n-butylperoxy n-butylborane sample. Such traces were difficult to avoid because of the relatively slow absorption of the second mol. of oxygen during the autoxidation of tri-n-butylborane.

(The autoxidation of tri-s-butylborane, 6 mM. in benzene at 25°C, was complete within five minutes; the autoxidation of tri-n-butylborane 8 mM. in benzene at 25°C, took thirty minutes for complete reaction)³.

The rate of polymerisation of vinyl acetate initiated by di-n-butyl n-butylperoxyborane increased throughout the period studied. Auto-acceleration of polymerisations is usually the result of an increase in the viscosity of the monomer-polymer mixture which is assumed to lower the termination rate constants in relation to the propagation rate constants. In this experiment using di-n-butyl n-butylperoxyborane as initiator, however, the polymerisation was only followed over about 3.5% reaction, and it does not seem probable that viscosity effects would be apparent at such a low level of conversion. It is possible that the increasing rate of polymerisation was due to an induced decomposition of the di-n-butyl n-butylperoxyborane brought about by vinyl acetate or polymer radicals, causing an increase in the rate of initiation.

The polymerisation rates can be converted into rates of initiation. The following is a typical reaction scheme for the polymerisation of a monomer M, initiated by a compound I, decomposing to radicals, R•.





The rate of polymerisation, R_p , is given by:

$$R_p = -\frac{d[M]}{dt} = k_1 [R^\bullet] [M] + k_p [RM_n^\bullet] [M] \quad (\text{xxiii})$$

The amount of monomer disappearing by reaction (xix) is minimal,

and hence: $R_p = k_p [RM_n^\bullet] [M] \quad (\text{xxiv})$

now $k_1 [R^\bullet] [M] = 2k_t [RM_n^\bullet]^2 \text{ (steady state)} \quad (\text{xxv})$

thus $[RM_n^\bullet] = \left(\frac{k_1 [R^\bullet] [M]}{2k_t} \right)^{\frac{1}{2}} \quad (\text{xxvi})$

Assuming a steady state concentration of R.

$$\frac{d[R^\bullet]}{dt} = 0 = 2k_d [I] - k_1 [R^\bullet] [M] \quad (\text{xxvii})$$

therefore $[R^\bullet] = \frac{2k_d [I]}{k_1 [M]} \quad (\text{xxviii})$

Substituting for $[R^\bullet]$ in (xxvi) yields:

$$[RM_n^\bullet] = \left(\frac{k_d [I]}{k_t} \right)^{\frac{1}{2}} \quad (\text{xxix})$$

and substituting for $[RM_n^\bullet]$ in (xxiv) gives:

$$R_p = k_p [M] \left(\frac{k_d [I]}{k_t} \right)^{\frac{1}{2}} \quad (\text{xxx})$$

from which $k_d = \frac{R_p^2}{[I][M]^2} \frac{k_t}{k_p^2} \quad (\text{xxxi})$

For vinyl acetate the values of k_t and k_p are well known and Matheson et al¹⁷ gives, at 60°C,

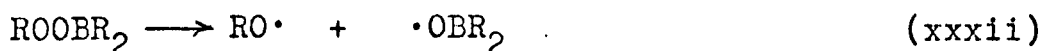
$$k_p = 3700 \text{ M}^{-1}\text{s}^{-1}$$

$$k_t = 7.4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$$

The rates of polymerisation of vinyl acetate at 60.5°C using di-n-butylperoxy n-butylborane ($5.7 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$), and di-s-butylperoxy s-butylborane ($7.5 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$), yield values for k_d of $1.5 \times 10^{-8} \text{ s}^{-1}$ and $2.6 \times 10^{-8} \text{ s}^{-1}$ respectively. The curve produced by initiation with di-n-butyl n-butylperoxyborane did not allow the calculation of an accurate polymerisation rate but an average value of $1.03 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$ yields a k_d of $2.6 \times 10^{-7} \text{ s}^{-1}$ at 25°C, using Matheson's data for k_p and k_t at this temperature ($1012 \text{ M}^{-1}\text{s}^{-1}$ and $2.94 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ respectively).

Thus, although the organoperoxyboranes do initiate the polymerisation of vinyl acetate, the rate at which they do so is far below the rate of decomposition, followed iodometrically, namely $2.0 \times 10^{-5} \text{ s}^{-1}$ for di-n-butylperoxy n-butylborane at 60.5°C, $2.13 \times 10^{-5} \text{ s}^{-1}$ for di-s-butylperoxy s-butylborane at 60.5°C, and $4.68 \times 10^{-5} \text{ s}^{-1}$ for di-n-butyl n-butylperoxyborane at 25°C. The difference between k_d and the first order rate constants determined iodometrically is too large to be ascribed to a low "initiator efficiency" (only a small proportion of the radicals produced actually initiating polymer chains) and it must be concluded that the homolytic route of decomposition of organoperoxyboranes is only of very minor importance to the decomposition as a whole.

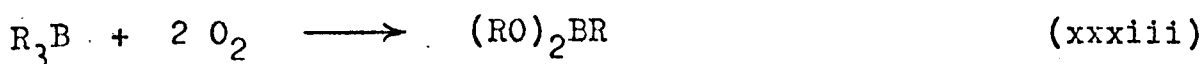
Ingold and Davies¹⁸ have reported that the autoxidation of dialkyl alkylperoxyboranes is initiated by the unimolecular decomposition of the peroxyborane to free-radicals:



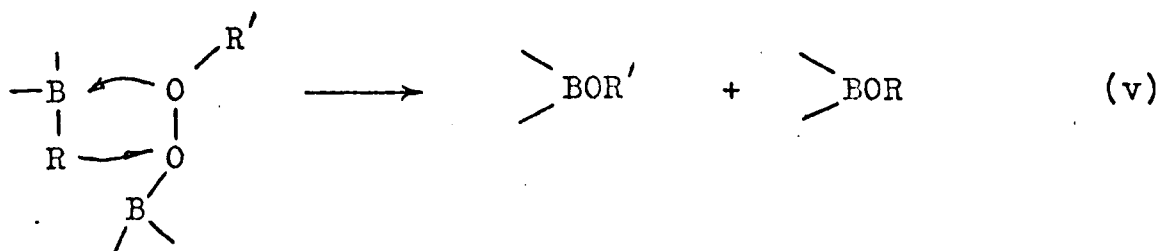
and gave rate constants for this process of $1.1 \times 10^{-5} \text{ s}^{-1}$ for di-n-butyl n-butylperoxyborane and $3.8 \times 10^{-4} \text{ s}^{-1}$ for di-s-butyl s-butylperoxyborane all at 30°C . Their results appear to be a contradiction of the facts reported in this thesis, but it must be remembered that their results were determined in the presence of oxygen and it does not seem unreasonable to suggest that they were actually studying an induced decomposition of the peroxyboranes.

2. The Reaction between Organoboranes and Organoperoxyboranes.

Prior to 1956 the autoxidation of a trialkylborane was believed to produce a boronate ester:

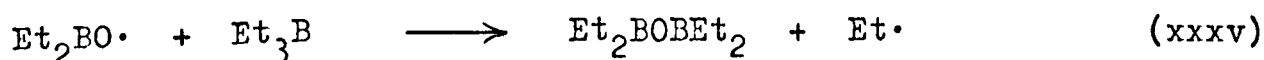
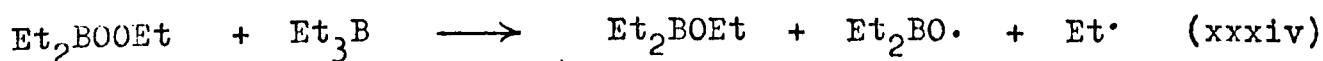


Subsequent studies demonstrated that in dilute solution and with efficient gas liquid mixing diperoxyboranes were obtained,^{1,2,3} and it seemed probable that a reaction occurred between peroxyborane and unreacted borane. This was confirmed by Murviss who reported that the yield of peroxide was reduced as the initial borane concentration was increased¹⁹ and he later reported that the addition of tri-n-hexylborane to a partially oxidised solution of tri-n-butylborane led to a large drop in the peroxide content⁹. Murviss suggested the following mechanism:



There is now considerable evidence in favour of a free-radical mechanism. Hansen reported that a mixture of borane and peroxyborane initiated the polymerisation of methyl methacrylate,²⁰ and more convincingly it has been recently demonstrated by electron spin resonance spectroscopy that such a reaction produced alkyl radicals, identified by their reaction with nitroxyls.¹⁸

Both Ingold and Davies,¹⁸ and Grotewold et al.¹⁰ have suggested the reaction between trialkylborane and dialkyl alkylperoxyborane as being responsible for the autocatalysis exhibited by organoborane autoxidations. Grotewold suggested the following mechanism:



Since it was now possible to obtain di-n-butyl n-butylperoxyborane in a pure form it was hoped that some progress could be made towards an understanding of the rate and mechanism of this reaction; firstly by iodometrically following the rate of loss of peroxide and secondly, an indirect method, by spectroscopically following the rate of removal of the radical traps galvinoxyl or triacetoneamine nitroxide.

The reaction was found to be too fast to be followed by either method, and no quantitative measurements could be made. All that can be said is that the reaction between tri-n-butylborane and di-n-butyl n-butylperoxyborane is extremely rapid being

virtually complete within ca. thirty seconds, at 25°C. Lowering of the temperature by 50°C appeared to have little significant effect on the rate of reaction, followed iodometrically (Figure 12) and it may be concluded that this is a process with a very small activation energy.

It was thought that the corresponding reaction of the more stable di-n-butylperoxy n-butylborane with tri-n-butylborane would be less vigorous and proceed at a measurable rate. This was not so, the reaction again being virtually complete within ca. thirty seconds at 25°C (when followed spectroscopically) and the disappearance of peroxide is shown in Figure 12..

One interesting point from this investigation was that for both the mono- and dialkylperoxyboranes, one mole. of borane destroyed ca. 0.6 mole of peroxide. This indicates that the reaction is not a simple bimolecular process, such as was proposed by both Murviss⁹ and Hansen,²⁰ but would tend to support the mechanism suggested by Grotewold et al.¹⁰.

Also, although by no means conclusive, was the supporting evidence for the radical mechanism provided by the fact that, these reactions rapidly removed both galvinoxyl and triacetoneamine nitroxide from solution, whereas the separate components did so only slowly (p. 135).

3. The Potential of Organoboranes and Derivatives as Free-Radical Polymerisation Initiators.

The organoperoxyboranes studied in this investigation were

a lot less stable than many organic peroxides, but their mode of decomposition, in the absence of any trialkylborane, was primarily by a non-radical pathway. The diButylperoxy butylboranes initiated the polymerisation of vinyl acetate with reasonable efficiency at temperatures above 50°C, but since this range is well served by the cheaper and more readily available dibenzoyl peroxide/amine or azo-bis-isobutyronitrile, the peroxyboranes appear to offer no particular advantages. Di-n-butyl n-butylperoxyborane initiated the polymerisation of vinyl acetate at 25°C and could well be useful at temperatures as low as 0°C. Its difficult preparation and instability at room temperature however, does not make it particularly attractive from a commercial point of view.

Although not studied in this investigation the evidence is convincing that both the autoxidation of organoboranes and the reaction between organoperoxyboranes and organoboranes act as efficient free-radical polymerisation initiators (Ch. 2). These systems could prove useful as low temperature initiators since the autoxidation of tributylboranes is still very rapid at -78°C³, and the limited evidence from this study indicates that the reaction between organoborane and organoperoxyborane has an almost negligible activation energy. The use of trialkylboranes as initiators has the additional advantage that traces of oxygen, which could otherwise act to the detriment of the polymerisation process, would be scavanged and used in the initiation reaction.

Our knowledge of the organoboranes has increased tremendously over the last five to ten years and it is now possible to

rationalize some of the earlier polymerisation studies with the benefit of hindsight.

Although by the early 1960's oxygen was known to play an important part in polymerisations initiated by trialkylboranes (see page 59), it was wrongly thought that its sole function was to produce a peroxide which then initiated the polymerisations. It is now clear that those workers using a trialkylborane-oxygen initiating system were studying polymerisations partly brought about by chain transfer from the autoxidation of the trialkylborane.

The studies of Bawn et al.²¹, Zutty and Welch,²² and Hansen,²⁰ can be conveniently grouped together since they were all supposed to pertain to polymerisations initiated by the reaction between organoboranes and organoperoxyboranes. There were two important differences between the work of Bawn et al. and the other two schools:

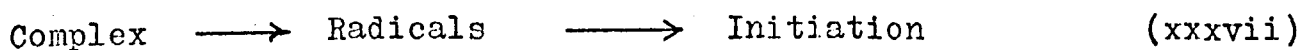
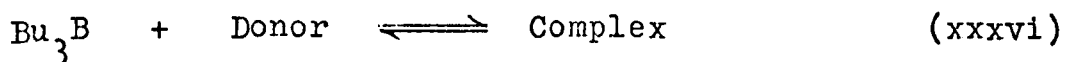
(a) Bawn et al. studied the polymerisation of methyl methacrylate by dilatometry whereas both Zutty and Welch, and Hansen determined reaction rates by the weight of polymer produced from methyl methacrylate polymerisations.

(b) Bawn et al. prepared the organoperoxyborane separately before mixing it with the organoborane. Zutty and Welch, and Hansen produced peroxide "in situ" by adding oxygen to the mixture of monomer and borane.

It is therefore clear that neither Zutty and Welch nor Hansen were studying polymerisation initiated purely by the reaction between organoborane and organoperoxyborane. The work of Bawn et al. must also be subject to some uncertainty since the technique of vacuum dilatometry is time consuming and they would

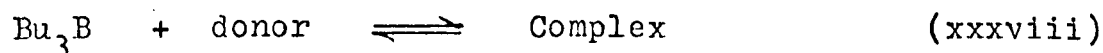
have been unaware of the great speed of the borane-peroxyborane reaction ($t_{\frac{1}{2}}$ ca. 10 sec.). Whether their measured initial rates of polymerisation were true initial rates resulting from the reaction between borane and peroxyborane, and not some secondary process, is debatable. That Bawn et al. were studying a different initiating process to both Zutty and Welch, and Hansen was shown by the differing activation energies determined for the polymerisation. Bawn et al. gave a value of 12.9 kcal. mole⁻¹ Zutty and Welch 4 kcal. mole⁻¹, and Hansen 2.4 kcal. mole⁻¹.

Kojima et al.²³ studied the polymerisation of methyl methacrylate initiated by tributylborane-oxygen in the presence of a variety of aromatic amines and proposed the following mechanism for the initiation:



They found that the rate of polymerisation was accelerated by the presence of pyridine and substituted pyridines relative to initiation by uncomplexed borane-oxygen, and that for a series of methyl substituted pyridines, the reactivity was the reverse of basicity. Kojima et al. suggested that this latter observation could be rationalized by reaction (xxxvii) becoming more facile.

Ingold and Davies¹⁸ have reported that complexed borane did not autoxidise and it is difficult to see how the borane-donor complex could give radicals in the manner suggested by Kojima et al. A more logical sequence of reactions leading to initiation would be:



On the basis of this mechanism, the increased rate of polymerisation with decreasing basicity of the donor is easily understood.

Borsini and Cipolla²⁴ have made the observation that for the initiating system borane-oxygen, the rate of polymerisation of vinyl chloride decreased if the oxygen to borane ratio was increased to a value greater than 0.3. In the presence of donors this decrease did not occur. This could be due to the rate of autoxidation, either in the presence of donors or at low concentrations of oxygen, being sufficiently slow to permit a reasonable extent of chain transfer from the autoxidation chain. Although they gave no data, if the work of Kojima et al. was carried out at a relatively high oxygen to borane concentration, the accelerating effect of donor complexing agents is explained.

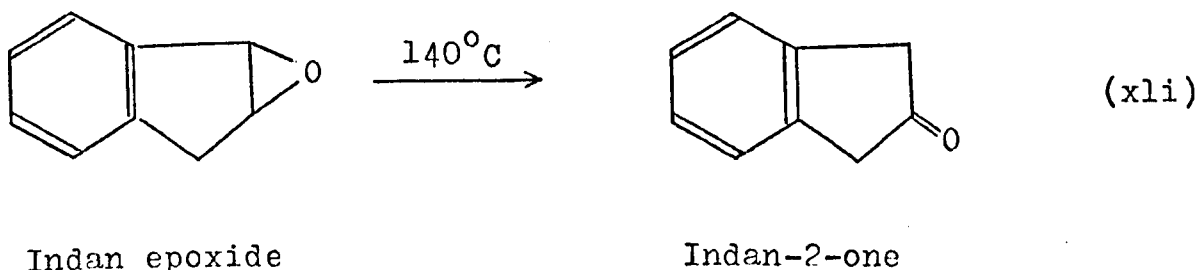
4. "Halcon Type" Reactions using Organoperoxyboranes.

The reaction of an olefin with an organic peroxide in the presence of a transition metal catalyst results in the formation of an epoxide,^{25,26,27} and this is generally known as the Halcon process. A typical reaction was²⁵:



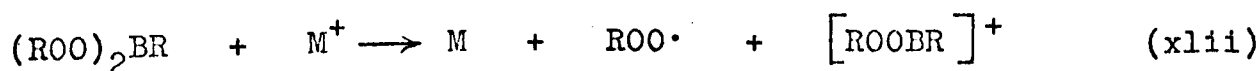
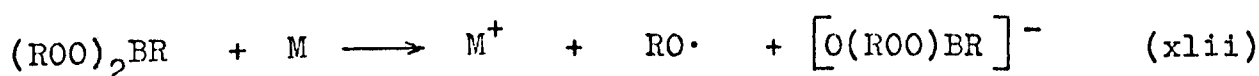
Following the work of Gould et al.²⁸ there appeared little doubt that such reactions did not involve a homolytic mechanism, since they reported that the epoxidation of cyclohexene with t-butylhydroperoxide was not catalysed by cobalt (II) complexes or di-t-butylperoxalate.

It was decided to investigate whether the organoperoxyboranes would partake in this process. The olefins chosen were cyclohexene, because of its ready availability, and indene because of its relatively greater reactivity. Experiments were conducted under a variety of conditions of temperature, time of reaction, and concentration and those described (page 139) are representative of the general procedure and technique. Only from indene at 40°C (18 hours) was any epoxide or epoxide derived product obtained, and then only in very low yield (ca. 1%). The product was indan-2-one (identified by comparison with an authentic sample) and was presumably formed from indan epoxide by a thermal rearrangement (on the chromatography column) in a manner analogous to the rearrangement of ethylene oxide to acetaldehyde.



The addition of molybdenum hexacarbonyl to a solution of di-n-butylperoxy n-butylborane was found to cause a rapid decomposition of the peroxide reducing the half-life from ca. 3×10^4 mins to ca. 30 mins at 25°C, with the formation of a

mixture of borate and boronate esters. On the basis of the carbon analysis (65.2%), this mixture appeared to be 43% borate, 57% boronate. Since the peroxide was completely reduced, this decomposition cannot have occurred by a simple catalysis of the alkyl 1,2 rearrangement, which would result in the formation of di-n-butoxy n-butylperoxyborane. Any attempt to propose a mechanism must be considered speculative, but possibly the presence of the transition metal catalyses the homolytic route of decomposition, initiating the process by such reactions as:

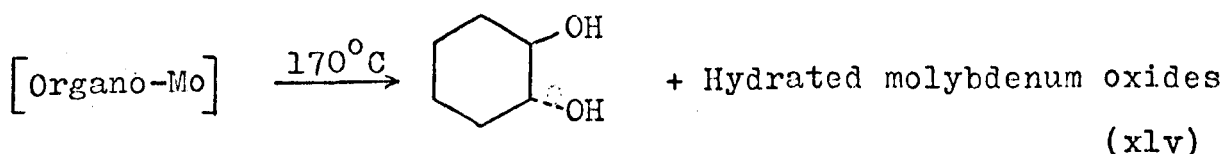
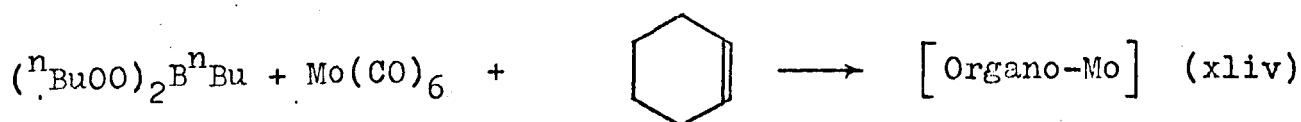


familiar reactions of organic peroxides.

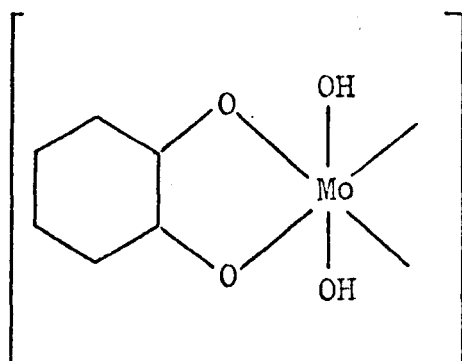
The instability of di-n-butylperoxy n-butylborane in the presence of molybdenum hexacarbonyl can be contrasted with the stability of t-butyl hydroperoxide, only 6% decomposition occurred in one hour at 87°C.²⁵ This difference in behaviour towards molybdenum hexacarbonyl explains the difference in the ability of these two peroxides to bring about the epoxidation of olefins.

An interesting aspect of this work arose when using a large amount of molybdenum hexacarbonyl (50 mol.% of the peroxide as opposed to the normal catalytic amount of 4 mol.%) with cyclohexene and di-n-butylperoxy n-butylborane. The solid isolated from the distillate contained molybdenum and an organic entity, but no carbon monoxide groups (absence of i.r. band at

ca. 2000 cm^{-1} , figure 15). This solid decomposed at 170°C to yield trans cyclohexane 1,2 diol and a hydrated molybdenum oxide:



The volatile complex, $[\text{Organo-Mo}]$, could possibly have been a molybdenum ester of trans 1,2 cyclohexane diol. The infra-red spectrum (Figure 15), although confirming the presence of a C-O grouping (C-O stretch, 1080 cm^{-1}) also indicated the presence of hydroxyl groups (O-H stretch, 3350 cm^{-1}), and $[\text{Organo-Mo}]$ could possibly be a hydroxy molybdenum ester:



Time did not permit further investigation of this reaction.

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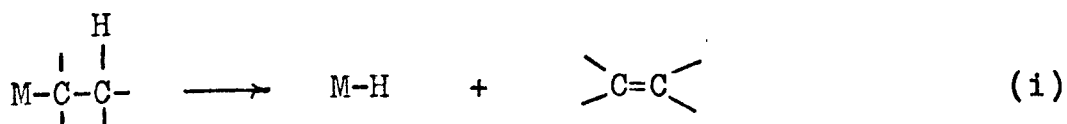
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CHAPTER 9

THE AUTOXIDATION OF ORGANOTRANSITION METAL COMPOUNDS.

It has been previously mentioned that simple alkyl and aryl derivatives of the transition metals were very unstable, in the absence of additional ligands, probably decomposing by a unimolecular homolytic route (Ch. 3). Work in the last five years, notably by Wilkinson *et al.*¹ and Lappert *et al.*² has shown that, provided the organic groups do not have β -hydrogens, fully alkylated organotransition metal compounds of reasonable stability could be prepared and isolated. The absence of β -hydrogens precludes the β -elimination reaction which has been suggested as the most facile route of decomposition¹:



Although the metal-carbon bond has been suggested as being quite strong and stable,³ the presence of vacant d orbitals on the early transition metal atoms made it seem most probable that these fully alkylated derivatives would undergo facile $\text{S}_{\text{H}}2$ reactions at the metal centre. Reports in the literature^{3,4} and elsewhere⁵ indicated that the organotransition metal compounds reacted vigorously with air and it was therefore decided to study their autoxidation as a possible example of $\text{S}_{\text{H}}2$ reactions at

transition metal atoms.

Initial studies were carried out on trimethylsilylmethyl derivatives of Groups IVA and VIA transition metals but later attention was turned to the benzyl derivatives because of greater availability and the probability of simpler reaction products. Finally hexaneopentyl bimolybdenum was prepared and studied in the hope that the greater steric shielding of these ligands would significantly affect the rate of autoxidation.

1. Uninhibited Autoxidation.

The extreme vigour of the interaction between early transition metal, σ -bonded, organometallics and oxygen was similar to that for other organometallics, which have been shown to autoxidise by a free radical mechanism.^{6,7} The reaction at 20°C was extremely facile, probably almost diffusion controlled, and had a half-life of ca. 10 secs.. In comparison, the autoxidation of tri-n-butylborane had a similar half-life, but took longer to go to completion because of the relatively slow second stage, dialkylperoxyborane to alkylldiperoxyborane (Figure 18).

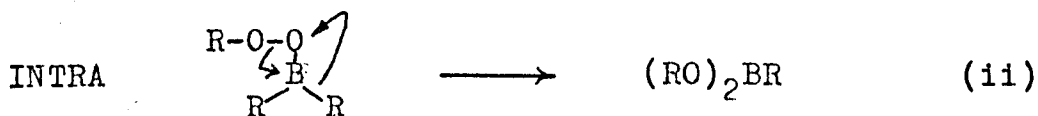
Lowering of the temperature to -74°C only had a really significant effect on the autoxidation of tetrabenzyl zirconium ($t_{\frac{1}{2}}$ ca. 2 mins.), although there was a slight slowing in the rates of autoxidation of all the other compounds studied ($t_{\frac{1}{2}}$ ca. 50 secs.) and a marginal increase in the amount of oxygen absorbed (Table 7).

This behaviour can be contrasted to the autoxidation of tri-n-butylborane at -74°C , at which temperature the absorption of the second mol. of oxygen was completely retarded.

These facts would appear to indicate that there is little activation energy difference between the first and subsequent stages of organotransition metal autoxidations.

A variety of solvents were used for the autoxidation (Table 6) and it has been reported by Russell and Hendry that the dielectric constant of a solvent affected the rates of autoxidation of a variety of hydrocarbons, the rate increasing with increasing dielectric constant.⁸ The effect, however, was relatively small and the slight differences in dielectric constants of the various solvents used in this study are unlikely to have greatly influenced the rate of autoxidation. The possibility of solvent effects due to radical attack on the solvent is also remote since the reaction of peroxy radicals with an organotransition metal compound is liable to be several orders of magnitude greater than the reaction of radicals at a saturated carbon atom. Thus, it can be reasonably assumed that solvent effects on the autoxidations investigated were negligible.

(i) Alkoxide Formation. The autoxidation of other organometallics result ultimately in the formation of alkoxy metal compounds, via peroxy intermediates.^{6,7} The alkoxides were formed by reduction of the peroxide and Davies et al. suggested that for boranes this occurred by an intramolecular rearrangement,⁹ whilst Murviss favoured an intermolecular reaction between peroxide and unreacted organometallic¹⁰:



Reaction (iii) will occur at high initial concentrations of organometallic, and in the absence of this reaction it has been possible to isolate peroxidic products from autoxidation reactions¹¹.

As described in the experimental section of this thesis, there was evidence that the major end-product from the organotransition metal autoxidations was the alkoxide, although it was not isolated.

The autoxidation of methyltitanium trichloride has been reported by Bestian and Beerman to produce methoxytitanium trichloride, 0.5 mol. of oxygen being consumed,¹² and recently Lappert et al. reported that they were able to isolate, and characterise, tetraneopentoxytitanium in 80% yield following the exposure of a solution of tetraneopentyltitanium to air.¹³

The compounds studied in this thesis were similar in this respect, for example, the proton magnetic resonance spectrum of an autoxidised solution of tetrakis (trimethylsilylmethyl) titanium showed the complete absence of the peak at 7.6 τ due to the methylene protons adjacent to the carbon-titanium bond which were present in the original solution. This would imply that all the titanium-carbon bonds had been broken during autoxidation and converted to a species having a new peak at 5.4 τ , which

is related to the value of 5.83 γ for tetraneopentoxytitanium reported by Lappert.¹³ The formation of tetrakis (trimethylsilylmethoxy) titanium was substantiated by the amount of oxygen absorbed, 0.5 mol. per alkyl group, and further substantiated by the identification of trimethylsilylmethanol as the major product following hydrolysis.

The hydrolysis of the autoxidation products of both tetrabenzyl zirconium and hexabenzyl tungsten was found to yield mainly benzyl alcohol, which was again indicative of alkoxide formation. The identification of benzyl alcohol following the autoxidation and hydrolysis of tetrabenzyl zirconium had been previously reported by Zucchini *et al.*⁴.

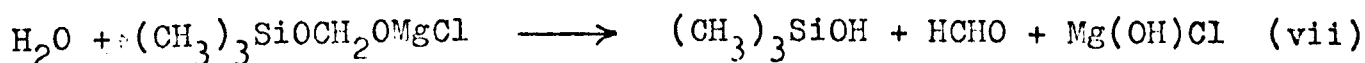
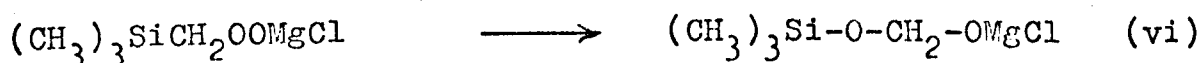
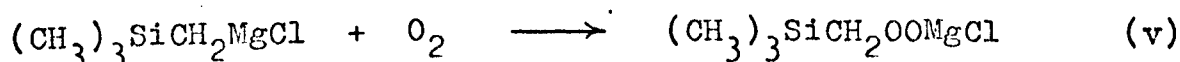
All of the compounds studied in this investigation were found to react with ca 0.5 mol. of oxygen per alkyl group at 20°C, and the overall reaction would therefore appear to be:



(ii) Peroxide Formation. Since it has been shown for many organometallics that alkoxides result from the decomposition of initially formed peroxides, it was logical to suspect their involvement in the systems under investigation.

It was not possible to detect significant amounts of peroxidic compounds following the autoxidation of the trimethylsilylmethyl transition metal organometallics, even when carried out at -74°C and at high dilution. However, there was some indirect evidence which suggested that at some stage alkylperoxy groups had been bonded to the metal. This came

from a comparison with the results of Eisch and Husk who had investigated the products from the autoxidation and hydrolysis of trimethylsilylmethyl magnesium chloride.¹⁴ They indentified, among other products, trimethylsilanol, formaldehyde, hexamethyldisiloxane, and as the major product trimethylsilylmethanol. Eisch and Husk explained the occurrence of these minor products as being the result of a rearrangement of the established¹⁵ alkylperoxy compound formed during autoxidation:



Brilkina and Shushunov have proposed an alternative route for the production of the hexamethyldisiloxane and formaldehyde, involving the reaction of the peroxide with the alkoxide.¹⁶

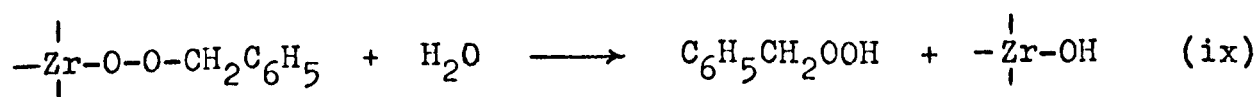
A full investigation of the hydrolysis products of autoxidised tetrakis (trimethylsilylmethyl) titanium was not carried out, because the primary aim of this section of work was to screen a number of compounds with a view to selecting one for detailed study. However, a g.l.c. examination of the hydrolysis products compared well with that from the hydrolysis products of autoxidised trimethylsilylmethyl magnesium chloride and many products appeared common to both. Since the formation of the

minor products almost certainly involved a trimethylsilylmethyl peroxy group, it would seem that, like the Grignard reagent, peroxy compounds were involved in the autoxidation of tetrakis (trimethylsilylmethyl) titanium.

More conclusive evidence came from subsequent studies on tetrabenzyl zirconium and hexabenzyl tungsten which resulted in the detection of unstable peroxidic products. At 20°C the autoxidation of tetrabenzyl zirconium yielded 4.5% of peroxidic material per alkyl group, whereas hexabenzyl tungsten gave 5%. At -74°C the yields of peroxide per alkyl group were 14.5% and 13.5% respectively.

Peroxide formation at -74°C was further substantiated by the fact that at this temperature, all of the compounds studied, in the absence of inhibitors, reacted with slightly more than 0.5 mol. of oxygen per alkyl group (Table 7), which is explained by the presence of small amounts of compounds of the type $\text{ROOM}(\text{RO})_{n-1}$.

The nature of the peroxide produced was investigated and it was found possible using thin layer chromatography, to isolate and identify benzyl hydroperoxide from the low temperature autoxidation of tetrabenzyl zirconium, following hydrolysis. This indicates that the peroxide produced by autoxidation was a true organoperoxytransition metal compound, and not a peroxo compound ($\text{M} \leq \text{O}$), nor a hydroperoxide of the type $\text{M}-\text{OOH}$.

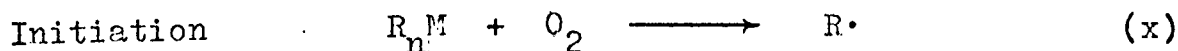


The amount of organoperoxytransition metal compound produced was very small, the majority of the oxygen absorbed being converted to alkoxide, via reactions (ii) and (iii). This is in contrast to trialkylborane autoxidations, in which nearly 100% of the oxygen absorbed is converted to organoperoxyborane, but more closely resembles the autoxidation of organolithium and organomagnesium compounds investigated by Davies and Roberts⁷. They suggested that the low yield of peroxide from these reactions was due to a facile reaction of the peroxide with unreacted organometallic (reaction (iii)). For the compounds studied in this section it is not possible to assess the relative contributions of reactions (ii) and (iii) towards the destruction of peroxide, but the importance of reaction (iii) to the autoxidation of Group IVA transition metal organometallics might be determined from a study of trialkoxy- or trichloro- alkyl derivatives, since reaction (ii) could not occur. Although some work has been carried out on compounds of this type and no evidence of peroxidic products was reported,¹⁶ it should be viewed with caution in the light of modern knowledge concerning concentration and temperature effects, oxygen starvation etc..

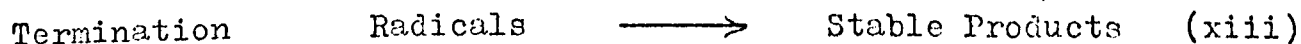
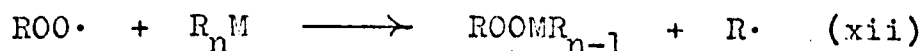
2. Mechanism.

So far it has been pointed out that the autoxidation of σ -bonded organotransition metal compounds has several similarities to the autoxidation of other organometallics, namely a fast, almost diffusion controlled reaction, the production of alkoxides and

the involvement of organoperoxy compounds. There is ample published evidence that organometallics such as Boron^{17,18}, Cadmium⁷, Zinc⁷, and Aluminium⁷ autoxidise by a free radical mechanism:

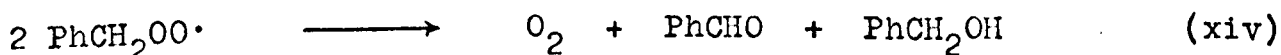


Propagation



It therefore seemed likely that a similar free-radical mechanism would be involved in the autoxidation of the σ -bonded organotransition metal compounds.

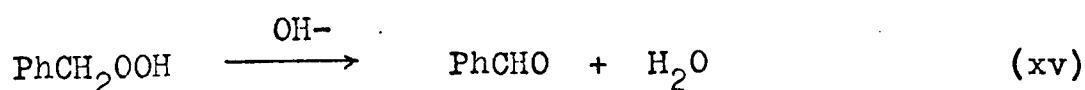
Following the autoxidation at 20°C of tetrabenzyl zirconium, significant quantities of benzaldehyde (7.5% per alkyl group), were indentfied in the hydrolysis products, in addition to benzyl alcohol. The termination reaction of two benzylperoxy radicals results in the formation of benzaldehyde, and is a well known step in hydrocarbon autoxidations¹⁹:



It would be a mistake, however, to look upon the indentification of benzaldehyde as good evidence of a free- radical mechanism, because the propagation chains should be long and reaction (xiv)

is therefore unlikely to yield a significant quantity of benzaldehyde. Also, alternative routes can be proposed to account for the formation of the benzaldehyde:

(a) Base catalysed decomposition of the benzyl hydroperoxide produced by hydrolysis¹⁹:



The base being the metal hydroxide also produced by hydrolysis.

(b) Decomposition of a benzylperoxy zirconium compound during the autoxidation.

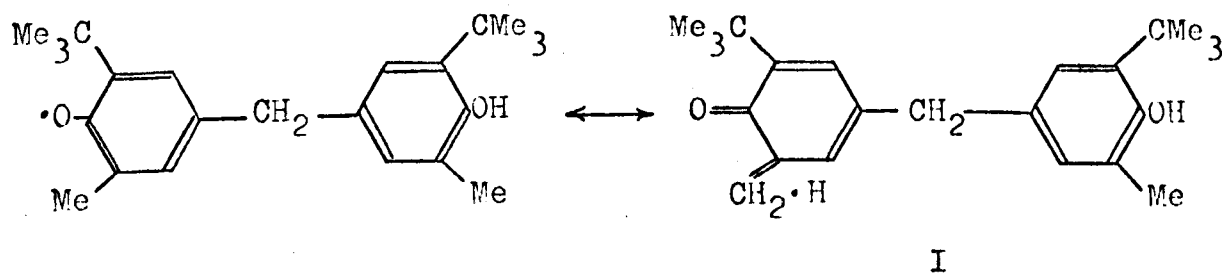
The autoxidation of tetrabenzyl zirconium at 20°C produced benzylperoxy zirconium (4.5% per alkyl group) and following hydrolysis benzyl hydroperoxide was obtained (0.95%). Route (a) therefore accounts for 3.55% of the benzaldehyde, and the remaining 3.95% could have been derived from alternative sources such as (b) or from others not considered above.

(i) Inhibition. It has been mentioned previously (Ch. 2) that the addition of small amounts of phenols, amines, or stable free-radicals can inhibit or retard the rate of oxygen absorption of free radical autoxidations. Allies and Brindley have compared the efficiencies of many inhibitors for trialkylborane autoxidations⁶, and a number of their more effective compounds were added to the organotransition metal autoxidations,

(a) Phenols. Of the phenolic compounds studied at 20°C, only 'Topanol 354' (2,6 di-*t*-butyl 4-methoxyphenol) when added to hexaneopentyl bimolybdenum had a detectable affect on the autoxidations. At -74°C, both 'Topanol 354' and 'Ethyl 720'

retarded the autoxidation of tetrabenzyl zirconium (Figure 20) which reflects the considerable reduction in the rate of autoxidation of this compound on lowering the temperature from 20°C to -74°C.

The two phenols used extensively in this study were Topanol 354, and Ethyl 720. Ethyl 720 has an electron releasing group in the ortho position, with respect to the hydroxyl group and this facilitates phenoxy radical formation resulting from hydrogen abstraction. Further, the phenoxy radical is stabilized by delocalisation (resonance structures such as I) and therefore an inactive radical with little tendency to initiate further chains results.



Allies and Brindley found that Ethyl 720 was one of the most successful phenolic antioxidants for trialkylborane autoxidations⁶. Topanol has three electron releasing groups all facilitating the removal of the hydroxyl hydrogen atom, and although there are no methyl substituents to stabilize the resultant phenoxy radical as for Ethyl 720, the ability of this radical to initiate fresh chains should be limited because of the bulky ortho groups.

The phenolic compounds are propagation suppressors (Ch.2), competing with the substrate for peroxy radicals. The fact

that they had little influence on the majority of reactions studied would indicate that the propagation step (reaction (xii)) was very fast for all stages of the organotransition metal autoxidations, i.e. the oxidation of the second and subsequent alkyl groups was not affected by phenols which is in contrast to the case of the trialkylboranes, when the step, peroxydialkylborane to diperoxyalkylborane was retarded by a variety of phenols⁶.

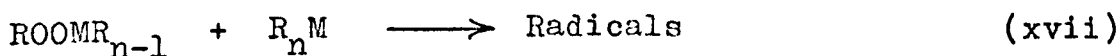
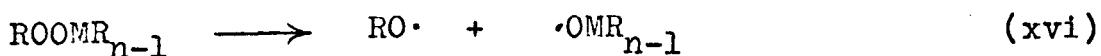
(b) Phenothiazine. This inhibitor, which acts both as a radical trap and a peroxide destroyer, was the most successful of the compounds used in this study. Its ability to act as a peroxide destroyer was reflected in the lower yield of peroxide obtained, when it was added to autoxidations (Table 7).

The effects of this inhibitor on the autoxidations are shown in Figures 19 and 20, all of the compounds except for hexakis(trimethylsilylmethyl) bimolybdenum and hexabenzyl bitungsten being significantly retarded either at 20°C or, as in the cases of tetrabenzyl zirconium and tetrakis(trimethylsilylmethyl)zirconium at -74°C. Phenothiazine caused a general slowing down in the rate of oxygen absorption, rather than a distinct break after the absorption of 1 mol. of oxygen which was observed for trialkylborane autoxidations⁶, and in this respect resembles the phenolic inhibitors previously mentioned.

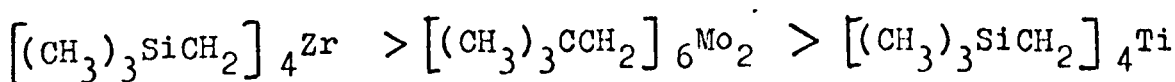
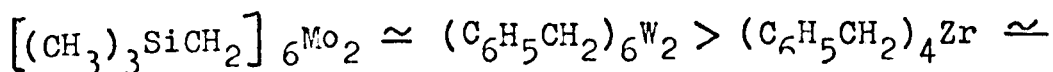
Phenothiazine could retard the rate of autoxidation in three ways:

- (a) Remove radicals produced directly from any initiation steps.
- (b) Remove peroxy radicals produced by the propagation steps.

- (c) Destroy peroxide which could take part in autocatalytic initiation processes such as:



The relative rates of the initiation, propagation, and autocatalytic initiation reactions, reflect the reactivity of a particular compound towards oxygen. The term "Oxidisability" frequently used, is referred to k_p/k_t and although this could not be measured in the case of these organometallic alkyls, a consideration of the effect of phenothiazine retardations allows the construction of a 'reactivity' series at 20°C:



The degree to which phenothiazine interferes with the rate of reaction by removal of peroxide can be considered as small since a large proportion of peroxide still remains after autoxidation in the presence of phenothiazine (ca. 70% of the yield in its absence). The effectiveness of phenothiazine can therefore be considered as a reflection of its ability to trap peroxy radicals, and the 'reactivity' series as a reflection of the rate of production of peroxy radicals by the organotransition metal compound. The processes involved in

the production of peroxy radicals, initiation and propagation, will both be influenced by the degree of steric crowding around the central metal atom. It is possible to rationalise some of the relative reaction rates on the basis of steric shielding, although it should be borne in mind that this is not the sole criterion of relative reactivity, such phenomena as radical stability, availability of low energy orbitals etc. being able to play an important part in determining the rate of autoxidation.

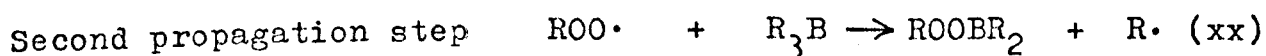
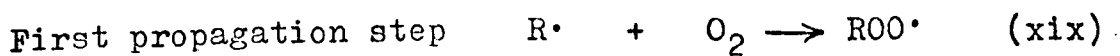
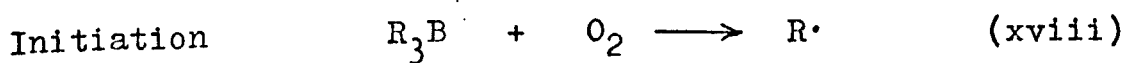
The observation that $[(CH_3)_3SiCH_2]_4Zr > [(CH_3)_3SiCH_2]_4Ti$, in the presence of phenothiazine, is compatible with the increased covalent radius of the zirconium atom compared to titanium.

The decrease in the covalent radii from silicon to carbon results in the well established increase in steric shielding in neopentyl compounds compared to trimethylsilylmethyl compounds. This phenomenon is manifested in several examples of classical organic chemistry, typically trimethylsilylmethylchloride undergoes S_N2 reactions, but neopentylchloride, almost exclusively S_N1 reactions. In the case of these organometallics the steric shielding is manifested in the extra air stability (in the presence of phenothiazine) of hexaneopentyl bimolybdenum compared to hexakis (trimethylsilylmethyl) bimolybdenum. Molecular models also clearly indicated greater steric hindrance to attack at the metal atom in the case of the neopentyl compound.

(c) Galvinoxyl. This compound had been shown by Allies and Brindley⁶, and by Davies and Roberts¹⁸, to be almost unique in its ability to give definite inhibition of

trialkylborane autoxidations and so in this study it was looked upon as the possible key to provide positive evidence of a free radical mechanism. It was therefore most unfortunate that galvinoxyl reacted directly with the organotransition metal compounds, and had little influence on the nature of the reaction. Davies and Roberts, in their studies on the autoxidation of a variety of organometallics, reported that galvinoxyl reacted with organolithium, organozinc, organocadmium, organo-aluminium and organomagnesium compounds, but in all cases except organolithium compounds and Grignard reagents, the reaction product interfered either with the rate or extent of the autoxidation⁶. This difference in behaviour is most probably the result of a difference in the nature of the reaction between galvinoxyl and the organometallic compound.

(ii) Autoxidation of Tetrabenzyl Zirconium in the Presence of Iodine. Iodine has been shown to be an effective inhibitor of trialkylborane autoxidations^{20,21}, and Brown and Midland demonstrated, by isolating alkyl iodide, that it acted as a propagation suppressor:



Iodine does not compete with organometallic for peroxy radicals, as do phenothiazine and phenols, but with oxygen for alkyl radicals and consequently its inhibiting power is dependent on its ability to suppress reaction (xix) rather than the second propagating step.

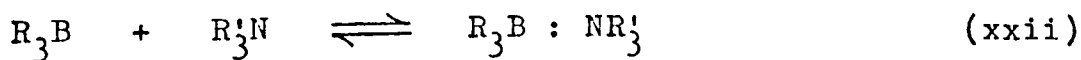
Iodine did not inhibit the autoxidation of tetrabenzyl zirconium, although the quantity of oxygen absorbed was reduced and the colour of the solution discharged during the course of the autoxidation. The absence of inhibition or retardation is possibly the result of a very fast propagation reaction.

The fact that iodine was trapping alkyl radicals was shown by the identification of benzyl iodide in the autoxidised solution. A blank experiment in the absence of oxygen was carried out to ensure that no benzyl iodide was produced by a direct reaction between the tetrabenzyl zirconium and iodine.

Lappert et al. had reported that trimethylsilylmethyl and related derivatives of zirconium did react directly with iodine²⁹ but significant quantities of benzyl iodide were not found in the blank experiment during the time of the autoxidation experiment (ca. 10 mins.). Consequently, the benzyl iodide observed must have been produced as a result of the autoxidation reaction, and was most probably formed by the trapping of alkyl radicals by iodine.

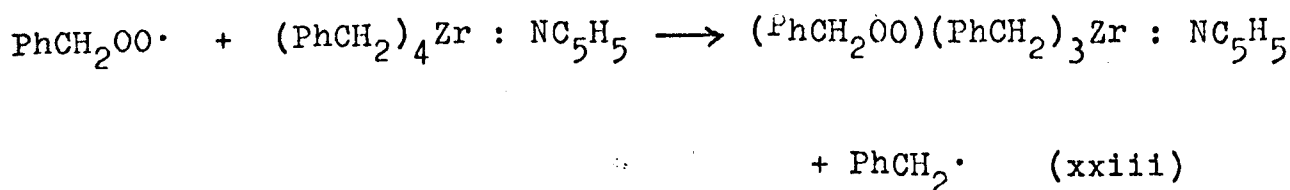
(iii) Autoxidation in the Presence of Donors. Recently Davies and Ingold²³ and Ingold et al.²⁴ demonstrated that the autoxidation of organoboranes was slowed considerably in the presence of pyridine. This was due to the well known

phenomenon of complex formation with amines:



In the presence of excess base the equilibrium is well to the right and so the concentration of free borane is reduced to a very low level. In this way, propagation rate constants for many organoboranes were measured, which had been inaccessible by other methods.^{23,24}

Felton and Anderson have recently reported that tetrabenzyl zirconium formed a 1:1 complex with pyridine, the equilibrium quotient for the reaction being 12.6 at 40°C²⁵, and therefore experiments were performed to test the effect of pyridine (up to 1000 fold excess) on the autoxidation of tetrabenzyl zirconium. Neither pyridine, nor the stronger base piperidine were found to influence significantly either the rate or extent of the reaction and it is suggested that, in contrast to organoboranes²³, an S_H2 reaction by radicals at the complexed metal atom can still occur:



Roberts and Ingold considered that an S_H2 reaction at a co-ordinatively unsaturated multivalent atom would not have a high activation energy, provided that the atom had low energy vacant orbitals available for increasing its co-ordination number.²⁶ In the complexed tetrahedral

organoborane, the boron atom has no vacant low energy orbitals, and consequently the possibility of an S_H^2 reaction occurring at this boron atom is remote. In contrast, the central zirconium atom of the 1:1 pyridine-tetrabenzyl zirconium complex has several low energy orbitals vacant and it is the presence of these orbitals which permit the attack by radicals on the complexed tetrabenzyl zirconium.

3. Rate of Reaction and the Influence of π -Bonding.

Although it has not been possible to show it unambiguously the accumulation of inferences is such, that it seems highly probable that the autoxidation of organotransition metal compounds occurs by a free radical chain mechanism. From the work with inhibitors it was apparent that the propagation stage was extremely facile, and these compounds would certainly appear to be more reactive towards oxygen than trialkylboranes.

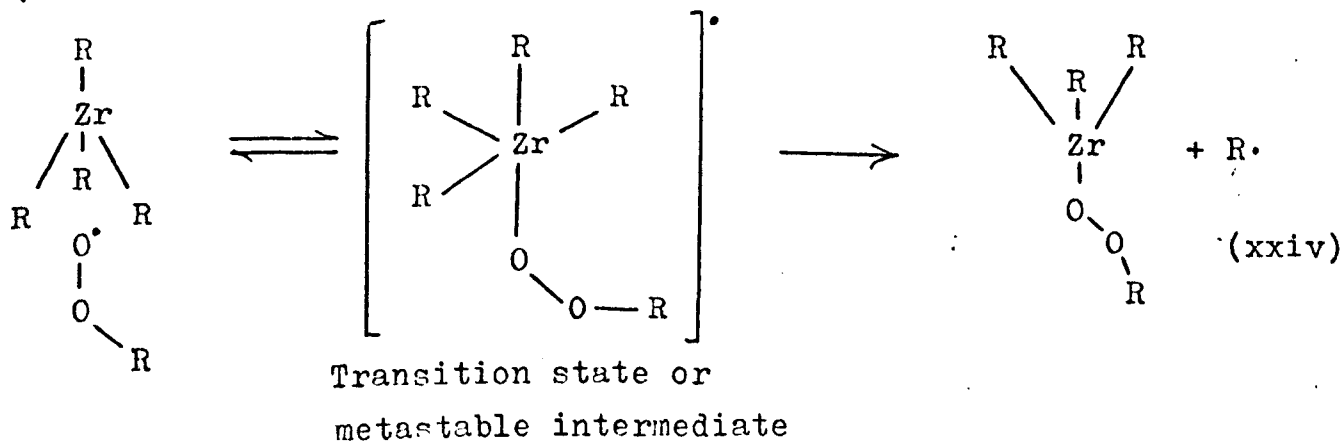
At 20°C all of the organotransition metal compounds studied, autoxidised at a rate approaching diffusion control and only the addition of phenothiazine, as was mentioned earlier, allowed the construction of a 'relative reactivity series'. The uninhibited autoxidation at -74°C showed that, of all the compounds studied, only the autoxidation of tetrabenzyl zirconium had a significant activation energy and was markedly slowed down by a reduction in temperature. This would appear to be anomalous since,

(a) The benzyl groups are less shielding than the trimethylsilylmethyl groups and thus the autoxidation of tetrabenzyl zirconium should be more facile and of lower activation energy than that of tetrakis (trimethylsilylmethyl) zirconium.

(b) The S_H^2 propagation reaction displaces a benzyl radical which will be more stable than the aliphatic radicals and hence should provide a "thermodynamic drive" to the autoxidation of tetrabenzyl zirconium. This fact has been reported for organoborane autoxidations by Ingold et al.²⁴.

An explanation of this anomalie may be associated with the observation of G.R. Davies et al. that the X-ray derived structure of tetrabenzyl zirconium was distorted from a perfect tetrahedron and they suggested that this was due to a non-bonding π -interaction between the aromatic rings and the metal atom.²⁷

The S_H^2 propagating reaction at the zirconium atom will involve a change from a tetrahedral structure to a trigonal bipyramid on attaining the 5-co-ordinate transition state (or metastable intermediate):



In the case of tetrabenzyl zirconium, in addition to the usual restrictions on the formation of the transition state, the 4 π -interactions must be perturbed i.e. the 4-co-ordinate structure is stabilized relative to the 5-co-ordinate structure, and thus the S_H2 reaction and the autoxidation will require a higher activation energy than in the absence of the π -interactions.

Other species capable of stabilising the tetrahedral structure relative to the trigonal bipyramid by π -interactions, include chloride, and oxygen containing functions such as alkoxides and hydroxides, and thus compounds such as trichloro- or trialkoxy- alkyltitanium and alkylzirconium should be more resistant to oxidation.

It has been reported that bis (π -cyclopentadienyl) dialkyl titanium compounds are far less reactive towards oxygen than the tetra-alkyl derivatives,¹⁶ and this can be readily explained using the above argument. The formation of cyclopentadiene to metal bonds requires a fairly strict stereochemistry and thus the 4 co-ordinate species will only tolerate fairly small changes in structure. The formation of the 5-co-ordinate transition state will disrupt the original structure quite considerably and it is therefore not surprising that the autoxidation of bis (π -cyclopentadienyl) dialkyl titanium compounds requires a relatively high activation energy. For these compounds there is an additional factor, viz. the availability of low energy orbitals. Whereas the tetra-alkyl derivatives have five such orbitals available for the incoming radical, the bis (π -cyclopentadienyl) dialkyl compounds only have two

(as a result of the 10 electrons donated by the cyclopentadienyl ligands) and this may well influence the rate of reaction.

4. Conclusions.

All of the compounds studied in this investigation were found to undergo a very vigorous reaction with oxygen, and because of this it was not possible to obtain conclusive evidence concerning the nature of the mechanism.

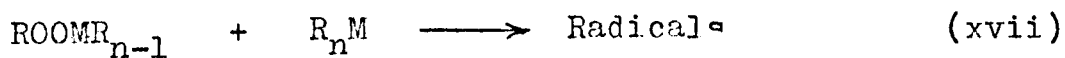
In order to study the mechanism further, it will be necessary to reduce the speed of the autoxidation and from the material presented in this chapter, two main lines of approach are apparent:

- (a) An increase of steric shielding of the metal atom.
- (b) The use of π -bonding ligands.

It has been pointed out, and demonstrated, that steric crowding can be increased by either a decrease in the size of the metal atom, or an increase in the bulk of the ligand. Lappert et al. have recently reported the synthesis of tetrakis (phenyldimethylsilylmethyl) titanium and tetrakis (diphenylmethylsilylmethyl) titanium²² and the autoxidation of these compounds could be sufficiently slow to enable a fruitful investigation of the mechanism to be carried out.

The effect of π -bonding ligands was not investigated in this study, but there does appear to be some justification for a brief study of trialkoxy alkyl and trichloro alkyl derivatives of titanium and zirconium. These compounds are readily prepared²⁸ and a brief study could not only provide information

concerning the mechanism of the autoxidation, but would also indicate the extent to which reaction (xvii) is responsible for the destruction of organoperoxy transition metal compounds.



If this reaction could be controlled, these compounds would enable the production, in high yield, of trialkoxy- or trichloroperoxy derivatives.

Both the available data^{16,22} and the theoretical consideration of transition state formation would indicate that the bis(η -cyclopentadienyl) dialkyl derivatives of Group IVA transition metals have enhanced air stability. Thus a bis(η -cyclopentadienyl) compound of titanium (IV) with two bulky alkyl groups should provide a suitable substrate for a detailed investigation.

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APPENDICES

1. Computer Program for Calculating First Order Rate Constants.

This program ("Forate") was written in the Algol 60 computing language suitable for use on the Elliott 4120 computer.

The input data was,

- (i) number of readings,
- (ii) titration result,
- (iii) time of reading.

The program evaluated $\ln \frac{a}{a-x}$ and plotted these values against time. The least squares line was calculated and drawn, together with the value of the slope which was the first order rate constant.

```
FORATE;
"BEGIN"
"REAL" C, R, M, SCX, SCY;
"INTEGER" J, N;
"LIBRARY" AXESON;

"REAL" "PROCEDURE" LSTSQLIN(X, Y, N, M, C, R);
"VALUE" N;
"REAL" M, C, R;
"INTEGER" N;
"ARRAY" X, Y;

"BEGIN"
"REAL" XSUM, YSUM, XSQSUM, YSQSUM, XYSUM, ZX, ZY;
"INTEGER" J;
XSUM:=YSUM:=XYSUM:=XSQSUM:=YSQSUM:=0.0;
"FOR" J:=1 "STEP" 1 "UNTIL" N "DO"
  "BEGIN"
    XSUM:=XSUM+X[J];
    YSUM:=YSUM+Y[J];
    XYSUM:=XYSUM+X[J]*Y[J];
    XSQSUM:=XSQSUM+X[J]*X[J];
    YSQSUM:=YSQSUM+Y[J]*Y[J];
  "END";
R:=XYSUM/N-(XSUM*YSUM/(N*N));
ZX:=SQRT(XSQSUM/N-(XSUM/N)2);
ZY:=SQRT(YSQSUM/N-(YSUM/N)2);
R:=R/ZX;
R:=R/ZY;
M:=R*ZY/ZX;
C:=(YSUM/N-R*(XSUM/N)*ZY/ZX);
"END" OF PROCEDURE LSTSQLIN;
"READ" N;
"BEGIN"
```



```

"REAL" "ARRAY" T,B,V(1:N);
"FOR" J:=1 "STEP" 1 "UNTIL" N "DO"
  "BEGIN"
  "READ" V(J),T(J);
  "IF" J "NE" 1 "THEN"
    "BEGIN"
    T(J):=T(J)*60;
    B(J):=V(1)/V(J);
    B(J):=LN(B(J));
    "END";
  "END";
  B(1):=0.0;
"PRINT" 'LS16'', 'TIME IN SECS', 'S6'', 'LN A/A-X';
"FOR" J:=1 "STEP" 1 "UNTIL" N "DO"
  "BEGIN"
  "PRINT" 'LS19'', SAMELINE, ALIGNED(5,0), T(J),
    'S8'', ALIGNED(1,4), B(J), 'L';
  "END";
  AXESON(0,T(N),0,B(N),SCX,SCY, 'TIME IN SECS', 'LN A/A-X');
"FOR" J:=1 "STEP" 1 "UNTIL" N "DO"
  "BEGIN"
  MOVEPEN(T(J)*SCX,B(J)*SCY);
  CENCHAR(3);
  "END" OF AXESON;
  LSTSQLIN(T,B,N,M,C,R);
  "IF" ((T(N)*M)+C)>B(N) "THEN"
    T(N):=(B(N)-C)/M;
  "IF" C>0 "THEN"
    "BEGIN"
    MOVEPEN(0,C*SCY);
    DRAWLINE(T(N)*SCX,((T(N)*M)+C)*SCY);
    "END"
  "ELSE"
    "BEGIN"
    MOVEPEN((-C/M)*SCX,0);
    DRAWLINE(T(N)*SCX,((T(N)*M)+C)*SCY);
    "END";
  MOVEPEN(T(N)*SCX/4,-200);
  "PRINT" PUNCH(5), 'RATE CONSTANTE', SCALED(4),M, 'S'', '1/SEC';
  "END";
"END";

```

2. Short courses attended during the period 1969 - 1973 in fulfilment of C.N.A.A. regulations.

1969 - 1970

Recent Advances in Gas-Liquid Chromatography Kingston Polytechnic
(1 day)

Mass Spectrometry Kingston Polytechnic (1 day)

Algol Programming Kingston Polytechnic (12 lectures)

1970 - 1971

Reactive Intermediates in Organic Chemistry Kingston Polytechnic
(1 day)

Chemical Society Annual Meeting - Synthetic Uses of Organometallic
Compounds University of Sussex (3 days)

Molecular Spectroscopy - Interpretation Kingston Polytechnic
(12 lectures)

1971 - 1972

Corrosion Resistant Reinforced Plastics Kingston Polytechnic
(1 day)

Practical Electronics Kingston Polytechnic (6 lectures)

During the course at Kingston Polytechnic I have given two research colloquia and attended various research colloquia given at this college, University College (University of London) and Royal Holloway College (University of London) on research or topics of general chemical interest.



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The published papers at the end of this thesis have been excluded at the request of the university.

Please contact the university for further information.