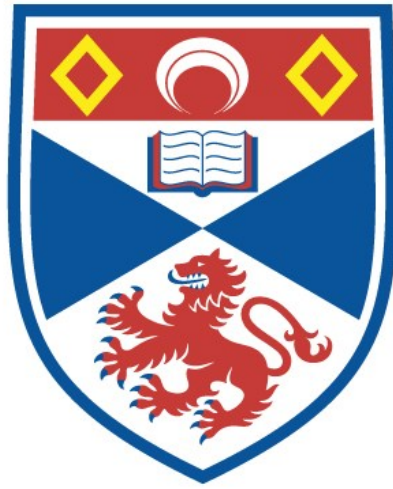


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SUMMARY

The photolysis of azocyclohexane and azoisopentane involves excited molecules which can be deactivated by collision or decompose into cyclohexyl or isopentyl (3-methylbutyl) radicals and nitrogen respectively. The ratio of the rate constants for disproportionation (k_d) to combination (k_c) have been calculated for many alkyl radicals. In the present work the ratio k_d/k_c , was calculated for the cyclohexyl and the isopentyl radical. The Arrhenius parameters for the hydrogen abstraction reaction, from the parent azo-compound, by the cyclohexyl and isopentyl radicals have been estimated.

The photolysis of azocyclohexane, carbon tetrachloride and cyclohexane at wavelengths greater than 300 nm has been investigated over a wide temperature range. At moderate temperatures a chain reaction ensues and the rate constants for the propagation steps were estimated. The really striking feature of the results is that they show that the combination of two cyclohexyl radicals is extremely slow. The only termination product from the photolyses of carbon tetrachloride-cyclohexane mixtures was hexachloroethane, and it is this slow combination of cyclohexyl radicals that accounts for this fact.

The reaction of cyclohexyl radicals with molecular oxygen proceeds by way of radical-radical reactions. The main products, cyclohexanone and cyclohexyl hydroperoxide can be predicted by the use of a simple mechanism. This mechanism gives rise to a simple rate law which is found to be obeyed. A cyclohexyl trioxyl radical is invoked to explain the formation of the minor products, cyclohexene and water.

When azo-n-butane is photolysed in the presence of molecular oxygen the reaction does not proceed by the same mechanism as the azocyclohexane study. Similarly, no chain mechanism is involved, only radical-radical reactions. The results are interpreted to account for product formation via cyclic intermediates. This involves the formation of an n-butyl tetroxyl radical which undergoes intramolecular reaction. All the products can be satisfactorily explained by reaction of these cyclic intermediates. The azocyclohexane study does not exhibit this type of reaction since the cyclohexane ring has such a rigid structure compared to the flexible n-butyl chain.

Decomposition of t-butyl-1-methyl-cyclohexyl-1-peroxide yielded products that can only be explained on the basis of a 1,5-rearrangement. For the rearrangement to operate, a six-membered transition state must be involved. The results do not indicate any general factors which influence the rearrangement but some interesting results are found for specific cases.

A STUDY OF THE

REACTIONS OF ALKYL RADICALS WITH MOLECULAR OXYGEN

A THESIS
PRESENTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
OF THE
UNIVERSITY OF ST. ANDREWS



ST. ANDREWS
OCTOBER 1974

Th 8679

The candidate entered Paisley College of Technology, in September 1966 and graduated from the Faculty of Pure Science with a First Class Honours Degree in Chemistry (C.N.A.A.) in July 1971.

The work described in this thesis was carried out in the Department of Chemistry, St. Andrews University between October 1971 and June 1974.

DECLARATION

I hereby declare that the work described in this thesis is a record of experiments carried out by me in the Chemistry Department of the University of St. Andrews, that it is my own composition and that it has not been previously submitted for a higher degree.

JAMES L. CURRIE

CERTIFICATE

I certify that JAMES LANG CURRIE, B.Sc., has spent ten terms of research work under my direction and that he has fulfilled the conditions of the Resolution of the University Court, 1967, No. 1 and as such he is qualified to submit this thesis for the degree of Ph.D.

PROFESSOR LORD TEDDER

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to Professor Lord Tedder for his constant encouragement and advice throughout the course of this work, and to Dr. H.W. Sidebottom for his many helpful ideas and discussions.

I would like to thank the Department of Chemistry of the University of St. Andrews for providing research facilities and to the Science Research Council for a Research Studentship.

I also wish to express my thanks to British Petroleum Chemical International Limited for facilities provided during my period of research at Great Burgh, Epsom, to my supervisor Dr. E.G.E. Hawkins for his expert guidance and friendly advice, to Dr. R. Large for coordinating the analysis results and to Dr. A.R. Metcalfe for taking over as my supervisor on Dr. E.G.E. Hawkins retirement.

My appreciation and thanks to Mrs. Maureen Sanders for her great patience in typing this thesis.

Finally, I thank my wife, Susan, for three happy years.

Some sections of the work contained in this thesis, have already been presented as papers for publication, to certain chemical journals.

Photolysis of Azocyclohexane Alone and in an Oxygen Atmosphere.

J. Chem. Soc., Faraday Transactions I., 70, 1851 (1974)

The Reaction of Cyclohexyl Radicals with Carbon Tetrachloride

Int. J. Chem. Kinet., 6 (4), 481 (1974)

The Reaction of Alkyl Radicals with Molecular Oxygen at Low

Temperatures (ambient \rightarrow 170°C)

Int. J. Chem. Kinet., in press.

TO MY MOTHER AND SUSAN

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INTRODUCTION

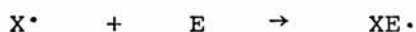
Molecules possessing an unpaired electron are called radicals. Radicals are usually a very reactive species and this results in their rapid disappearance by reaction with themselves or with other substances which may be present. In some instances radicals can have quite long lifetimes. Gomberg¹ first showed the existence of free radicals by observing one of these stable radicals in solution.

The first detection of a free radical was made by Paneth and Hofeditz² who showed that free methyl radicals, formed by the thermal decomposition of lead tetramethyl, deposited a metallic mirror on the walls of a tube through which a carrier gas was flowing. Subsequent work by Rice and co-workers³ showed that free radicals could be detected in the thermal decomposition of a large number of organic compounds.

The reactions of free radicals can be grouped into four main classes:

- (a) Addition reactions
- (b) Transfer reactions
- (c) Decomposition reactions
- (d) Radical-Radical reactions

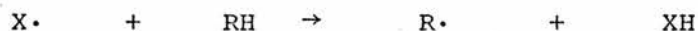
The greatest attention has been focussed on the addition reaction (a) of the type



This not only takes the form of addition across an olefinic double bond⁴ but also addition to aromatic systems⁵ and across acetylinic triple bonds⁶.

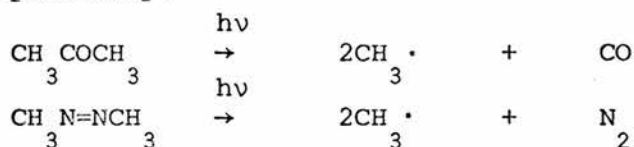
The second class of reactions (b) have also been well investigated. These radical transfer reactions usually involve the abstraction of a hydrogen atom from the substrate^{7,8} but more recently bromine, chlorine and iodine^{9,10} atom abstractions have become more common. It was concluded by Hass and co-workers¹¹,

from the chlorination of alkanes, that the ease of hydrogen atom abstraction was in the order tertiary > secondary > primary for a series of unsubstituted alkanes. Although this effect has been found to be general for all free radicals, differing selectivities are found for different radicals ^{7,8}.



Radical decomposition reactions (c) have been largely ignored while radical-radical reactions (d) have only recently been exploited for their importance in calculating absolute rates for transfer reactions. Almost all absolute values for the rate constants of radical molecule reactions are calculated from measurements relative to radical-radical reactions. The absolute rate constants for combination reactions of the smaller radicals have been known for some time but the rate constants for combination of alkyl radicals (except $\text{CH}_3\cdot$) are either unknown or very uncertain ($\text{CH}_3\cdot$ ^{12,13}, $\text{CF}_3\cdot$ ¹⁴, $\text{CClF}_2\cdot$ ¹⁵, $\text{CCl}_3\cdot$ ^{16,17}). It was originally supposed that the rate for combination of alkyl radicals was the same as that for methyl (k_c , methyl = $10^{10.5} \text{ l m}^{-1} \text{ s}^{-1}$), but recent work by Hiatt and Benson¹⁸⁻²¹ showed that this was not the case.

The main clean source of alkyl radicals has been ketones or azo-compounds. Acetone and azomethane irradiated at wavelengths >300nm produce two methyl radicals and a molecule of carbon monoxide and nitrogen respectively.



The carbon monoxide or nitrogen formed can be used as a monitor on the rate of radical formation. In the present work azo-compounds were used as the source of alkyl radicals.

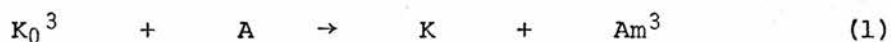
One of the main fields of chemical research over the past 70 years has been the study of hydrocarbon oxidation. The work originated in the form of complete degradation of organic products into carbon dioxide and water. This was followed by the study of combustion and flames. In more recent years attention has been turned to the kinetics of the primary processes that occur when hydrocarbons are reacted with oxygen. Originally it was supposed that the intermediates formed in the oxidation of hydrocarbons were aldehydes and ketones but now it is almost certain that hydroperoxides are the main intermediates. This type of work has become even more important in recent years with the problems associated with atmospheric pollution. The study of hydrocarbon oxidation can help give a better insight into the primary photochemical processes that occur when waste gaseous materials are introduced into the atmosphere.

This thesis was instigated to look more closely into alkyl radical addition to molecular oxygen and to study the fate of the alkyl peroxy and alkoxy radicals formed in the reactions. Work was also carried out to reconcile the apparently conflicting results from the literature on the study of trichloromethyl radicals with cyclohexane.

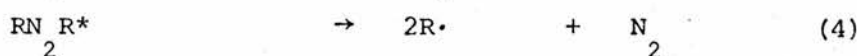
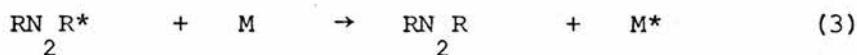
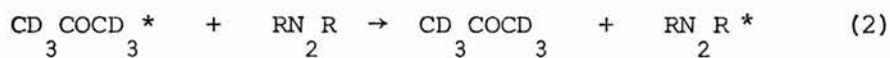
PART I

INTRODUCTION

The photochemistry of aliphatic azo-compounds was developed largely because of their usefulness as sources of free radicals. It has been known for a long time that azoalkanes do not phosphoresce or fluoresce when irradiated at any wavelengths at which they absorb. They have also been shown to efficiently quench the phosphorescence from triplet ketones. Rebbert and Ausloos²² showed that the fluorescent emission from acetone and biacetyl was not affected by azoalkanes; only the phosphorescence. They concluded from this, that energy transfer occurs only from an excited triplet ketone to an azoalkane molecule. This energy transfer is a physical process as shown by (1) and not a chemical reaction.



Where K_0^3 is the ketone molecule in a low vibrational level of the triplet state from which level phosphorescence is generally assumed to occur. Am^3 is an azoalkane molecule excited to the m^{th} vibrational level of the triplet state. Rebbert and Ausloos also experimented with the photosensitized decomposition of azoalkanes in order to obtain information about the fate of the triplet excited azoalkane. In the photolysis of acetone-d₆ at 313 nm in the presence of relatively small concentrations of azoalkanes (azomethane and azoethane) it is the excited azoalkane molecule formed in energy transfer reaction (2) which decomposes to give two alkyl radicals for each nitrogen molecule produced in reaction (4).

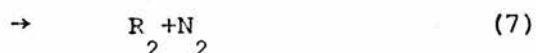


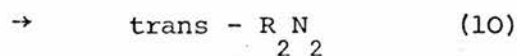
Step (3) shows collisional deactivation from the triplet state of the azoalkane, to the ground state. The probability of deactivation

should fall with decreasing pressure; this was found to be the case. Similarly, the longer the dissociative lifetime of the triplet azoalkane the higher the probability of deactivation.

More recently Collier, Slater and Calvert ²³ have investigated the photochemistry of 1,1'-azoisobutane. They found that decomposition was accompanied by cis-trans isomerisation. It was also found that the triplet level of the azo-compound lies below that for biacetyl and acetone. Thus energy transfer from these ketones may be used to populate the triplet state of the azoalkane. However, when biacetyl was used as the donor no decomposition occurs. With acetone, as Rebbert and Ausloos found, decomposition was observed. Work on azoisopropane ²⁴ in solution and in the gas phase, again showed cis-trans isomerisation was accompanying the decomposition. At low pressures the quantum yield of decomposition of azoisopropane, ϕ_{dec} , was unity at 366 nm; no cis-trans isomerisation was observed. This is in agreement with the decomposition of azomethane ^{25,26} at low pressures where ϕ_{dec} is near unity. More complex azoalkanes show that a significant fraction of the light excited molecules do not decompose but are stabilized by a second-order kinetic process (3). In the azoisopropane studies an increase of pressure decreased the decomposition yield and increased the yield of isomerisation.

The dissociation of azoalkanes in the long wavelength region can be summarised by the reaction sequence below.

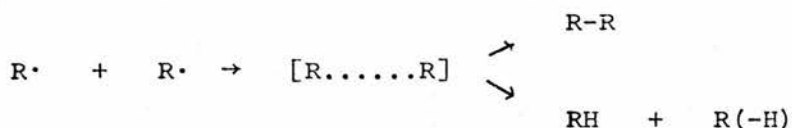




Where M represents either an azoalkane molecule or some other added molecule; the prime on the products of the reaction designates some non-dissociative, vibrationally excited molecules.

Although primary process (7) occurs about 1% in the photolysis of azomethane it appears to be much less important in the higher azoalkanes. The excited molecule mechanism, reactions (5) and (8), hold well for other azoalkanes studied: Azoethane ^{27,28}, azoisopropane ^{24,29}, azo-n-butane ³⁰ and azoisobutane ³¹.

Azoalkanes have been used to determine the ratio of rate constants for disproportionation to combination for alkyl radicals. In the past it has been assumed that the same transition state existed for disproportionation and combination reactions.



This was concluded because the ratio of rate constants for disproportionation to combination (k_d/k_c) remained constant over a wide temperature range in the gas phase ^{7,32}. Recently this hypothesis has been put in doubt by results from work in the liquid phase. Gillis ³³ found that k_d/k_c for ethyl and isopropyl radicals in liquid methane was greater than the ratio in the gas phase by a factor of about 2.5. He also found that the activation energy for combination, exceeded that for disproportionation by $290 \pm 30 \text{ cal mol}^{-1}$ for ethyl radicals and by $255 \pm 25 \text{ cal mol}^{-1}$ for

isopropyl radicals. It was concluded that k_d/k_c depends both on temperature and phase which is in accord with other workers.

Sheldon and Kochi ³⁴ found k_d/k_c for ethyl radicals in n-pentane was the same as the gas phase value, while k_d/k_c for isopropyl radicals was almost twice that for the best gas phase estimate. Dixon and co-workers ³⁵ found a difference in activation energy between the combination and disproportionation reactions for ethyl radicals reacting in a cage in liquid isooctane, ($E_c - E_d \approx 400 \text{ cal mol}^{-1}$). Konar ³⁶ concluded from his work on the correlation of k_d/k_c with entropy change that $E_c \neq E_d$, therefore the disproportionation and combination reactions cannot have exactly the same transition state structure. This agrees with proposals made by Benson ³⁷; both reactions involve different transition states with considerable ionic character and there could be more contribution from ionic states to the transition state for disproportionation.

An activation energy difference should also be observed in the gas phase even though the difference in the liquid phase is not pronounced. The activation energy difference should take the form of a temperature dependence for k_d/k_c . James and Stuart ³⁸ photolysed 2,2'-azoisobutane to effect a source of t-butyl radicals. They concluded that $E_c - E_d = 250 \text{ cal mol}^{-1}$ for the mutual interaction of t-butyl radicals. Reid and Le Roy ³⁹ studied the reaction of ethyl radicals with molecular hydrogen in the gas phase and tentatively concluded that $E_c - E_d = 900 \text{ cal mol}^{-1}$ for ethyl radicals.

It is therefore quite probable that disproportionation and combination proceed by way of different transition states with very small activation energies. The activation energy for combination is slightly larger than that for disproportionation.

Previous studies of azoalkanes, azoethane ²⁷, azo-n-propane ⁴⁰, azoisopropane ²⁹, azo-n-butane ³⁰, azoisobutane ³¹ etc have given the rates of disproportionation to combination for the ethyl, n-propyl, isopropyl, n-butyl and isobutyl radicals. More recently the ratio of k_d/k_c has been found for large branched alkyl radicals ⁴¹ and for small alkyl radicals, the latter being formed by the mercury photo-sensitized hydrogenation of olefins in the gas phase ⁴². As yet no reliable ratio exists for the cyclohexyl radical in the gas phase and the ratio for isopentyl radicals has not previously been reported. This work was initiated to determine an accurate k_d/k_c ratio for the cyclohexyl and isopentyl radicals by photolyses of the parent azo-compounds.

PART I SECTION I

THE PHOTOLYSIS OF AZOCYCLOHEXANE

PART I SECTION I

EXPERIMENTAL

1. Materials

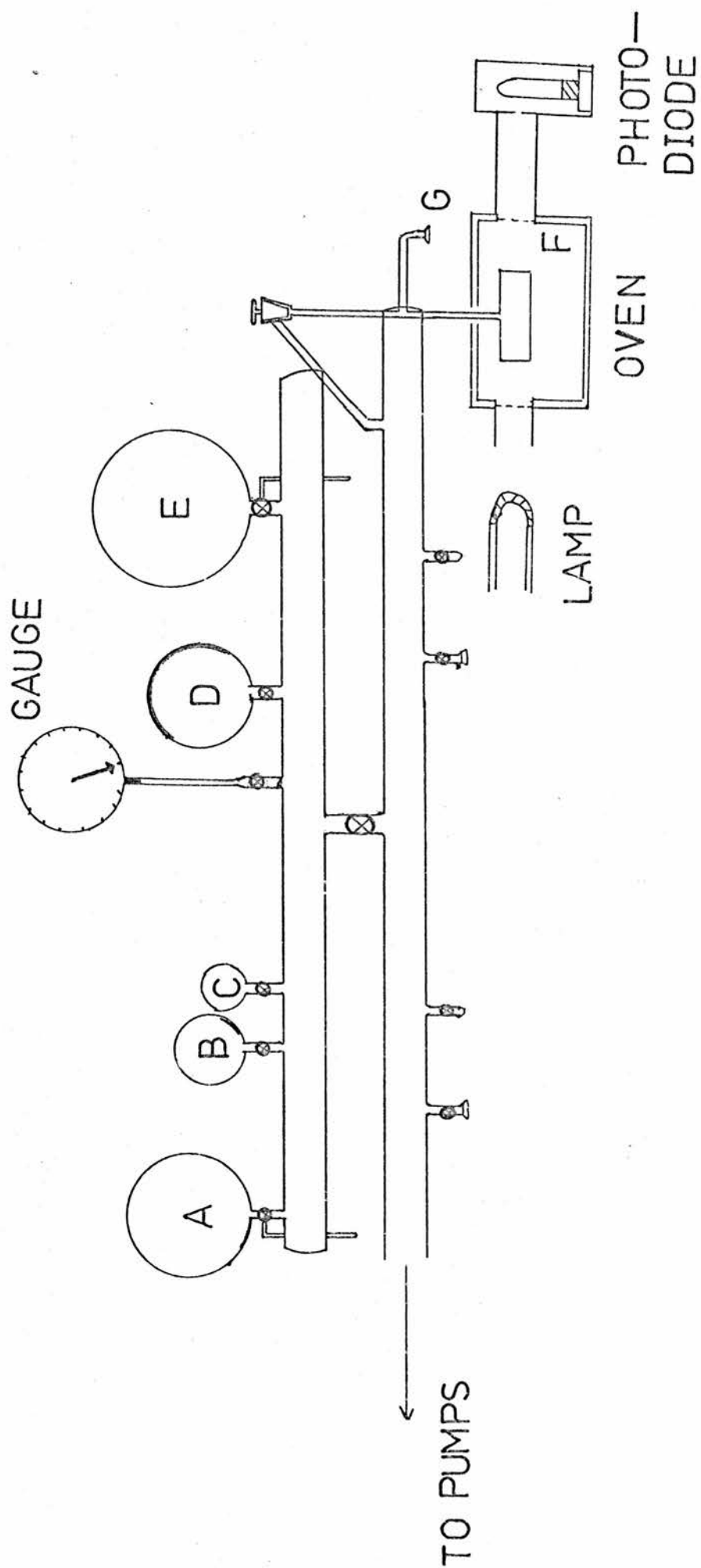
Cyclohexane (Fisons spectrograde reagent) was trap to trap distilled on the vacuum line before use and was found to contain no impurities by gas/liquid chromatography. Cyclohexene (Fisons laboratory reagent) and bicyclohexyl (Aldrich Chemical Co.) were used without further purification for identification purposes. Azocyclohexane was prepared from N,N' -dicyclohexylsulphamide, which was prepared by the method of R. Sowada⁴³.

Cyclohexylamine (99g; 1 mol), pyridine (64 cm³) and petroleum spirit (40-60°C; 300 cm³) were treated dropwise with stirring with sulphuryl chloride (32 cm³) in petroleum spirit (40-60°C; 100 cm³) at -20°C. After the addition the mixture was stirred for 1 hour at room temperature. The petroleum spirit was distilled off and the residue treated with concentrated hydrochloric acid (90 cm³) in water (500 cm³). The mixture was then cooled, filtered at the pump, and the crude product refluxed with a mixture of concentrated hydrochloric acid (150 cm³): ethanol (150 cm³): water (150 cm³): for 1½ hours. The product was filtered at the pump as a flaky white solid. The product was recrystallized from aqueous ethanol.

% yield = 54 M.Pt. 152-154°C (Lit⁴³ 154.4°C).

Azocyclohexane was prepared by a method similar to that of R. Ohme and H. Preuschhof⁴⁴. Sodium (8.5g) was reacted with dry methanol (250 cm³) to form sodium methoxide. This was added to N,N' -dicyclohexylsulphamide (17 g) and sodium hypochlorite (300 cm³; 1.5 M). The solution was stirred for 2 days at ~50°C. The upper layer, which was a sweet smelling oil was separated and any methanol present removed on a rotary evaporator. The liquid was then shaken with petroleum spirit

FIGURE I-1



(40-60°C) and the lower aqueous layer discarded. The petroleum spirit was removed on a rotary evaporator and the straw coloured liquid left to cool, when near colourless crystals were formed. The product was recrystallized from absolute methanol and dried under vacuum. Gas/liquid chromatographic analysis of the product revealed no residual impurity.

% yield = 25 M.Pt. 33-34°C (Lit⁴⁵ 34.5°C)

2. Apparatus

A conventional mercury free vacuum system made of 'pyrex' glass was used (fig. I.1, P. 10). The reactant volumes were measured by the bulbs A (2478 cm³), B (62 cm³), C (149 cm³), D (500 cm³) and E (5000 cm³). The reaction vessel F (146 cm³) was cylindrical in shape and also made of 'pyrex' glass. A side arm G attached close to the reaction vessel could be isolated from the main line. With a small tube attached the product mixture from the reaction vessel could be distilled into the tube without the possibility of the mixture distilling on the walls of the main vacuum line. The vacuum was maintained by means of a 'Speedivac' oil vapour diffusion pump (model 102A) backed by a 'Speedivac' single stage rotary pump (model 1SC50B). The pressure measurements were taken by a barometrically compensated 'Speedivac' capsule dial gauge (model CG3). The range of the gauge was 0-100 torr. The reaction vessel was heated by a cylindrical furnace whose temperature was controlled by a 0-250 volt 'Variac' transformer (type 71A). The temperature, measured by a mercury in glass thermometer was invariant over the volume occupied by the reaction vessel and remained constant to within $\pm 2^\circ\text{C}$ for any experiment. The light source was an 'Hanovia'

u.v.s. 220 medium pressure mercury arc lamp. The beam emitted passed through a circular hole in the side of the furnace (dia. 5 cm) on to the plane circular face of the reaction vessel.

3. Procedure

A weighed amount of azocyclohexane was placed in a small tube and attached to the side arm G (fig. I.1). The material was 'degassed' several times and then introduced into the evacuated reaction vessel by cooling the vessel with liquid nitrogen. The distillation was speeded up by gently warming the small tube with a hot air blower. After the distillation was complete the reaction vessel was closed to the main line. Cyclohexane which was 'degassed' and stored on the line in a tube, fitted with a teflon tap, was allowed to expand into the line and bulb (A or B). When a suitable pressure had registered the bulb tap was closed and the cyclohexane in the line redistilled into the storage tube by cooling in liquid nitrogen. The measured amount was then distilled from the bulb into the reaction vessel by previous procedure. The pre-heated furnace was then raised into position and the temperature allowed to stabilize. During this time the lamp was switched on and left to warm up. Usually 10 minutes was adequate for this. The experiment was started by simultaneously starting the timing device and raising the shutter which covered the aperture. After the experiment was completed the furnace was removed and the reaction vessel surrounded with liquid nitrogen. After ~2 hours the reaction vessel was pumped down with the liquid nitrogen still in position. This pumping should only remove the nitrogen formed from the photolysis of the azo-compound. The furnace was again raised into position and the products distilled into a small tube attached to the side arm G (fig. I.1). At this point a

known volume and pressure of n-pentane was distilled into the tube. This was necessary because under the analytical conditions used the azocyclohexane peak was not observed. Therefore, a peak of known concentration must be present on the chromatogram to calculate the concentrations of the products.

4. Analysis

A Griffin and George D6 gas chromatograph was used for all the analysis. The peaks were recorded using a Honeywell Brown potentiometric recorder (1mV). The detector employed by the instrument was a gas density balance. The relationship $q = KAM/M - m$ holds (q = sample weight, K = constant, M = molecular weight, A = peak area and m = molecular weight of carrier gas). Hence the concentration of any material is given by $q/M = KA/M - m$:

The separation of the products was obtained by using a 6' X $\frac{3}{8}$ " column packed with 28.6% by weight of tritolyl phosphate on 100/120 mesh Celite. The samples were introduced into the column by stainless steel capillary needles (2, 4 and 6 ul).

The peak areas were measured using either a Honeywell Precision Integrator or a Du Pont 310 Curve Resolver.

Usually about 4 or 5 analyses were made of a reaction mixture and an average concentration for each component obtained.

5. Identification of Products

Only 3 peaks were observed from gas/liquid chromatographic analysis. Cyclohexane, cyclohexene and bicyclohexyl were all identified by comparison of retention times with those for authentic samples.

To separate and measure the peaks accurately two sets of chromatograms were required. The column was first operated at 40°C, nitrogen flow rate 32 cm³/min and then at 130°C, nitrogen flow rate 175 cm³/min.

6. Results

The products formed in the gas phase photolysis of azocyclohexane were cyclohexene, cyclohexane and bicyclohexyl. The concentrations for each of the products in the reaction mixtures were found and the rates of their formation calculated, as shown in table I.1.

TABLE I.1 Rates of Product Formation in the Photolysis of Azocyclohexane at Wavelengths greater than 300nm

TEMP (°C)	Rc-C6H12	Rc-C6H10	R(c-C6H11)2	R N2	$\frac{Rc-C6H10}{R(c-C6H11)2}$	$\frac{(Rc-C6H12)_5 \times 10^2}{R^{\frac{1}{2}}(c-C6H11)2 [(c-C6H11)2N2]}$
87	0.608	0.395	0.391	0.893	1.01	1.38
95	0.674	0.435	0.439	0.994	0.99	1.46
108	0.922	0.588	0.542	1.30	1.08	1.84
124	1.00	0.463	0.421	1.15	1.10	3.35
135	1.13	0.478	0.503	1.31	0.95	3.72
160	1.77	0.633	0.879	2.08	0.72	4.91
179	2.46	0.782	0.711	2.33	1.10	8.07
187	4.62	1.36	1.47	4.46	0.93	10.9

All Rates (R) in mol l⁻¹ s⁻¹ x 10¹⁰ Photolysis Time = 5.4x10⁴s. [(c-C6H11)2N2] = 2.47x10⁻⁴ mol l⁻¹

$$\frac{(Rc-C6H12)_5 \times 10^2}{R^{\frac{1}{2}}(c-C6H11)2 [(c-C6H11)2N2]} , \quad 1^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}} \text{ s}^{-\frac{1}{2}} \quad (P.38)$$

where $(Rc-C6H12)_5 = (Rc-C6H12)_{total} - (Rc-C6H10)_{4d}$ and $R_{N2} = Rc-C6H10 + R(c-C6H11)2 + \frac{1}{2}(Rc-C6H12)5$

A least squares plot of $\log_{10} \frac{(Rc-C_6H_{12})_5}{R^{\frac{1}{2}}(c-C_6H_{11})_2 [\text{Azo}]}$ versus $10^3/T$ (P.25)

(fig. I.2) gave a straight line of slope = -1.44 ± 0.24

and intercept = 4.12 ± 0.095

A least squares plot of $\log_{10} R_{N_2}$ versus $10^3/T$ (fig I.3) gave a straight line of slope = -0.67 ± 0.38 (P. 26)

and intercept = 2.8 ± 0.15

PART I SECTION II

THE PHOTOLYSIS OF AZOISOPENTANE

PART I SECTION II

EXPERIMENTAL

1. Materials

3-Methylbut-1-ene (Fluka Chemicals Ltd.) was used without further purification for identification purposes. Azoisopentane was made from N,N'-diisoamylsulphamide which was prepared by the method described in Section I. The sulphamide was a flaky white solid.

% Yield = 38 M.Pt. 104-106°C

Azoisopentane was prepared by a similar method to that described in Section I for the preparation of azocyclohexane. N,N'-diisoamylsulphamide (3g; 12.7m Mol), sodium hydroxide (1.01g; 25.4m Mol), sodium hypochlorite (1.88g; 25.4m Mol: 16.9cm³ of 1.5M NaOCl) and pentane (4cm³) were stirred together until all the sulphamide was dissolved (~15 hours), with occasional ice-bath cooling to keep the temperature below 36°C. The pentane layer was then separated, dried over anhydrous magnesium sulphate and purified by preparative gas/liquid chromatography. The instrument used was a Pye 105, preparative gas/liquid chromatograph employing a 7ft glass column packed with 20% by weight of dinonyl phthalate on 60-100 mesh 'Embacel'. With a nitrogen flow rate of 250 cm³/min and column temperature 100°C the azo-compound was obtained >99.9% pure. The nitrogen flow rate was obtained by setting the injector nitrogen pressure to 50lb f/in² and the column pressure to 30lb f/in². The sample size for injection was ~250 µl.

2. Apparatus

The reaction vessel (149cm^3) was again cylindrical in shape, but for these experiments was made of 'quartz' glass. The furnace had two apertures. The entrance hole allowed light to irradiate the cell and the exit hole allowed the light to fall on to a photo-diode tube which was connected to an amplifier. The entrance hole was covered by a circular piece of 'pyrex' glass, while the exit aperture was covered by a circular piece of 'quartz' glass. The photo-diode and amplifier acted as a monitor on the light passing through the cell. The remaining apparatus has already been described in Section I.

3. Procedure

Azoisopentane was 'degassed' and stored in a darkened tube on the line. The liquid was allowed to expand into the line and bulb D. The pressure could not be measured as it was too low to register accurately on the gauge (0-40 torr). The runs were then carried out as described in Section I. Cyclohexane was added, after completion of the runs, as a concentration reference.

4. Analysis

The analysis was carried out as described in Section I. The most satisfactory stationary phase, for separating the products was 20% by weight silicone oil on 60-100 mesh 'Embacel'.

5. Identification of Products

For runs between $40-170^\circ\text{C}$ only four product peaks were observed from gas/liquid chromatographic analysis. 2-Methylbutane (isopentane),

3-methylbut-1-ene (isopentene) and 2,7-dimethyloctane were identified by mass spectrometry. The fourth peak will be discussed later and should be of no importance in this work. The sample for mass spectral analysis was photolysed for 3 hours at 100°C using an 'Hanovia' medium pressure arc lamp. The spectra were measured on an A.E.I. MS 902 instrument with a g.l.c. inlet from a Pye 104 gas/liquid chromatograph. About a 10 μ l injection was made into the 7' glass column packed with 20% by weight silicone oil on 60-100 mesh 'Embacel', with helium as carrier gas. The column was initially operated at 30°C and gas pressure 10lb f/in² finally reaching 120°C and gas pressure 20lb f/in². This ensured that all the peaks were well separated on entering the ionisation chamber of the mass spectrometer.

Two sets of chromatograms were necessary for complete separation of products from kinetic runs. The column was first operated at 30°C, nitrogen flow rate 20 cm³/min and then at 100°C, nitrogen flow rate 230 cm³/min.

6. Results

The products formed in the gas phase photolysis of azoisopentane (azo-2-methylbutane) were isopentene (3-methylbut-1-ene), isopentane (2-methylbutane) and 2,7-dimethyloctane. The rates of their formation are shown in Table I.3.

TABLE I.2Mass Spectra of the Products formed in the Photolysis of Azoisopentane

Product		Authentic	
m/e	%	m/e	%
55	100	55	100
42	45	27	30
29	40	42	27
27	38	29	26
41	38	39	26
39	33	70	26
70	21	41	21
53	13	53	8

3-Methylbut-1-ene

Product		Authentic	
m/e	%	m/e	%
43	100	43	100
41	98	42	87
42	92	41	68
57	80	57	55
39	61	29	46
29	50	27	41
27	43	39	21
56	23	56	17

2-Methylbutane

Product		Authentic	
m/e	%	m/e	%
43	100	43	100
57	75	57	81
41	54	41	53
27	26	27	33
29	25	71	30
42	24	99	28
99	19	29	26
71	15	42	23

2,7-Dimethyloctane

TABLE I.3 Rates of Product Formation in the Photolysis of Azoisopentane at Wavelengths greater than 300nm.

TEMP (°C)	REACTION TIME	[Azo]	Ri-C5H10	R(i-C5H11)2	Ri-C5H12	R N2	$\frac{Ri-C5H10}{R(i-C5H11)2}$	$\frac{(Ri-C5H12)5 \times 10^2}{R^2(i-C5H11)2[Azo]}$
42	1.8	2.00	0.507	7.03	0.869	7.72	0.072	0.683
62	1.8	2.12	0.660	7.70	1.15	8.61	0.086	0.833
82	2.16	1.97	0.762	9.20	1.80	10.5	0.083	1.74
102	1.8	2.03	0.906	10.66	2.53	12.38	0.085	2.45
123	1.8	2.32	1.210	14.70	4.52	17.57	0.082	3.723
148	1.8	3.95	1.290	15.15	14.12	22.85	0.085	8.35
172	1.44	3.85	1.540	18.5	25.6	32.1	0.083	14.60
201	0.72	3.00	6.120	43.2	76.0	84.3	0.142	35.40

All Rates (R) in mol l⁻¹ s⁻¹ x 10¹⁰ [Azo] , mol l⁻¹ x 10⁴

$\frac{(Ri-C5H12)5 \times 10^2}{R^2(i-C5H11)2[Azo]}$, l^{1/2} mol^{-1/2} s^{-1/2} (Page 38)

$R^2(i-C5H11)2[Azo]$

Reaction time, s x 10⁻⁴ where (Ri-C5H12)₅ = (Ri-C5H12) total - (Ri-C5H10)_{4d}

and R_{N2} = Ri-C5H10 + R(i-C5H11)₂ + 1/2(Ri-C5H12)₅

A least squares plot of $\log_{10} \frac{(i-C_5H_{11})_2 \times 10^3}{R^{\frac{1}{2}}(i-C_5H_{11})_2[Azo]}$ versus $10^3/T$ (P.27)

(fig. I.4) gave a straight line of slope = -1.455 ± 0.32

and intercept = 5.337 ± 0.12

A least squares plot of $\log_{10} R_{N_2} [Azo]$ versus $10^3/T$ (fig. I.5) (P.28)

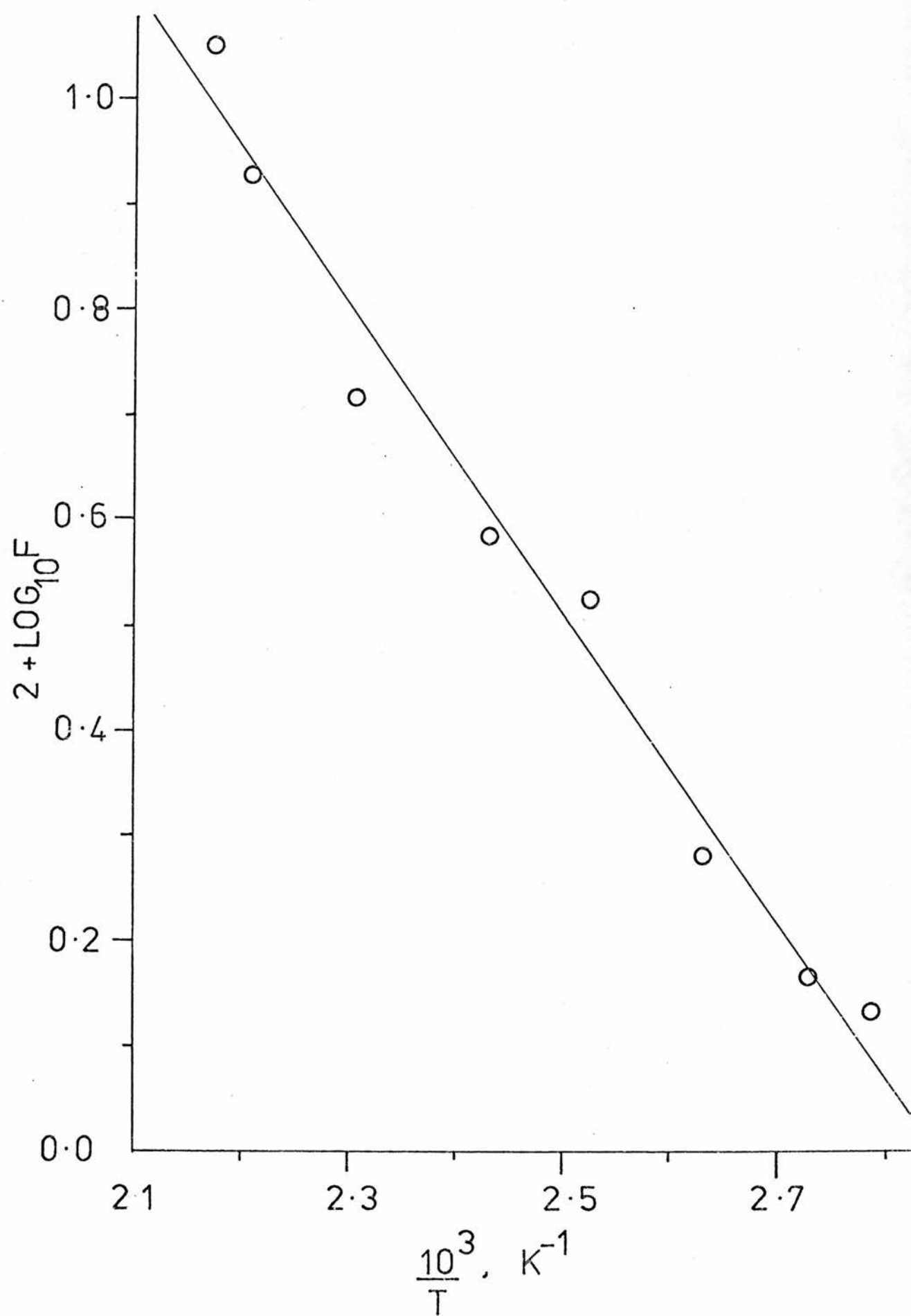
gave a straight line of slope = -0.991 ± 0.43

and intercept = 3.203 ± 0.159

The above plot (fig. I.5) is not a good straight line and the activation energy derived from the gradient can only be regarded as a very crude approximation.

CAPTIONS FOR THE FIGURES

- Figure I.2 Plot of $\log_{10} \frac{(Rc-C_6H_{12})_5}{R^{\frac{1}{2}}(c-C_6H_{11})_2 [(c-C_6H_{11})_2 N_2]}$ versus the
reciprocal of temperature (table I.1)
- Figure I.3 Plot of $\log_{10} R_{N_2}$ versus the reciprocal of
temperature (table I.1)
- Figure I.4 Plot of $\log_{10} \frac{(Ri-C_5H_{12})_5}{R^{\frac{1}{2}}(i-C_5H_{11})_2 [(i-C_5H_{11})_2 N_2]}$ versus the
reciprocal of temperature (table I.3)
- Figure I.5 Plot of $\log_{10} R_{N_2} [Azo]$ versus the reciprocal
of temperature (table I.3)
- Figure I.6 The Ultraviolet Absorption Spectrum of Azocyclohexane.



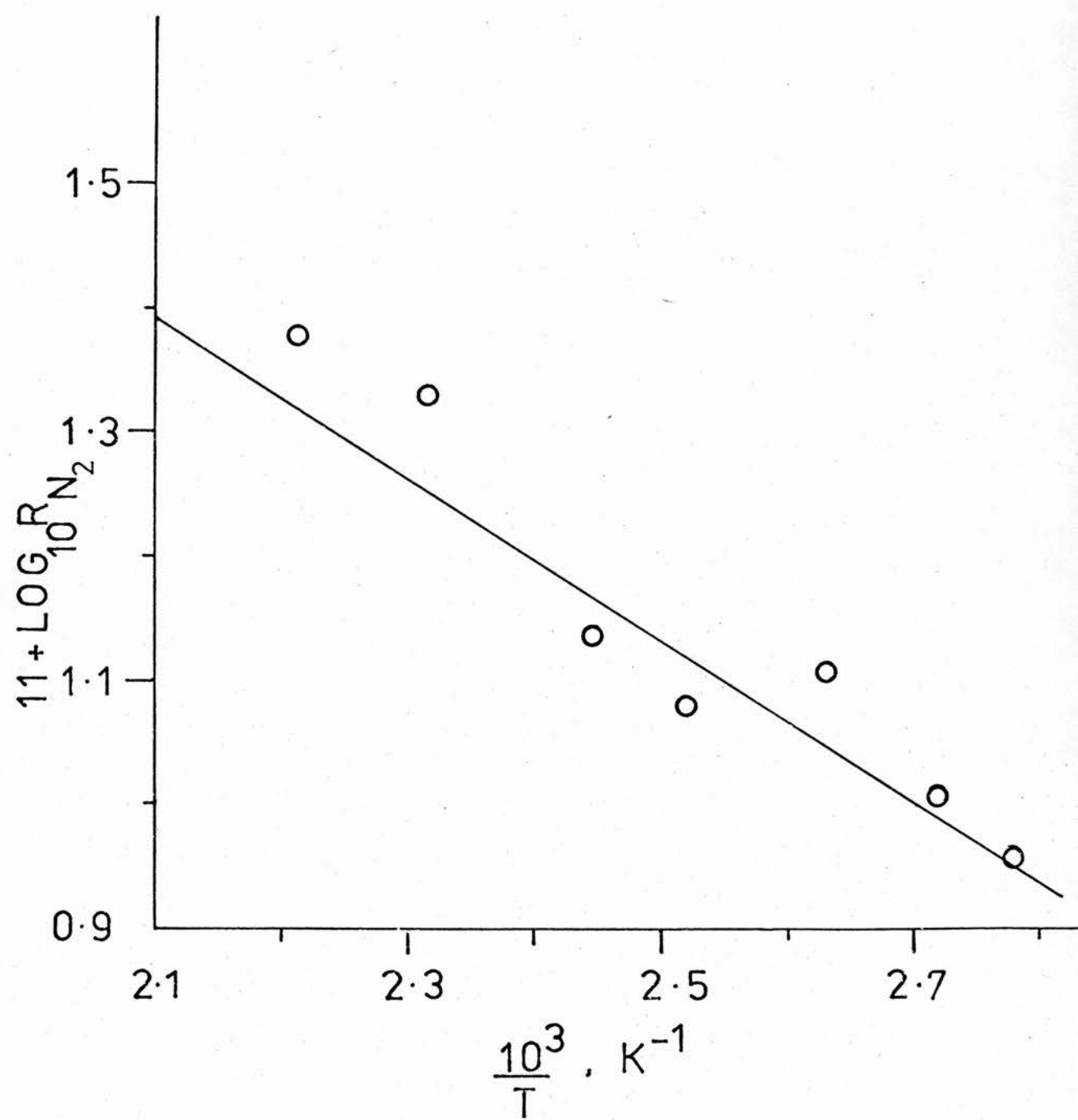


FIGURE I·4

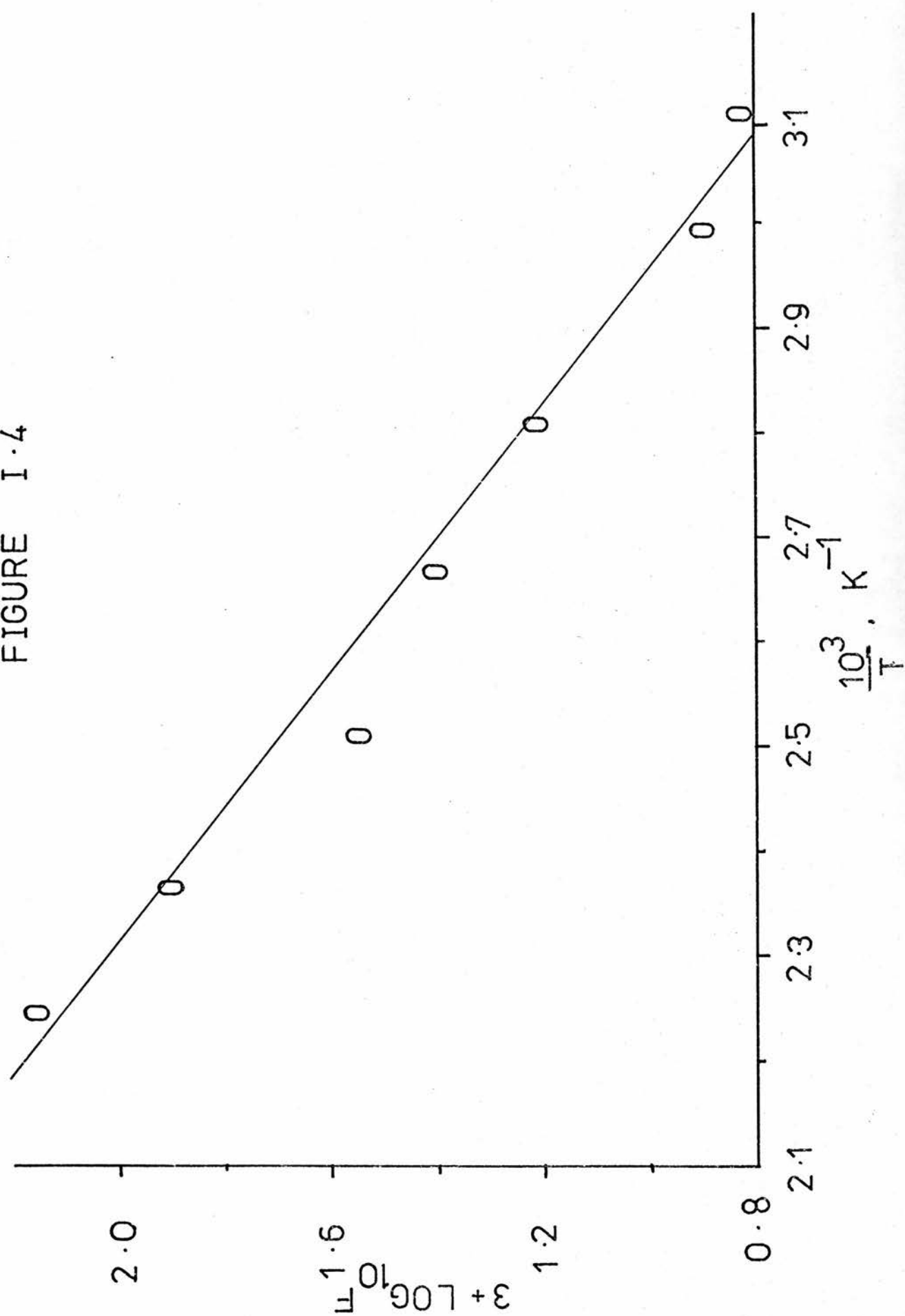


FIGURE I.5

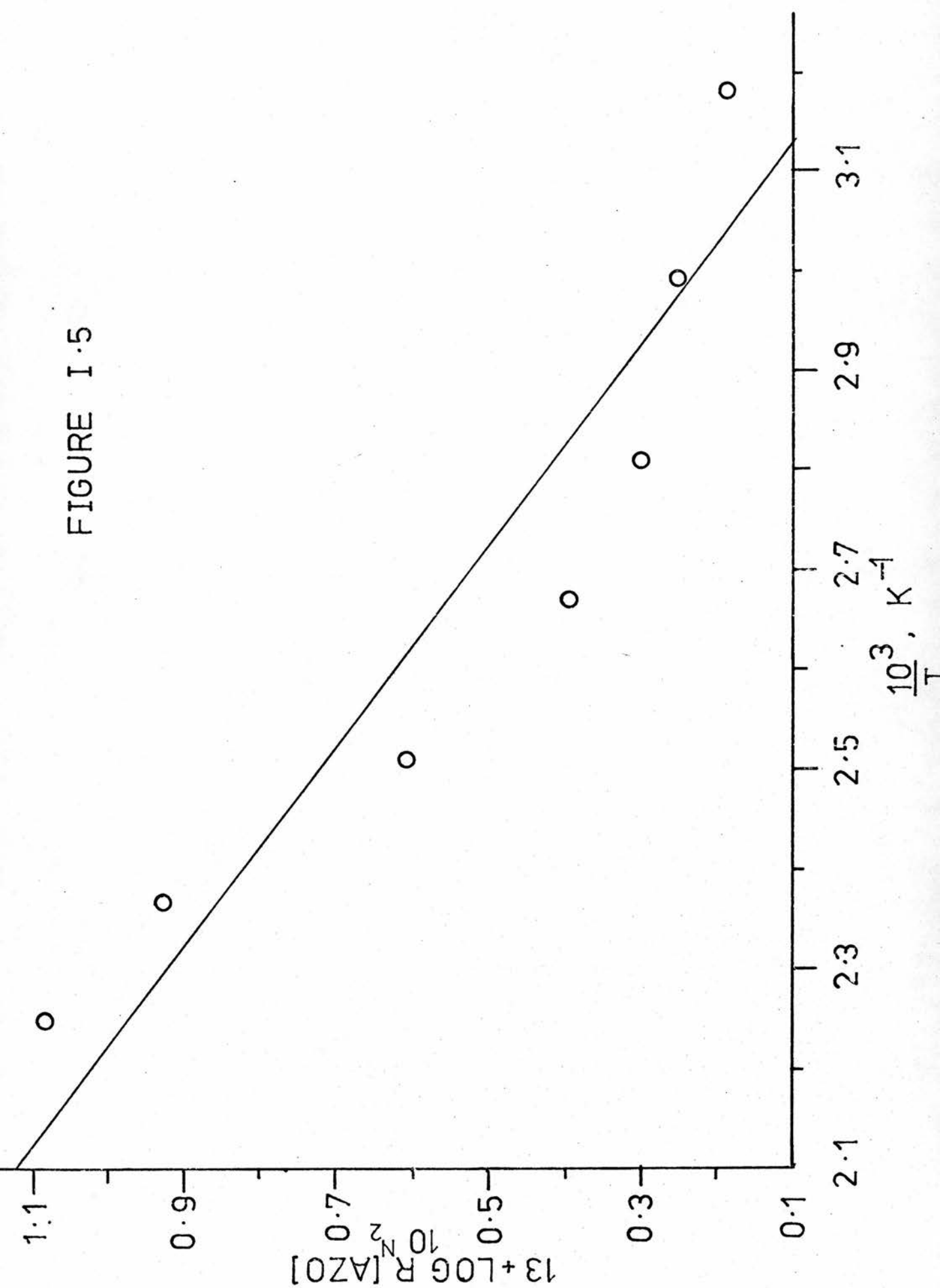
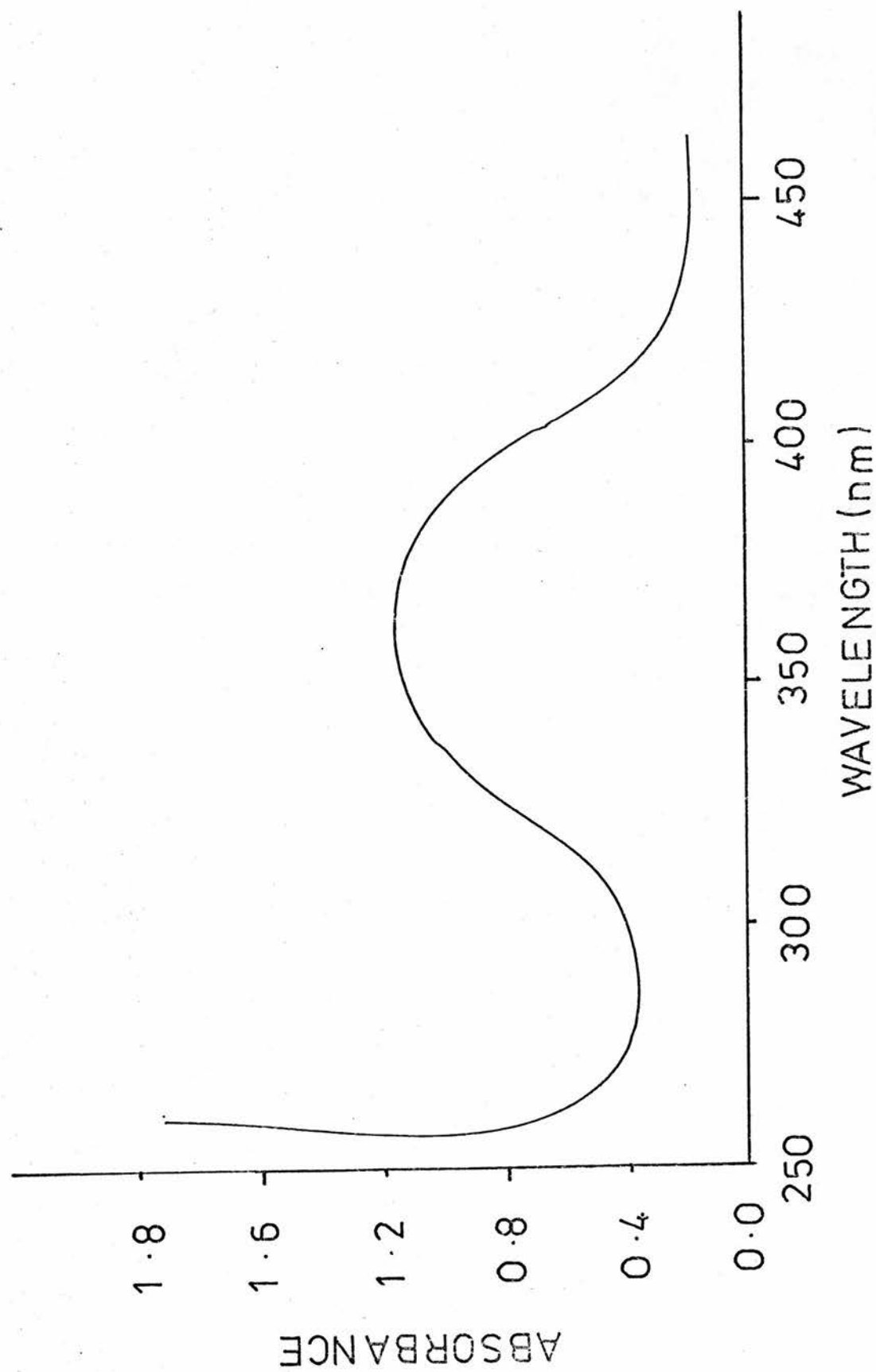


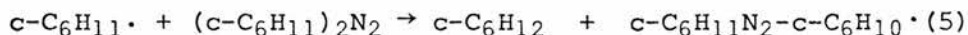
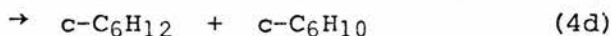
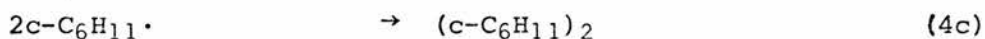
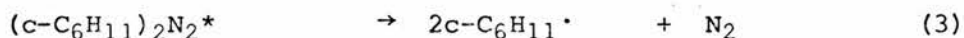
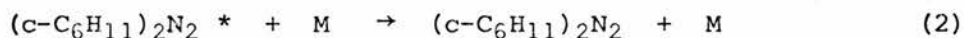
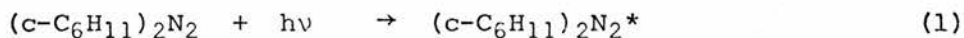
FIGURE I · 6



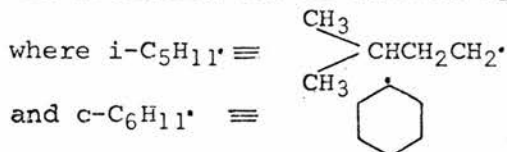
PART I

DISCUSSION

The ultraviolet absorption spectrum of azocyclohexane (fig. I.6) shows a maximum at 362 nm. This is in the same range as the absorption of other azoalkanes ⁴⁶, (trans azomethane, $\lambda_{\text{max}} = 340$ nm; trans azoethane, $\lambda_{\text{max}} = 355$ nm; trans azo-n-propane, $\lambda_{\text{max}} = 356$ nm; trans azo-n-butane, $\lambda_{\text{max}} = 368$ nm). It has been universally agreed that this weak transition at ~ 355 nm in the azoalkanes involves the excitation of an electron from the highest filled non-bonding orbital, n , to the lowest empty orbital π^* . The photolysis of azocyclohexane using a medium pressure mercury arc lamp through a 'pyrex' glass reaction vessel (313 nm and 366 nm) gave three products, which can be rationalized using the following reaction sequence.

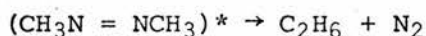


where $(c\text{-C}_6\text{H}_{11})_2\text{N}_2^*$ represents an excited state of azocyclohexane. The same mechanism as above applies for the photolysis of azoisopentane (>300 nm). The mechanism can be written by inserting $i\text{-C}_5\text{H}_{11}$ in place of $c\text{-C}_6\text{H}_{11}$ where $i\text{-C}_5\text{H}_{11}\cdot \equiv$



The products from the azoisopentane photolysis were 2-methylbutane ($i\text{-C}_5\text{H}_{12}$), 3-methylbut-1-ene ($i\text{-C}_5\text{H}_{10}$) and 2,7-dimethyloctane ($(i\text{-C}_5\text{H}_{11})_2$).

The above mechanism has already been used extensively by previous workers in this field.^{22,23,24,29,30,31} Some workers found that an intramolecular extrusion process occurs about 1% with azomethane^{22,47,48}



This process does not apply in the photolysis of azocyclohexane since in the presence of oxygen no bicyclohexyl was observed. In the azoisopentane system the addition of oxygen left only a trace of 2,7-dimethyloctane. The oxygen in these cases was acting as a very efficient radical scavenger.

Application of the steady-state approximation to reactions (1) through (5) yields the following equations:-

where $\text{R}^{\cdot} = \text{c-C}_6\text{H}_{11}^{\cdot}$ or $\text{i-C}_5\text{H}_{11}^{\cdot}$

$$\frac{d[\text{R}_2\text{N}_2]^*}{dt} = 0 = \text{Ia} - k_2[\text{R}_2\text{N}_2]^*[\text{M}] - k_3[\text{R}_2\text{N}_2]^*$$

$$\therefore [\text{R}_2\text{N}_2]^* = \frac{\text{Ia}}{k_3 + k_2[\text{M}]}$$

$$\text{since } \text{R}_{\text{N}_2} = k_3[\text{R}_2\text{N}_2]^*$$

$$\therefore \text{R}_{\text{N}_2} = \frac{k_3 \text{Ia}}{k_3 + k_2[\text{M}]} \quad (\text{A})$$

$$\text{From reaction (3) } \text{R}_{\text{N}_2} = 2\text{R}^{\cdot}$$

$$\therefore \text{R}_{\text{N}_2} = \text{R}_{\text{R(H)}} + \text{R}_{\text{R}_2} + \frac{1}{2} (\text{R}_{\text{RH}})_5 \quad (\text{B})$$

Where Ia = absorbed light intensity and R is the rate of formation of the indicated product. The final term in function (B) refers to the cyclohexane (RH) or isopentane (RH) formed in the hydrogen atom abstraction reaction (5) and can be estimated from,

$$(R_{RH})_5 = (R_{RH})_{\text{total}} - (R_{RH})_{4d}$$

since $(R_{RH})_{4d} = (R_{R(-H)})_{4d}$

$$\therefore (R_{RH})_5 = (R_{RH})_{\text{total}} - (R_{R(-H)})_{4d} \quad (C)$$

where the terms on the right hand side of equation (C) refer to the total cyclohexane or isopentane rate and the rate of cyclohexene or isopentene formed in the disproportionation reaction (4d) respectively.

Assuming a value of k_2 no larger than the collision number ($3.2 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$). Calvert and co-workers have determined the value of $k_3 \geq 2.5 \times 10^9 \exp -3,800 \text{ cal/RT s}^{-1}$ and $4.5 \times 10^9 \exp -4,800 \text{ cal/RT s}^{-1}$ for the unimolecular decomposition of electronically excited azo-n-butane³⁰ and azoisobutane³¹ respectively. Making the assumption that similar rate parameters will be applicable to azocyclohexane and azoisopentane photolyses, equation (A) can be written in the approximate form

$$R_{N_2} = \frac{k_3 I_a}{k_2 [R_2 N_2]} \quad (D)$$

Since $k_2 [M]$ is the dominant term in the denominator for the experimental conditions at temperatures below 160°C . This approximation can be made by considering the following argument.

Assuming reaction (2) occurs on every collision, then

$$\begin{aligned} k_2 [M] &= 3.2 \times 10^{11} \times 2.47 \times 10^{-4} & k_2 &= \text{collision number} \\ &= 7.9 \times 10^7 \text{ s}^{-1} & &= 3.2 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{and } [M] &= [R_2 N_2] \\ &= 2.47 \times 10^{-4} \text{ mol l}^{-1} \end{aligned}$$

for azocyclohexane.

taking $k_3 = 3.5 \times 10^9 \exp(-4,300/RT) \text{ s}^{-1}$

(k_3 is an average of Calvert and co-workers^{30,31} results)

at 87°C , $k_3 = 8.5 \times 10^6 \text{ s}^{-1}$

at 160°C , $k_3 = 2.3 \times 10^7 \text{ s}^{-1}$

(at 179°C , $k_3 = 2.9 \times 10^7 \text{ s}^{-1}$)

(at 187°C , $k_3 = 3.2 \times 10^7 \text{ s}^{-1}$)

These last two values are approaching too close to $k_2[M]$ to make assumption, $k_2[M] > k_3$.

Therefore the Arrhenius plot of function (D) was restricted to results obtained below 160°C . A reasonable Arrhenius plot was obtained (fig. I.3) for azocyclohexane and this yielded a value of the activation energy for the decomposition of excited azocyclohexane, $E_3 = 3.1 \text{ k cal mol}^{-1}$. This is in reasonable agreement with the results obtained by Calvert and co-workers of $3.8 \text{ k cal mol}^{-1}$ for the decomposition of excited azo-n-butane³⁰ and $4.8 \text{ k cal mol}^{-1}$ for excited azoisobutane³¹.

Using the same procedure for azoisopentane as was used for azocyclohexane, the results in table I.3 were used to obtain an Arrhenius plot (fig. I.5); yielding a value of the activation energy for the decomposition of excited azoisopentane, $E_3 = 4.5 \text{ k cal mol}^{-1}$. This value is in good agreement with the results obtained by Calvert and co-workers and also for the azocyclohexane study.

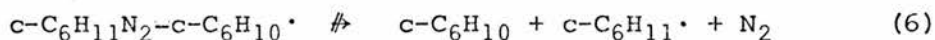
Turning to the azocyclohexane photolysis and assuming bicyclohexyl and cyclohexene are formed exclusively via the combination of cyclohexyl radicals from reaction (4) (P. 30) then the data in table I.1 can be used to provide an estimation for the ratio of the rate constants for disproportionation to combination. An estimate for the ratio $k_d/k_c = 0.99 \pm 0.10$ was found over the

temperature range 87-187°C. Neglecting experimental errors the ratio k_d/k_c for cyclohexyl radicals was found to be temperature independent over the range studied. At temperatures above 200°C a thermal reaction occurs, therefore the temperature was kept below 200°C for the kinetic runs. This temperature independence for the ratio k_d/k_c is in agreement with most other studies carried out in the gas phase. Calvert and co-workers have shown that there is no temperature dependence for k_d/k_c in the region 20-127°C for n-butyl³⁰ radicals and 20-168°C for isobutyl³¹ radicals. Gunning and Stock⁴⁹ found no temperature dependence for cyclopentyl radicals in the range 26- 250°C. It was mentioned earlier that certain workers had found a small activation energy difference between the disproportionation and combination processes, particularly in solution. Because of experimental errors the temperature dependence for k_d/k_c could go undetected.

Assuming that 2,7-dimethyloctane and 3-methylbut-1-ene are formed only from the combination of isopentyl radicals from reaction (4), (P. 30) then the data in table I.3 can be used to provide an estimate for k_d/k_c . This estimate was found to be, $k_d/k_c = 0.082 \pm .002$ over the temperature range 42-172°C. Neglecting experimental errors this ratio was also found to be temperature independent.

Photolysis studies of azoalkanes indicate a possible alternative path to reaction (4d) for the formation of cyclohexene or isopentene. Hydrogen atom abstraction from the parent azoalkane by the alkyl radical with subsequent decomposition of the ensuing radical has been proposed to account for the increased amounts of butene and isobutene formed in the higher temperature photolysis of azo-n-butane³⁰ and

azoisobutane ³¹ respectively. The consistency of the ratio k_d/k_c for cyclohexyl and isopentyl radicals suggests the analogous reaction for the formation of cyclohexene or isopentene is unimportant in the present work.



In the case of azoisopentane, there is the possibility that 3-methylbut-2-ene could be formed (abstraction of the tertiary hydrogen atom by the isopentyl radical). Since this compound is not observed and the ratio k_d/k_c remains constant with temperature this reaction can be neglected^{30,31}.

Presumably the major fate of the azocyclohexyl radicals formed in reaction (5) will be in radical-radical reactions either homogeneously or at the reaction vessel wall. In the case of the azoisopentyl radical a product peak was observed on chromatograms of reaction mixtures which has been tentatively identified as the combination product of two azoisopentyl radicals.

The determined value for $k_d/k_c = 0.99 \pm 0.10$ for the cyclohexyl radical obtained in this work is somewhat higher than the value of 0.45 estimated by Gunning et al ⁵⁰ using the mercury photosensitized decomposition of cyclohexane. However it is in excellent agreement with a more recently determined value of 1.1 ± 0.14 ⁵¹ determined in the liquid phase at 23°C, and may be compared with a value of 1.0 ⁴⁹ determined for cyclopentyl radicals in the gas phase. Table I.4 shows some values of k_d/k_c for cyclohexyl radicals in different phases. The results show a general agreement with the value found in this work.

TABLE I.4

Phase	k_d/k_c	Reference
gas	0.99 ± 0.1	this work
gas	0.45	50
liquid	1.1 ± 0.14	51
liquid	1.3 ± 0.4	52
liquid	1.47	53
liquid	1.25	54
solid	0.33 ± 0.2	55

As yet there have been no reported measurements for the ratio k_d/k_c for isopentyl radicals.

Sheldon and Kochi ³⁴ normalized the values of k_d/k_c by dividing through by the number of β -hydrogen atoms available for disproportionation. These ratios are quite consistent, 0.06 for primary radicals, 0.2 for secondary radicals and 0.8 for tertiary radicals. Table I.5 shows the normalized values for various radicals. The values used in the table for k_d/k_c are either the best estimate available or if there is some doubt then an average of the reported values.

The normalized value for the cyclohexyl radical is quite close to the values for other secondary radicals (0.2); the normalized value for the isopentyl radical is slightly lower than the predicted 0.06 for primary radicals.

TABLE 1.5

Radical	k_d/k_c	$k_d/k_c(n^b)$	Reference
$\text{CH}_3\text{CH}_2\cdot$	0.14	0.047	7
$\text{CH}_3\text{CH}_2\text{CH}_2\cdot$	0.16	0.08	7
$\text{CH}_3\dot{\text{C}}\text{HCH}_3$	0.69	0.115	56
$\text{CH}_3\dot{\text{C}}\text{HCH}_3$	1.2	0.2	34
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\cdot$	0.14	0.07	30
$(\text{CH}_3)_2\text{CHCH}_2\cdot$	0.075	0.075	31
$\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCH}_3$	$\sim 1.0^*$	0.2	7,34
$(\text{CH}_3)_3\text{C}\cdot$	$\sim 4.6^*$	0.51	7,34,38,57,58
$\text{c-C}_4\text{H}_7\cdot$	$\sim 0.475^*$	0.12	34
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$	0.2	0.1	59
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\cdot$	0.082	0.041	this work
$\text{c-C}_5\text{H}_9\cdot$	1.0	0.25	49
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$	0.14	0.07	60
$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$	0.14	0.07	7
$\text{c-C}_5\text{H}_9\text{CH}_2\cdot$	<0.1	<0.1	34
$\text{c-C}_6\text{H}_{11}\cdot$	0.99	0.25	this work
$\text{c-C}_8\text{H}_{15}\cdot$	0.52	0.13	61
$\text{c-C}_{10}\text{H}_{19}\cdot$	1.4	0.35	61

where (n^b) is the number of β -hydrogen atoms

* average of the reported values

The increase of the normalized value $k_d/k_{c(n^b)}$ in the order tertiary > secondary > primary must be influenced by other factors than purely statistical ones.

The increasing ratio of cyclohexane to cyclohexene and isopentane to isopentene can be satisfactorily explained by the hydrogen atom abstraction reaction (5). The rate data in table I.1 can be used to obtain rate parameters for hydrogen atom abstraction by cyclohexyl radicals, while the data in table I.3 can be used to obtain rate parameters for hydrogen atom abstraction by the isopentyl radical. The rate parameters can be found by the use of function (E).

$$\frac{k_5}{k_{4c}^{1/2}} = \frac{(R_{RH})_5}{R_{R_2}^{1/2} [R_2 N_2]} \quad (E)$$

where $R \cdot = c\text{-C}_6\text{H}_{11} \cdot$ or $i\text{-C}_5\text{H}_{11} \cdot$

Equation (E) is found as follows:-

$$\begin{aligned} R_{R_2} &= k_{4c} [R \cdot]^2 \\ (R_{RH})_5 &= k_5 [R \cdot] [R_2 N_2] \end{aligned}$$

$$\therefore \frac{(R_{RH})_5}{R_{R_2}^{1/2}} = \frac{k_5 [R_2 N_2]}{k_{4c}^{1/2}}$$

$$\frac{k_5}{k_{4c}^{1/2}} = \frac{(R_{RH})_5}{R_{R_2}^{1/2} [R_2 N_2]}$$

$$\text{where } (R_{RH})_5 = (R_{RH})_{\text{total}} - (R_{RH})_{4d}$$

$$\text{also } (R_{RH})_{4d} = (R_{R(-H)})_{4d}$$

By using the Arrhenius equation in the form $k = Ae^{-E/RT}$ and taking

logarithms,

$$\log_{10} \frac{(R_{RH})_5}{R_2^{1/2} [R_2N_2]} = \log_{10} \frac{A_5}{A_{4C}^{1/2}} - \frac{(E_5 - \frac{1}{2} E_{4C})}{2.303 RT}$$

An Arrhenius plot of $2 + \log_{10} \frac{(R_{RH})_5}{R_2^{1/2} [R_2N_2]}$ versus $10^3/T$

(for azocyclohexane, fig. I.2, P. 25) gave a straight line of slope

$$\frac{-(E_5 - \frac{1}{2} E_{4C})}{2.303R} \quad \text{and intercept} \quad \log_{10} \frac{A_5}{A_{4C}^{1/2}}$$

Least squares treatment gave,

$$\text{slope} = -1.45 \pm 0.23$$

$$\text{intercept} = 4.12 \pm 0.09$$

$$\therefore \frac{-(E_5 - \frac{1}{2} E_{4C})}{2.303R} = -1.45 \pm 0.23 \quad \text{and} \quad \log_{10} \frac{A_5}{A_{4C}^{1/2}} = 4.12 - 2.0$$

$$\therefore E_5 - \frac{1}{2} E_{4C} = 6.6 \pm 1.0 \text{ k cal mol}^{-1} \quad \text{and} \quad \log_{10} \frac{A_5}{A_{4C}^{1/2}} = 2.12 \pm 0.09$$

assuming, $E_{4C} = 0$

This relationship yields an estimate of

$$\frac{k_5}{k_{4C}^{1/2}} = 10^{2.1 \pm 0.1} \exp(-6,600 \pm 1,000 \text{ cal}/RT) \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$$

for cyclohexyl radicals.

An Arrhenius plot of $3 + \log_{10} \frac{(R_{RH})_5}{R_2^{1/2} [R_2N_2]}$ versus $10^3/T$

(for azoisopentane, fig. I.4, P. 27) gave a straight line of slope

$$\frac{-(E_5 - \frac{1}{2}E_{4C})}{2.303R} \text{ and intercept } \log_{10} \frac{A_5}{A_{4C}^{\frac{1}{2}}}$$

Least squares treatment gave,

$$\text{slope} = -1.455 \pm 0.32$$

$$\text{intercept} = 5.34 \pm 0.12$$

$$\therefore \frac{-(E_5 - \frac{1}{2}E_{4C})}{2.303R} = -1.455 \pm 0.32 \text{ and } \log_{10} \frac{A_5}{A_{4C}^{\frac{1}{2}}} = 5.34 - 3.0$$

$$\therefore E_5 - \frac{1}{2}E_{4C} = 6.7 \pm 1.5 \text{ and } \log_{10} \frac{A_5}{A_{4C}^{\frac{1}{2}}} = 2.34 \pm 0.12$$

assuming $E_{4C} = 0$

This relationship yields an estimate of

$$\frac{k_5}{k_{4C}^{\frac{1}{2}}} = 10^{2.3 \pm 0.1} \exp(-6,700 \pm 1,500 \text{ cal/RT}) \text{ l}^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}} \text{ s}^{-\frac{1}{2}}$$

for isopentyl radicals.

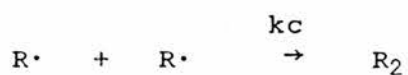
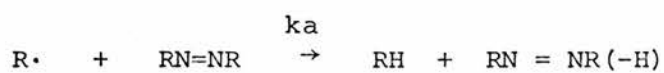
Taking the rate for combination of cyclohexyl radicals ⁶², $k_{4C} = 1.0 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$, independent of temperature, then $k_5 = 10^{5.6 \pm 0.1} \exp(-6,600 \pm 1,000 \text{ cal/RT}) \text{ l mol}^{-1} \text{ s}^{-1}$. This result is compared with previous data for alkyl radical hydrogen atom abstraction reactions involving azoalkanes, table I.6. (P. 41)

Taking the rate for combination of isopentyl radicals as similar to the rate for combination of ethyl radicals ²⁰, $k_{4C} = 10^{9.6} \text{ l mol}^{-1} \text{ s}^{-1}$, then $k_5 = 10^{7.1 \pm 0.1} \exp(-6,700 \pm 1,500 \text{ cal/RT}) \text{ l mol}^{-1} \text{ s}^{-1}$. This result is also compared with results from table I.6.

TABLE I.6

P	$\log_{10} \frac{A_a}{A_c^{1/2}}$ ($l^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$)	E_a (k cal mol ⁻¹)	Reference
CH ₃	3.3	8.7	47
	3.4	8.7	64
	3.4	8.6	38
C ₂ H ₅	2.7	7.5	65
	3.2	8.0	27
n-C ₃ H ₇	3.1	7.9	40
n-C ₄ H ₉	3.0	7.1	30
c-C ₆ H ₁₁	2.1	6.6	this work
i-C ₃ H ₇	1.9	6.5	66
	2.0	6.7	29
i-C ₄ H ₉	2.3	6.7	31
i-C ₅ H ₁₁	2.3	6.7	this work

Arrhenius Parameters for the Reactions



It is difficult to place the Arrhenius parameters for abstraction on an absolute scale since the combination rates for many of the radicals are not accurately known. However, all present evidence suggests that radical combination activation energies are close to zero. It is interesting to note that for the reactions where abstraction is from a secondary site (i.e. ethyl, n-propyl and n-butyl) the activation energies are in close agreement. Similar agreement is also found for the isopropyl and isobutyl radical results where a tertiary hydrogen atom abstraction occurs.

Cyclohexyl radicals are secondary radicals. They should abstract a secondary hydrogen atom from azocyclohexane. The activation energy for this abstraction compares well with those for similar abstraction reactions involving azoalkanes (table I.6. P. 41). The pre-exponential factor ratio is lower than the similar ratio for primary alkyl radicals. This means that, not only is the combination of cyclohexyl radicals considerably slower than ethyl radicals (k_c , cyclohexyl = $10^{7.0}$; k_c , ethyl = $10^{9.6}$ $\text{l mol}^{-1} \text{s}^{-1}$)²⁰, but radical transfer reactions such as hydrogen atom abstractions must also have lower A-factors. Comparison of the results for ethyl and isopropyl radicals reveals a similar trend. Although the reaction with isopropyl radicals involves a tertiary hydrogen atom abstraction it is difficult to understand the lowering of the ratio of A-factors $A_a/A_c^{1/2}$ by an order of magnitude. Since recent results suggest that the combination of isopropyl radicals is somewhat slower than that for ethyl radicals (k_c , isopropyl = $10^{8.6}$ $\text{l mol}^{-1} \text{s}^{-1}$)²⁰ (a more recent value of this combination rate by Golden and co-workers⁶³

found only a slight difference between the isopropyl value and the reported ethyl²⁰ value, k_c , isopropyl = $10^{9.5} \text{ l mol}^{-1} \text{ s}^{-1}$) a quite marked drop in the A-factor for isopropyl hydrogen atom abstraction is observed for isopropyl compared to ethyl radicals. It appears, therefore, that the slow combination of cyclohexyl radicals is not a special characteristic of the combination reaction, but is due to a group property at the radical itself.

The activation energy and pre-exponential factor ratio for isopentyl radicals abstracting a tertiary hydrogen atom from azoisopentane are consistent with the results of similar abstraction reactions from azoalkanes (table I.6. P. 41). The isopentyl results compare favourably with the results obtained for the isopropyl and isobutyl radicals. All three radicals abstract a tertiary hydrogen atom from the parent azoalkane.

From the photolysis of azoisopentane above 170°C , more products appear in the reaction mixture. These products must originate from the decomposition of the isopentyl radical. Similarly, the n-butyl³⁰ and isobutyl³¹ radicals have been shown to decompose at these temperatures. At $\sim 200^\circ\text{C}$ the main decomposition product, from the photolysis of azoisopentane, appears to be isobutane (2-methylpropane) with smaller amounts of propane and propene. Since isobutyl and n-propyl radicals are now present in the system, isomers of nonane and octane could now be formed; by combination of these radicals with isopentyl radicals. At present, 2,6-dimethylheptane has been tentatively identified from mass spectra data. The mechanism by which these decomposition products are formed is beyond the scope of this work.

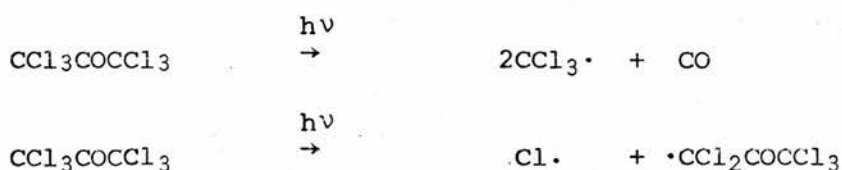
PART II

THE PHOTOLYSIS OF AZOCYCLOHEXANE IN THE
PRESENCE OF CYCLOHEXANE AND CARBON TETRACHLORIDE

PART II

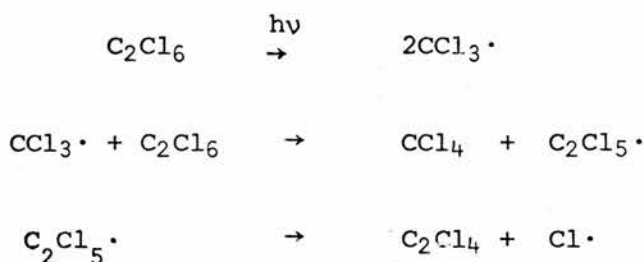
INTRODUCTION

The main difficulty in studying the trichloromethyl radical has been the limited number of convenient sources. Trifluoromethyl radicals can be produced from hexafluoroacetone. Trichloromethyl radicals can be produced in an analogous reaction from hexachloroacetone but the occurrence of another primary photolytic process yields chlorine atoms which are more reactive than the trichloromethyl radical.

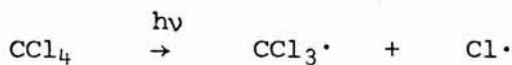


Hexachloroacetone is also too involatile for many purposes.

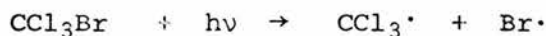
Hexachloroethane was originally reported not to yield trichloromethyl radicals but more recent work⁶⁷ showed that the primary initiation was trichloromethyl radical production. Subsequent reaction of the trichloromethyl radical again yielded the more reactive chlorine atom.



Wijnen and co-workers^{68,69,70} have studied the photolysis of carbon tetrachloride in the presence of ethane/ethylene mixtures and in the presence of ethyl chloride. Again chlorine atoms were formed which could either add to ethylene or abstract a hydrogen atom from ethane.



Bromotrichloromethane has been used successfully by a number of workers for the production of trichloromethyl radicals. The bromine atom produced is not as reactive as a chlorine atom.



Trichloromethyl radicals have also been produced from the γ -radiolysis of carbon tetrachloride⁷¹ or chloroform⁷². Both the above processes were used to study the telomerisation of ethylene.

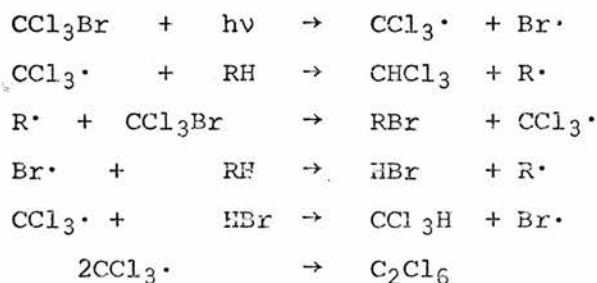
Most of the early work on trichloromethyl radicals involved liquid phase studies and were essentially qualitative in nature. A major contribution to this work was made by Karasch and co-workers^{73, 74} who studied the addition of halomethyl radicals to olefins.

To find the absolute values for the rates of addition to olefins by the trichloromethyl radical the rate of recombination of the radical must be known. The rate of combination of the trichloromethyl radical was first determined in the liquid phase by Melville and co-workers⁷⁵. Their value of $k = 10^{8.0} \text{ l mol}^{-1} \text{ s}^{-1}$ was later confirmed by Bengough and co-workers⁷⁶ under similar conditions. The first gas phase estimate was made by Goldfinger and his co-workers⁷⁷ who combined the rate data from studies of chlorination of several chloromethanes. Since this involves the ratios of a number of experimentally determined quantities an accumulation of errors can result. This seems to be the case since their value of $k = 10^{8.8}$

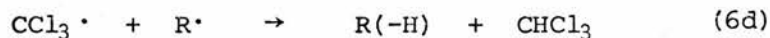
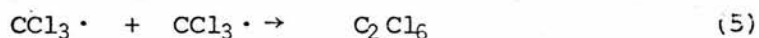
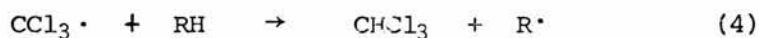
$1 \text{ mol}^{-1} \text{ s}^{-1}$, was nearly two powers of ten lower than the value obtained from a more recent rotating sector study by Tedder and Walton⁷⁸. Their system involved the photo-addition of bromotrichloromethane to ethylene. From their data the rate of combination of trichloromethyl radicals was $k = 10^{10.9} \text{ l mol}^{-1} \text{ s}^{-1}$. De Mare and Huybrechts¹⁶ measured the rate of combination of trichloromethyl radicals in the gas phase from the photochlorination of chloroform and found $k = 10^{9.66} \text{ l mol}^{-1} \text{ s}^{-1}$. Finally White and Kuntz¹⁷ measured the rate of combination from the photolysis of carbon tetrachloride in cyclohexane and found $k = 10^{9.59} \text{ l mol}^{-1} \text{ s}^{-1}$ and also from the pyrolysis of hexachloroethane, $k = 10^{9.7} \text{ l mol}^{-1} \text{ s}^{-1}$.

The Arrhenius parameters for the addition of trichloromethyl radicals to olefins have recently been recalculated by Tedder, Walton and Sidebottom⁸⁰ because the photolysis of bromotrichloromethane was found to be temperature dependent.

Relatively few radical transfer reactions of the trichloromethyl radical have been studied in the gas phase compared to the methyl and trifluoromethyl radicals. Tedder and McGrath⁸¹ studied the hydrogen atom abstraction reactions of the trichloromethyl radical from simple alkanes. This work was later extended by Tedder and Watson⁸². They generated the trichloromethyl radicals by photolysing bromotrichloromethane at 366 nm. The mechanism can be represented as follows:-



They showed that the major chain propagating step was hydrogen abstraction by trichloromethyl radicals rather than bromine atoms. This enabled them to determine the activation energy differences between a trichloromethyl radical abstracting a primary, secondary or tertiary hydrogen atom from substituted butanes. More recently Wampler and Kuntz⁸³ have obtained the Arrhenius parameters for the abstraction of hydrogen atoms from several alkanes by the trichloromethyl radical. They photolysed carbon tetrachloride in the presence of an alkane and showed the reaction proceeds via the following reaction scheme.



Under their experimental conditions reactions (6c) and (6d) did not occur to a detectable extent.

The most studied radical transfer reaction of the trichloromethyl radical is the abstraction of a hydrogen atom from cyclohexane. This reaction has been extensively studied in both the liquid and gas phase. The first liquid phase study was by Henglein and co-workers⁸⁴. They studied the γ -radiolysis of carbon tetrachloride and cyclohexane mixtures. They found a chain reaction operating which yielded

chloroform and chlorocyclohexane. The chain termination products were cyclohexene, bicyclohexyl, trichloromethylcyclohexane and hexachloroethane. The cyclohexene and bicyclohexyl products were probably formed together in the same solvent cage⁸⁵. Another liquid phase study was carried out by Stone and Dyne⁸⁶. They studied the γ -radiolysis of cyclohexane in dilute solutions of carbon tetrachloride and chloroform. They found a radical chain reaction was operating with chain termination by dimerisation of trichloromethyl radicals to give hexachloroethane. The cross-termination product, trichloromethylcyclohexane was also observed. Similarly, the cyclohexene and bicyclohexyl products could be formed within the solvent cage.

White and Kuntz¹⁷ studied the gas phase photolysis of carbon tetrachloride in cyclohexane, using the rotating sector technique. They reported that the only termination product under their experimental conditions was hexachloroethane and proposed that k_3 must be much greater than k_4 (see mechanism P. 47).

The purpose of this work was to reconcile the apparently conflicting results of Wijnen and Kuntz. Wijnen found all possible termination products from the photolysis of carbon tetrachloride and ethylene/ethane mixtures. Kuntz on the other hand found hexachloroethane as the sole termination product from the photolysis of carbon tetrachloride in cyclohexane. Kuntz's argument that $k_3 > k_4$ seems somewhat doubtful since k_4 is fast enough to produce chains of intermediate length. It appears from Wijnen's data that k_3 for ethyl radicals is sufficiently slow to allow termination in ethyl radicals, and it is not clear why the corresponding reaction for cyclohexyl radicals does not produce termination in cyclohexyl radicals. The first objective in the present work was to determine k_3 for cyclohexyl radicals.

PART II
EXPERIMENTAL

1. Materials

Carbon tetrachloride (Fisons analytical reagent) and cyclohexane (Fisons spectrograde reagent) showed no impurities on gas/liquid chromatographic analysis and were used without further purification. Cyclohexene (Fisons spectrograde reagent), chloroform (Fisons analytical reagent), chlorocyclohexane (B.D.H. laboratory reagent), hexachloroethane (Aldrich Chem. Co.) and bicyclohexyl (Aldrich Chem. Co.) were used without purification for identification purposes. Azocyclohexane was prepared as described in part I (section I).

2. Apparatus

The light intensity was varied by placing gauzes of different mesh sizes between the lamp and the reaction vessel. The gauze transmissions had previously been calibrated on a 'Unicam' SP800 ultraviolet spectrophotometer. For the gas phase reactions the same apparatus was used as described in part I (section I). The solution phase studies were carried out using a small cylindrical reaction vessel with two 'quartz' glass windows (dia. 2cm.) and internal volume 1.7 cm³.

3. Procedure

Carbon tetrachloride and cyclohexane were bulb to bulb distilled prior to use. For the gas phase studies the reactants were introduced into the reaction vessel as described in part I

(section I). For the solution phase studies a known weight of azocyclohexane was placed in the reaction vessel and then the vessel and contents were 'degassed' on the line. Known volumes and pressures of carbon tetrachloride and cyclohexane were distilled into the vessel by cooling the vessel in liquid nitrogen. The reaction vessel tap was closed and the vessel placed in front of the lamp. A shutter and a piece of 'pyrex' glass were fixed between the lamp and reaction vessel. The lamp was switched on and after 10 minutes the shutter was removed. After the reaction was completed the reaction vessel tap was opened slowly to the air and the contents poured into a small vial with a screw-on cap.

4. Analysis

The most satisfactory stationary phase for separating the products was 28.6% by weight tritolyl phosphate on 100-120 mesh Celite. The analysis was carried out as described in part I (Section I).

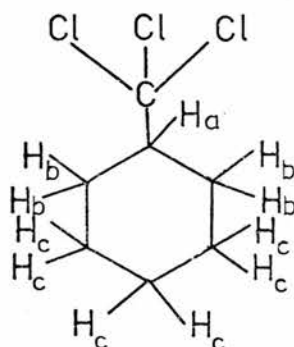
5. Identification of Products

For the gas phase reactions a typical chromatogram showed six product peaks. Cyclohexene, chlorocyclohexane, chloroform, hexachloroethane and bicyclohexyl were identified by comparison of retention times with those for authentic samples. From the liquid phase studies three product peaks were observed from a chromatogram of the reaction mixture. Chlorocyclohexane and chloroform were identified by comparison of retention times with

those for authentic samples. The unknown peak which appeared in the chromatograms of both the liquid and gas phase studies was tentatively identified as trichloromethylcyclohexane since it appeared on the chromatogram between the peaks for hexachloroethane and bicyclohexyl. Gas/liquid chromatographic coupled mass spectrometry confirmed the identification of the other product peaks but the breakdown pattern of the trichloromethylcyclohexane was not conclusive for absolute identification. Since this compound could not be synthesised easily a sample was collected from the solution phase studies. Several solution phase reactions were carried out using a 200-watt super high pressure mercury arc coupled to a Bausch and Lomb high-intensity monochromator as the light source ($\lambda=360$ nm). The combined reaction mixtures were then separated with a Pye 105 preparative chromatograph using a 7' glass column packed with 28.6% tritolyl phosphate at 120°C . The required sample was collected in a high efficiency trap cooled by liquid nitrogen. A nuclear magnetic resonance spectrum was run on a solution of the sample in carbon tetrachloride using a Varian HA-100 spectrometer at 100 Hz with tetramethylsilane as the internal standard.

N.M.R. Analysis Table II.1

τ	Statistical Weight	Multiplicity	No of Protons	Assignment
8.58	2	Singlet	1	Ha
8.43	13	Multiplet	6	Hc
7.63	9	Multiplet	4	Hb



6. Results

The products formed in the liquid phase photolysis of azocyclohexane in the presence of carbon tetrachloride and cyclohexane were chlorocyclohexane, chloroform and trichloromethylcyclohexane. The concentration for each of the products was found and the rates of their formation calculated.

1. Variation of Light Intensity

A series of experiments were carried out with fixed amounts of reactants and constant reaction time. The light intensity was varied by inserting wire gauzes between the light source and reaction vessel. A 'pyrex' glass filter was also present to allow only light of wavelength >300 nm to enter the reaction vessel thus precluding photolysis of carbon tetrachloride.

Table II.2

Relative Intensity %	[Azocyclohexane]	R_{CHCl_3}	R_{RCl}	R_{RCCl_3}
100	0.275	3.52	11.79	5.26
48	0.279	2.56	7.18	1.94
28	0.282	2.34	5.89	1.52

All Rates (R) in $\text{mol l}^{-1} \text{ s}^{-1} \times 10^7$

[], mols l^{-1}

$[\text{c-C}_6\text{H}_{12}] = 3.22$; $[\text{CCl}_4] = 1.288$

Reaction Time = $5.4 \times 10^4 \text{ s}$.

A least squares plot of $\log_{10} R_{\text{CHCl}_3}$ versus \log_{10} (relative intensity), (fig. II.1) gave a straight line of slope = 0.329 ± 0.13

A least squares plot of $\log_{10} R_{\text{RCl}}$ versus \log_{10} (relative intensity), (fig. II.1) gave a straight line of slope = 0.554 ± 0.15

A least squares plot of $\log_{10} R_{\text{RCCl}_3}$ versus \log_{10} (relative intensity), (fig. II.1) gave a straight line of slope = 0.997 ± 0.44

2. Variation of Reaction Time

A series of experiments were carried out with fixed amounts of reactants and constant light intensity but for various lengths of time.

Table II.3

Reaction Time	[Azocyclohexane]	$[\text{CHCl}_3] \times 10^2$	$[\text{RCl}] \times 10^2$	$[\text{RCCl}_3] \times 10^2$
11.64	0.290	2.84	8.54	4.31
5.82	0.285	1.78	6.54	2.67
2.91	0.285	0.87	2.84	0.80

Reaction time, $\text{s} \times 10^{-4}$

[], mols l^{-1}

Relative Intensity (%) = 100.

$[\text{c-C}_6\text{H}_{12}] = 3.22$;

$[\text{CCl}_4] = 1.288$

3. Variation of Reactant Concentrations

A series of experiments were carried out with constant light intensity over a fixed period of time. The concentrations of cyclohexane and carbon tetrachloride were varied.

Table II.4

[c-C ₆ H ₁₂]	[CCl ₄]	[Azocyclohexane]	[CHCl ₃] x 10 ²	[RCl] x 10 ²	[RCCl ₃] x 10 ²
3.22	0.32	0.223	1.77	8.42	3.38
0.32	3.22	0.224	2.62	5.86	3.07
4.51	0.19	0.224	2.27	7.10	3.69
1.61	1.61	0.225	2.30	4.38	2.38

[], mols l⁻¹

Reaction Time = 5.4 x 10⁴s

Relative Intensity (%) = 100

The products formed in the gas phase photolysis of azocyclohexane in the presence of carbon tetrachloride and cyclohexane were chlorocyclohexane, chloroform, hexachloroethane, trichloromethylcyclohexane, bicyclohexyl and cyclohexene. The concentration for each of the products in each reaction mixture was found and the rates of their formation calculated.

4. Variation of Reaction Temperature

A series of experiments were carried out with uniform light intensity and over a fixed period of time. The reactant concentrations remained constant within each series.

Table II.5 (Series A)

TEMP (°C)	R_{CHCl_3}	R_{RCI}	$R_{\text{C}_2\text{Cl}_6}$	R_{RCCl_3}	R_{R_2}	$R_{\text{R}(-\text{H})}$
130	1.21	1.33	-	0.389	-	-
146	1.55	1.90	0.140	0.327	0.168	0.146
149	1.70	2.98	0.180	0.285	0.183	0.159
155	2.84	4.21	0.286	0.461	0.128	0.102
170	5.15	6.96	0.403	0.427	0.102	0.102
202	10.80	14.10	0.689	0.389	0.107	0.126

All Rates (R) in $\text{mol l}^{-1} \text{ s}^{-1} \times 10^{10}$

[], $\text{mol l}^{-1} \times 10^4$ Reaction Time = $4.89 \times 10^4 \text{ s}$

$[\text{R}_2\text{N}_2] = 2.47$; $[\text{c-C}_6\text{H}_{12}] = 4.65$; $[\text{CCl}_4] = 11.2$

Table II.6 (Series B)

TEMP (°C)	R_{CHCl_3}	R_{RCI}	$R_{\text{C}_2\text{Cl}_6}$	R_{RCCl_3}	R_{R_2}	$R_{\text{R}(-\text{H})}$
111	1.23	1.08	-	0.511	-	-
135	2.48	2.20	-	0.511	-	-
148	3.03	2.29	0.141	0.389	-	-
162	5.05	6.41	0.205	0.386	0.202	0.182
177	8.06	8.24	0.286	0.368	0.164	0.164
201	10.80	11.90	0.205	0.429	0.307	0.327

All Rates (R) in $\text{mol l}^{-1} \text{ s}^{-1} \times 10^{10}$

[], $\text{mol l}^{-1} \times 10^4$ Reaction Time = $4.89 \times 10^4 \text{ s}$

$[\text{R}_2\text{N}_2] = 2.47$; $[\text{c-C}_6\text{H}_{12}] = 11.2$; $[\text{CCl}_4] = 4.65$

Table II.7 (Series A)

TEMP (°C)	$\frac{R_{\text{RCCl}_3}}{(R_{\text{C}_2\text{Cl}_6} \cdot R_{\text{R}_2})^{1/2}}$	$\frac{R_{\text{CHCl}_3} \times 10^2}{R_{\text{C}_2\text{Cl}_6}^{1/2} [\text{RH}]}$ ($1^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$)	$\frac{R_{\text{RCl}} \times 10^2}{R_{\text{R}_2}^{1/2} [\text{CCl}_4]}$ ($1^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$)	$\frac{R_{\text{CHCl}_3} \times R_{\text{RCl}} \times 10^4}{R_{\text{RCCl}_3} [\text{RH}] [\text{CCl}_4]}$ ($1 \text{ mol}^{-1} \text{ s}^{-1}$)
130	-	-	-	7.94
146	2.1	8.91	4.14	17.3
149	1.6	8.62	6.22	34.1
155	2.4	11.4	10.5	49.8
170	2.1	17.4	19.46	161
202	1.4	28.0	38.5	752

Series B

111	-	-	-	4.99
135	-	-	-	20.5
148	-	7.21	-	34.2
162	1.9	9.96	30.7	161
177	1.7	13.5	43.8	347
201	1.7	21.3	46.2	575

A least squares plot of $\log_{10} \frac{R_{\text{CHCl}_3} \times 10^2}{R_{\text{C}_2\text{Cl}_6} [\text{RH}]}$ versus $10^3/T$ (fig. II.3)

gave a straight line of slope = -2.18 ± 0.24

and intercept = 8.01 ± 0.13

A least squares plot of $\log_{10} \frac{R_{\text{CHCl}_3} \times R_{\text{RCl}} \times 10^4}{R_{\text{RCCl}_3} [\text{CCl}_4] [\text{RH}]}$ versus $10^3/T$ (fig. II.4)

gave a straight line of slope = -4.77 ± 0.84

and intercept = 12.92 ± 0.36

CAPTIONS FOR THE FIGURES

- Figure II.1 Plot of \log_{10} (rate of product formation) versus \log_{10} (relative intensity). (table II.2).
- Figure II.2 Plot of Concentration (products) versus Time (table II.3).
- Figure II.3 Plot of $\log_{10} \frac{R_{\text{CHCl}_3}}{R_{\text{C}_2\text{Cl}_6} [\text{RH}]}$ versus the reciprocal of temperature; open circles, data from the photolysis ($\lambda=250$ nm) of carbon tetrachloride-cyclohexane mixtures; closed circles, data from the photolysis ($\lambda>300$ nm) of the azocyclohexane, cyclohexane, carbon tetrachloride system, (table II.7). The open circle points were results furnished by Dr. H.W. Sidebottom⁹⁴.
- Figure II.4 Plot of $\log_{10} \frac{R_{\text{CHCl}_3} \times R_{\text{RCl}}}{R_{\text{RCCl}_3} [\text{RH}] [\text{CCl}_4]}$ versus the reciprocal of temperature; closed circles, data from Series A, open circles data from Series B (table II.7)

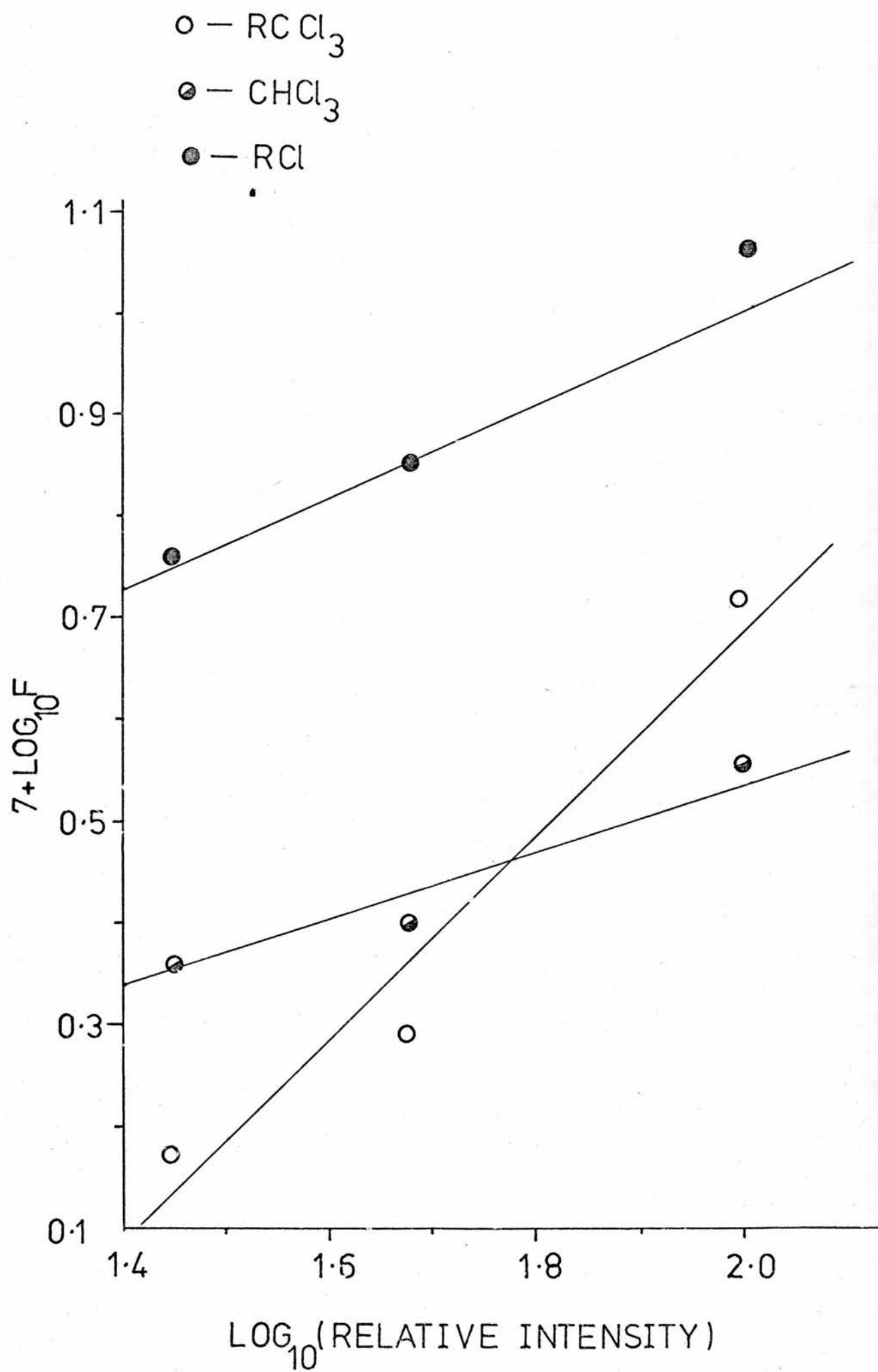
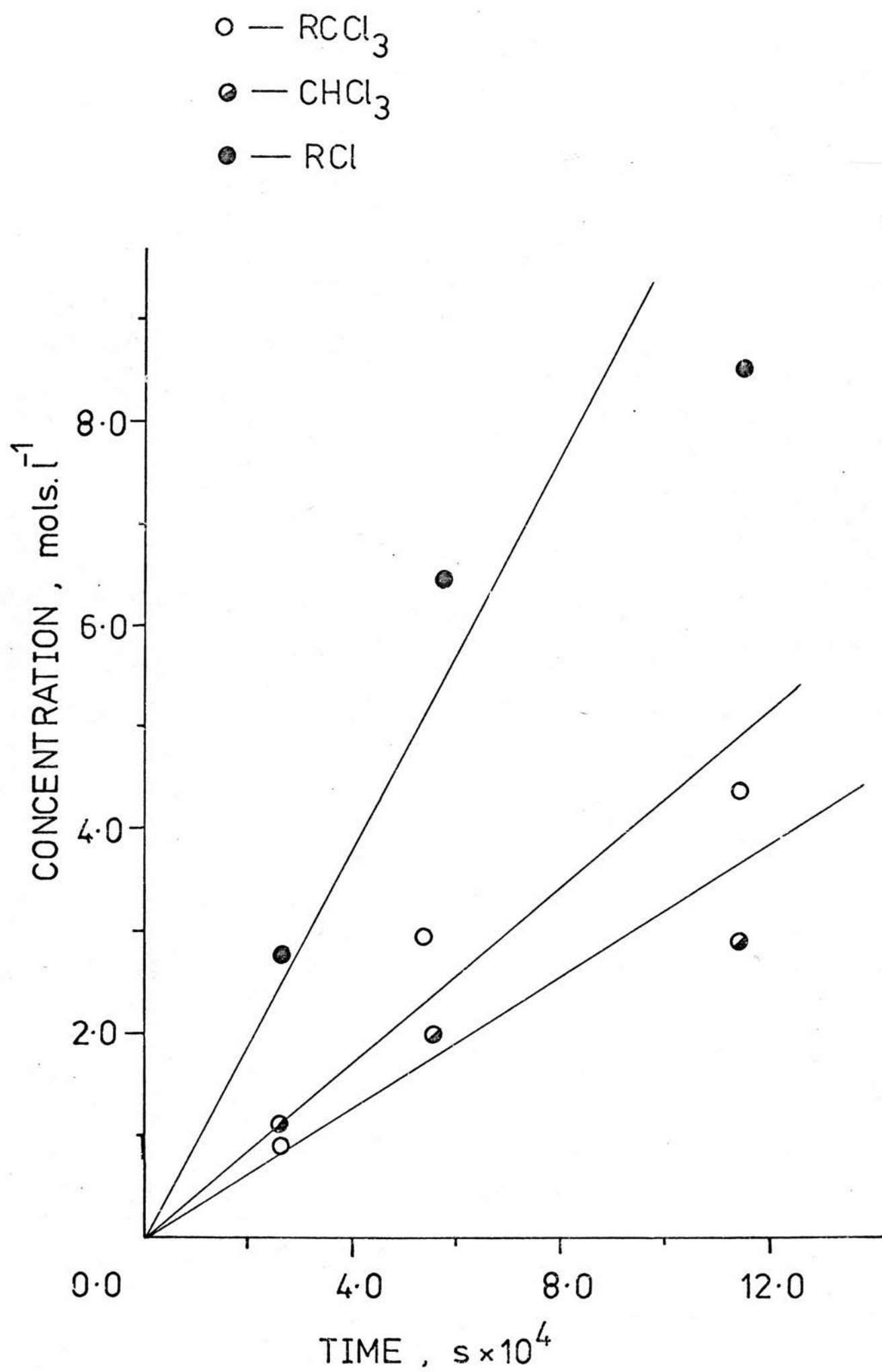
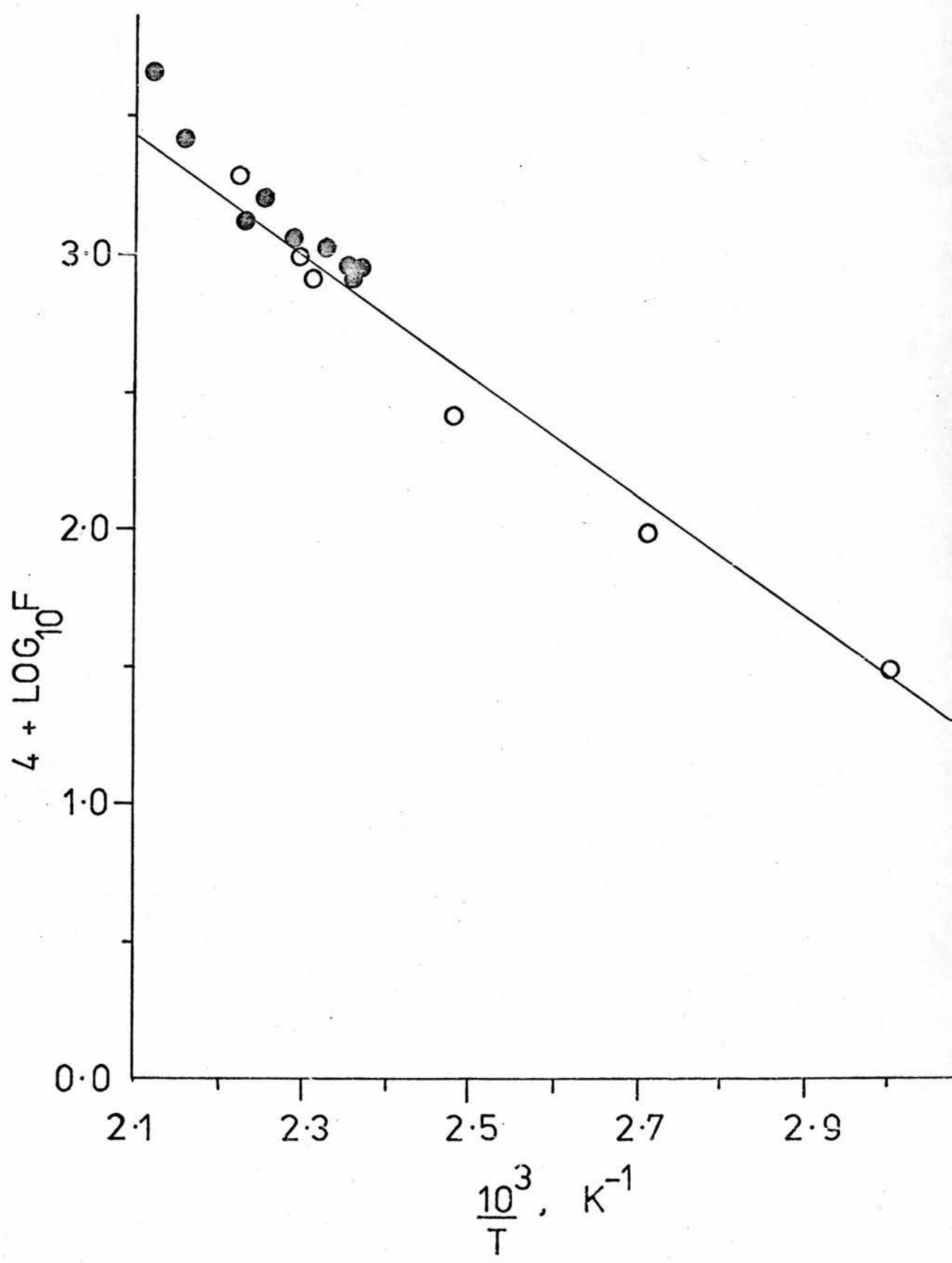
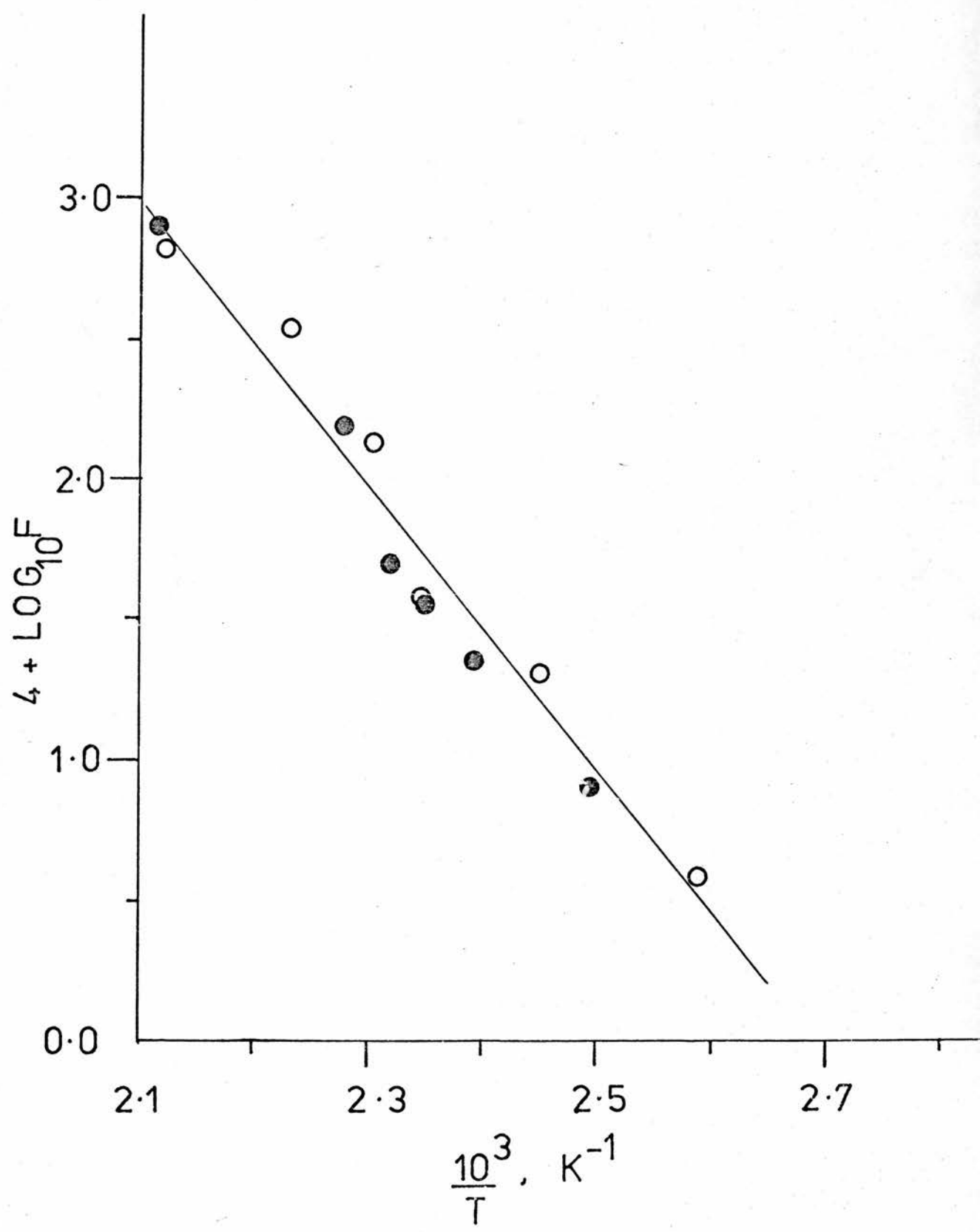


FIGURE II · 2







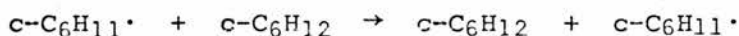
PART II
DISCUSSION

The photolysis of azocyclohexane has been fully discussed in Part I (section I). The important feature was that photolysis of azocyclohexane at >300 nm yielded cyclohexyl radicals and nitrogen. In the azocyclohexane-carbon tetrachloride-cyclohexane system, the production of cyclohexyl radicals is the initiation process.

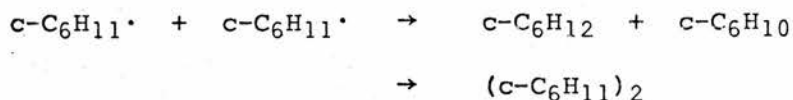
The cyclohexyl radical produced from the photolysis of azocyclohexane in carbon tetrachloride and cyclohexane has three possible reaction paths. It could abstract a chlorine atom from carbon tetrachloride thus producing the trichloromethyl radical.



The cyclohexyl radical could also abstract a hydrogen atom from cyclohexane but this would produce another cyclohexyl radical and a product indistinguishable from one of the reactants.



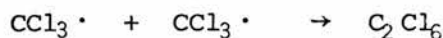
The radical could also terminate by disproportionation and combination.



The only other possible reaction which has not yet been mentioned is the abstraction of a hydrogen atom by the cyclohexyl radical from azocyclohexane. This reaction should have little importance since carbon tetrachloride is in large excess over azocyclohexane.

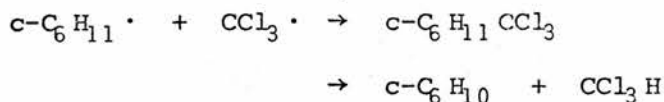
If chlorine atom abstraction is the main pathway for the cyclohexyl radical then the trichloromethyl radical formed has

several reactions possible.

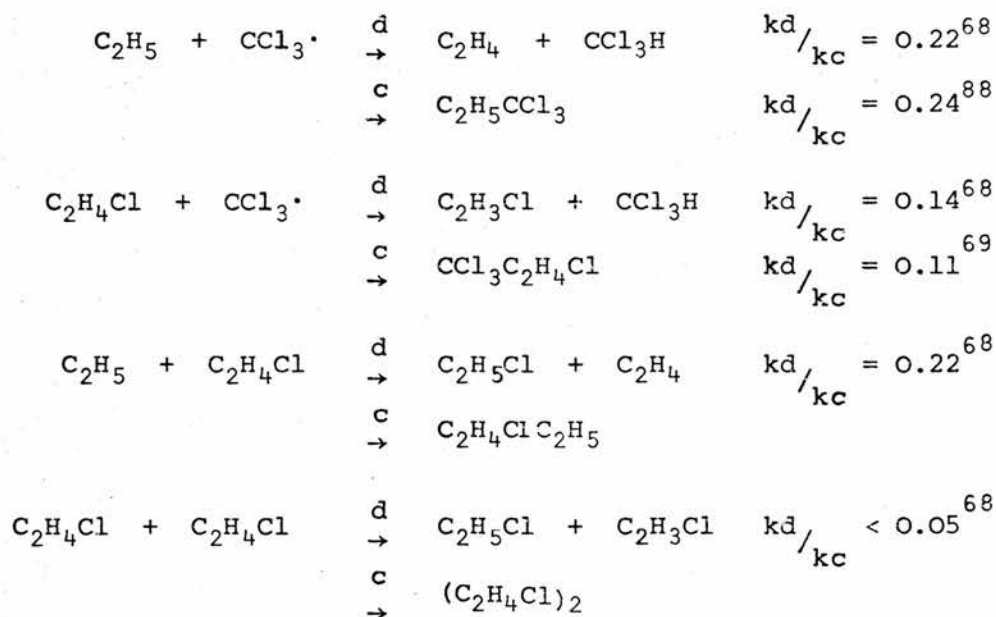


Again the abstraction of a hydrogen atom from azocyclohexane is highly unlikely due to the large excess of cyclohexane.

The only other reaction that is possible is the collision of a cyclohexyl and trichloromethyl radical to give the cross-combination or disproportionation products.



There appear to have been no reports of disproportionation involving trichloromethyl radicals⁸⁷ but the disproportionation to combination ratio for trichloromethyl and ethyl radicals is reported⁶⁸. Work has also been carried out on the disproportionation to combination ratios for some other haloalkyl radicals.

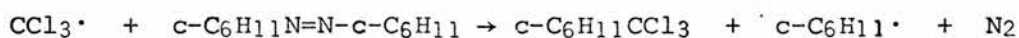


From these disproportionation to combination ratios one is led to expect extensive disproportionation between trichloromethyl and cyclohexyl radicals. From column 7 table II.5 (P. 55) appreciable amounts of cyclohexene are reported but these amounts arise from disproportionation between two cyclohexyl radicals. From part I (section I) the disproportionation to combination ratio for cyclohexyl radicals was calculated to be 0.99. Looking at columns 6 and 7 table II.5 (P. 55) the ratio between the rate of cyclohexene production and bicyclohexyl production is almost unity. The experimental error involved is probably sufficient to allow at least a small part of the cyclohexene to come from disproportionation between trichloromethyl and cyclohexyl radicals, but this is much smaller than expected. From the solution phase results table II.2 - table II.4, large amounts of trichloromethylcyclohexane are found, but no cyclohexene. This would indicate that disproportionation between trichloromethyl and cyclohexyl radicals is negligible.

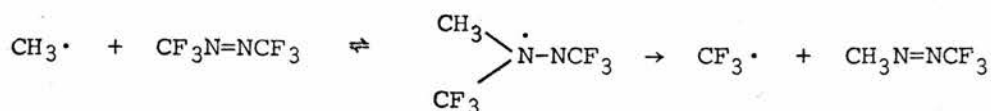
The important difference between previous studies^{17,84,86} and this work for the reactions of cyclohexyl radicals and trichloromethyl radicals is the presence of the azo-compound; the reactions of this compound with trichloromethyl radicals had to be investigated. The reaction of cyclohexyl radicals and the azo-compound can be neglected since from part I (section I) no reaction of this type was observed or has been reported from similar studies^{30,31} although this might only be true under certain conditions.

From the azocyclohexane experiments with carbon tetrachloride the major termination step was the formation of trichloromethylcyclohexane. This product was absent from the work of White and

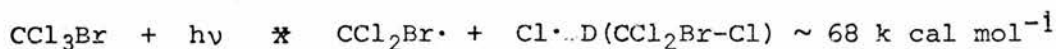
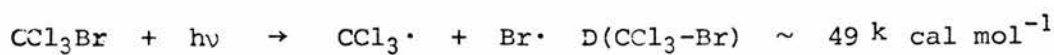
Kuntz¹⁷ who photolysed carbon tetrachloride in the presence of cyclohexane and found hexachloroethane as the only termination product. There exists the possibility that trichloromethyl-cyclohexane is not formed from trichloromethyl radicals and cyclohexyl radicals but from a direct reaction between trichloromethyl radicals and azocyclohexane.



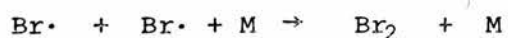
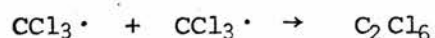
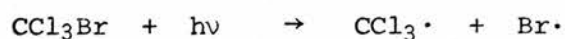
From the literature data available trifluoromethyl radicals can add across an azo double bond, while methyl radical addition to azo-compounds is well known⁸⁹.



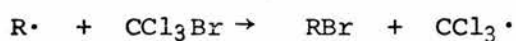
An experiment was carried out to test this reaction between trichloromethyl radicals and azocyclohexane. The source of trichloromethyl radicals was bromotrichloromethane since this compound does not produce the highly reactive chlorine atom. The light source was a 200 watt super high pressure mercury arc coupled to a Bausch and Lomb high intensity monochromator. This arrangement gave a monochromatic source of ultraviolet radiation centred at 250 nm with a 10 nm band width. The azocyclohexane should not be affected by light at this wavelength (see fig. I.6, P.29). Although there is sufficient energy in the light source to break the C-Cl bond in bromotrichloromethane it has been shown that only the weakest bond of a polyhalogenated methane is broken on photolysis i.e. C-Br bond.



The bromotrichloromethane (Schuchart Ltd.) was purified by preparative gas/liquid chromatography before use. Bromotrichloromethane ($1.68 \times 10^{-3} \text{ mol l}^{-1}$) and azocyclohexane ($1.73 \times 10^{-4} \text{ mol l}^{-1}$) were photolysed for four hours at 110°C in a cylindrical quartz reaction vessel (149 cm^3). The products were analysed as described in experimental section. The products obtained were chloroform, bromocyclohexane (trace) and hexachloroethane (main product). Bromine and hydrogen bromide were probably present in the system but were not analysed. From previous studies^{78,82,91} for the photolysis of bromotrichloromethane with alkenes or alkanes the following mechanism should be applicable:-

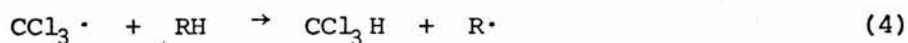
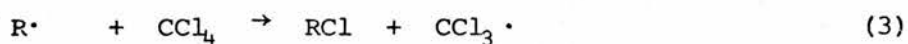
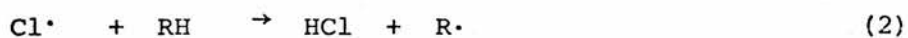
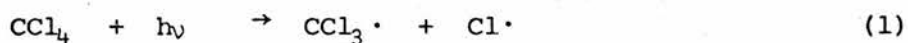


The most likely source of bromocyclohexane is from the photolysis of azocyclohexane (will probably absorb a small quantity of light even at low wavelengths) producing cyclohexyl radicals which will abstract a bromine atom from bromotrichloromethane.



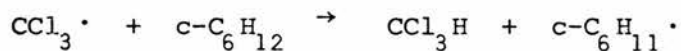
With the absence of trichloromethylcyclohexane the addition of trichloromethyl radicals to azocyclohexane to give trichloromethylcyclohexane can be neglected.

It has already been stated in the introduction to part II that the photolysis of carbon tetrachloride has been used by a number of workers as a source of trichloromethyl radicals. Wijnen and co-workers^{68,69,70} have studied the photolysis of carbon tetrachloride in the presence of ethane/ethylene mixtures and in the presence of ethyl chloride. Kuntz and his colleagues have investigated the photolysis of carbon tetrachloride in the presence of alkanes and cycloalkanes^{17,83}. Both groups suggest the same basic mechanism which can be summarised as follows:-



White and Kuntz¹⁷ studied the photolysis of carbon tetrachloride in the presence of cyclohexane and found the only termination product was hexachloroethane. They argued that $k_3 > k_4$ so that the steady state concentration of trichloromethyl radicals was greater than that of cyclohexyl radicals. From the results in this work (tables II.5 and II.6) chain lengths from between 2-8 require that k_3 is reasonably fast. On the other hand all three termination products are observed with the cross-termination product generally predominating.

Although the literature data available is limited it is also very contradictory. Mayo and Edwards⁹² studied the solution phase, thermal decomposition of acetyl peroxide and found that the methyl radicals produced abstract hydrogen atoms from cyclohexane five times faster than they abstract chlorine atoms from carbon tetrachloride. This result was obtained by measuring the methane and methyl chloride formed in the reaction. This result was put in doubt by the work of De Tar and Wells⁶⁰ who studied the reactivity of the 1-hexyl radical in abstracting hydrogen and halogen atoms. They argued that Mayo and Edwards had not taken into account the cross-transfer reaction which converts much of the solvent (carbon tetrachloride and cyclohexane) into chloroform and chlorocyclohexane.

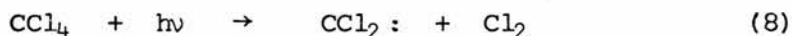


Since chloroform is a very good hydrogen atom-donor and a very poor chlorine atom-donor, the yield of methane would be higher than warranted by the reactivity of cyclohexane itself towards

the methyl radical. The solution phase results for the 1-hexyl radical shows that this radical abstracts a chlorine atom from carbon tetrachloride fifty times faster than a hydrogen atom from cyclohexane.

More recently Pritchard and co-workers⁹³ studied the reaction of methyl radicals with carbon tetrachloride in the gas phase and obtained k_3 ($R\cdot = \text{CH}_3\cdot$) = $10^{10.2} \exp -13,400 \text{ cal/RT}$. This contains an abnormally high pre-exponential term but even so leads one to predict a lower rate for k_3 than for k_4 in the 150°C temperature range for a system involving secondary alkyl radicals. Further evidence suggesting that chlorine atom abstraction from carbon tetrachloride is a difficult process comes from its reaction with trifluoromethyl radicals, k_3 ($R\cdot = \text{CF}_3\cdot$) = $10^{7.9} \exp -10,400 \text{ cal/RT}$.

Work in this laboratory by Sidebottom⁹⁴ on the photolysis of carbon tetrachloride and cyclohexane at 250nm gave results which are in excellent agreement with those of White and Kuntz¹⁷ over the temperature range they studied ($110 - 175^\circ\text{C}$). It has been generally accepted that the photolysis of carbon tetrachloride at 250 nm yields trichloromethyl radicals and chlorine atoms. However, another photolytic process was observed, yielding dichlorocarbene and molecular chlorine.



Although this alternative path makes only a minor contribution it can have an important effect in the low temperature, non-chain runs. Hexachloroethane was the only termination product observed not only in the region $110 - 175^\circ\text{C}$ but over the whole temperature

range investigated (35-285°C). It was found however that the yield of hexachloroethane decreases at temperatures above 160°C until at the highest temperatures only traces were detectable. It is convenient to consider the data in two halves,

a) up to 160°C

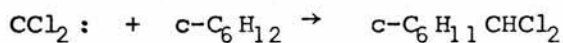
and

b) 160 - 285°C

At the lowest temperatures the reaction is in a non-chain region and the relation

$$R_{\text{RCI}} = R_{\text{CHCl}_3} + R_{\text{C}_2\text{Cl}_6}$$

should hold. Examination of the results shows that there is an excess of chlorocyclohexane. This can be explained by examining the subsidiary photochemical process, reaction (8, P.70). Both White and Kuntz and the present investigators have found small amounts of tetrachloroethylene and dichloromethylcyclohexane, which are presumably formed from dichlorocarbene.



Although the contribution from this alternative photolytic process is small it has an important effect in the non-chain region. Molecular chlorine will take part in the following transfer process



If the molecular chlorine is dissociated it will still lead to

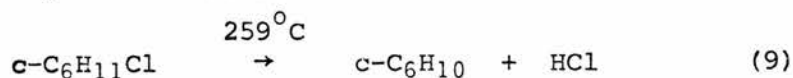
extra cyclohexyl radicals and hence to extra chlorocyclohexane.

In the remaining low temperature ($<160^{\circ}\text{C}$) runs the material balance is consistent with the mechanism.

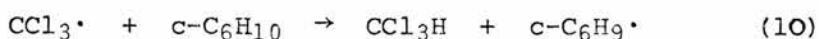
In the high temperature range the yield of C_2Cl_6 after reaching a maximum falls off with increasing temperature. At the same time the yield of cyclohexene increases. In this region the chains are long and according to the mechanism (P. 68)



should be observed. In practice it was found that $\text{RCHCl}_3 > \text{R-C}_6\text{H}_{11}\text{Cl}$, with the inequality increasing as the temperature rises. This could be due to an alternative route leading to chloroform or the loss of chlorocyclohexane. Extra chloroform could be derived from the disproportionation reaction (6d) but from the results already discussed this cannot be the explanation. Chlorocyclohexane shows no sign of photochemical decomposition under the experimental conditions used, but at temperatures above 160°C thermal decomposition sets in. A quantitative pyrolysis of chlorocyclohexane ($2.2 \times 10^{-3} \text{ mol l}^{-1}$) in a quartz reaction vessel (149 cm^3) at 259°C for 15 hours gave cyclohexene ($1.5 \times 10^{-4} \text{ mols l}^{-1}$) and hydrogen chloride (9) although cyclohexene was the only product analysed. The percentage decomposition was 6.8%.

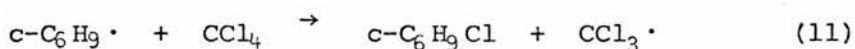


Cyclohexene has two allylic positions and reaction with trichloromethyl radicals is particularly facile⁹⁵.

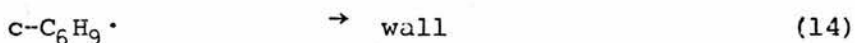
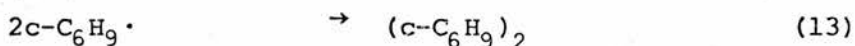
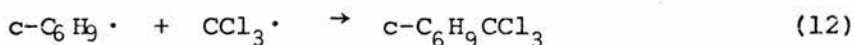


A similar experiment with hexachloroethane yielded only insignificant amounts of tetrachloroethylene.

Thermal decomposition of chlorocyclohexane thus increases the $[\text{CHCl}_3]_f/[\text{c-C}_6\text{H}_{11}\text{Cl}]_f$ ratio by both decreasing chlorocyclohexane and increasing chloroform. The high reactivity of cyclohexene means that it acts as a radical trap for trichloromethyl radicals; as the temperature increases above 160°C the yield of hexachloroethane decreases as more of the trichloromethyl radicals react with cyclohexene (10). When cyclohexene is added to the system the rate of production of hexachloroethane is almost completely suppressed. The fate of the unreactive cyclohexenyl radicals formed in reaction (10) is uncertain. Chlorine abstraction from carbon tetrachloride (11) is likely to be very slow and chlorocyclohexene is only found at high temperatures.



The main fate of such an unreactive allylic radical will be in termination reactions (12), (13) and (14).



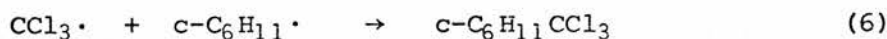
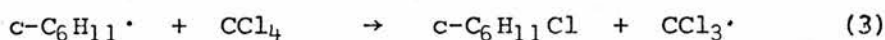
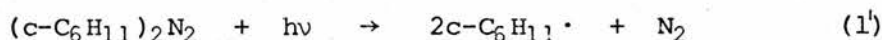
Small traces of trichloromethylcyclohexene were detected.

Photolysis of carbon tetrachloride in the presence of cyclohexane thus leads to a very complicated system. At low temperatures there is no chain process and the course of the reaction is entirely governed by the two initiation and the available

termination processes. At an intermediate temperature range a reasonable chain process involving reactions (3) and (4) is observed.

It is now convenient to look more closely at the results from the photolysis of azocyclohexane in the presence of carbon tetrachloride and cyclohexane.

The solution phase studies tables II.2 - II.4 (P. 52) yielded three products which can be explained by the following simple mechanism.



Application of the steady-state approximation to this mechanism gives the conditions,

$$\frac{d[CCl_3\cdot]}{dt} = 0 ; \quad \frac{d[c-C_6H_{11}\cdot]}{dt} = 0.$$

The rate of initiation can be expressed by Rate (1') = ϕI_a , where ϕ is the quantum yield for decomposition of azocyclohexane and I_a is the light absorbed.

Therefore ($R\cdot = c-C_6H_{11}\cdot$)

$$(i) \quad \frac{d[R\cdot]}{dt} = 0 = 2\phi I_a + k_4[CCl_3\cdot][RH] - k_3[R\cdot][CCl_4] - k_6[CCl_3\cdot][R\cdot]$$

$$(ii) \quad \frac{d[CCl_3 \cdot]}{dt} = 0 = k_3[R \cdot][CCl_4] - k_4[CCl_3 \cdot][RH] - k_6[CCl_3 \cdot][R \cdot]$$

Addition of (i) and (ii).

$$\begin{aligned} 0 &= 2\phi Ia - 2k_6[CCl_3 \cdot][R \cdot] \\ \therefore [CCl_3 \cdot] &= \frac{\phi Ia}{k_6[R \cdot]} \end{aligned} \quad (A)$$

since

$$\begin{aligned} \frac{d[RCCl_3]}{dt} &= k_6[R \cdot][CCl_3 \cdot] \\ &= \frac{k_6[R \cdot]\phi Ia}{k_6[R \cdot]} \\ &= \phi Ia \end{aligned} \quad (B)$$

Integrating if reaction goes to <5% conversion

$$\text{i.e.} \quad [RN = NR]_f = [RN = NR]_i \quad (f - \text{final, } i - \text{initial})$$

$$[RCCl_3]_f = \phi Ia \, t. \quad (C)$$

$$\text{since} \quad \frac{d[RC1]}{dt} = k_3[R \cdot][CCl_4]$$

$$\begin{aligned} \text{and} \quad \frac{d[CHCl_3]}{dt} &= k_4[CCl_3 \cdot][RH] \\ &= \frac{k_4[RH] \phi Ia}{k_6[R \cdot]} \quad (\text{from (A)}) \end{aligned}$$

$$\begin{aligned} \text{therefore} \quad \frac{d[RC1]}{dt} \times \frac{d[CHCl_3]}{dt} &= k_3[R \cdot][CCl_4] \times \frac{k_4[RH] \phi Ia}{k_6[R \cdot]} \\ &= \frac{k_3 k_4 [CCl_4][RH] \phi Ia}{k_6} \end{aligned}$$

Hence $[RCl]_f \times [CHCl_3]_f \propto I_a$

A straight forward relationship between the incident light intensity I_o , and the absorbed light intensity I_a can be derived by assuming that the Beer - Lambert law is obeyed.

ie.
$$\log_{10} \frac{I_o}{I_o - I_a} = \epsilon l [RN = NR]$$

where ϵ = molar extinction coefficient of azocyclohexane and l = the reaction cell path length (cm)

$\therefore \ln \frac{I_o}{I_o - I_a} = \beta l [RN = NR] \text{ where } \beta = 2.303$
($\text{cm}^{-1} \text{ l mol}^{-1}$)

$\therefore \frac{I_o}{I_o - I_a} = \exp (\beta l [RN = NR])$

$\therefore 1 - \frac{I_a}{I_o} = \exp (-\beta l [RN = NR])$

expanding the series

$$1 - \frac{I_a}{I_o} = 1 - \beta l [RN = NR] + \frac{\beta^2 l^2 [RN = NR]^2}{2!} \dots$$

Since β and $[RN = NR]$ are both small, only the first two terms of the expansion need be used. (compared to 1)

$$1 - \frac{I_a}{I_o} = 1 - \beta l [RN = NR]$$

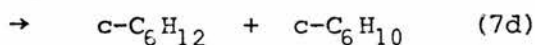
$\therefore I_a = I_o \beta l [RN = NR]$

Therefore I_a is always very small and directly proportional to I_o .

From a least squares plot of $\log_{10} R_{\text{RCl}}$ versus \log_{10} (relative intensity), (fig. II.1, P. 59) a straight line was obtained, the gradient of which was found to be 1.0 ± 0.44 . From equation (B) (P.75) the gradient required for a first order dependence of the termination product with light intensity should be 1.0. For the incident and absorbed intensity to be proportional to one another the concentration of absorber, azocyclohexane, must remain constant during these experiments. The rate of production of chain products has a $I^{1/2}$ dependence with the light intensity. Thus a log-log plot of rate of formation versus relative intensity gives a gradient of 0.55 ± 0.15 for RCl and 0.33 ± 0.13 for CHCl_3 (fig. II.1, P. 59).

From the results in table II.3 (P. 53) a plot of $[\text{RCCl}_3]$ versus time (fig. II.2, P. 60) was a straight line passing through the origin in agreement with equation (C) (P.75).

The photolysis of azocyclohexane in the presence of carbon tetrachloride and cyclohexane in the gas phase can best be described by the following reaction sequence.



The Rates (R) of product formation are given by:-

$$R_{\text{CHCl}_3} = k_4 [\text{CCl}_3 \cdot] [\text{RH}]$$

$$R_{\text{RCl}} = k_3 [\text{R} \cdot] [\text{CCl}_4]$$

$$R_{\text{RCCl}_3} = k_6 [\text{R} \cdot] [\text{CCl}_3 \cdot]$$

$$R_{\text{R}_2} = k_7 [\text{R} \cdot] [\text{R} \cdot]$$

Hence

$$\frac{R_{\text{CHCl}_3}}{R_{\text{C}_2\text{Cl}_6}^{\frac{1}{2}}} = \frac{k_4 [\text{RH}]}{k_5} \quad (\text{D})$$

By using the Arrhenius equation in the form $k = Ae^{-E/RT}$ and taking logarithms.

$$\log_{10} \frac{R_{\text{CHCl}_3}}{R_{\text{C}_2\text{Cl}_6}^{\frac{1}{2}} [\text{RH}]} = \log_{10} \frac{A_4}{A_5^{\frac{1}{2}}} - \frac{(E_4 - \frac{1}{2} E_5)}{2.303RT}$$

The plot of $4 + \log_{10} \frac{R_{\text{CHCl}_3}}{R_{\text{C}_2\text{Cl}_6}^{\frac{1}{2}} [\text{RH}]}$ versus $10^3/T$ (fig. II.3, P.61)

was a straight line of slope $= \frac{-(E_4 - \frac{1}{2} E_5)}{2.303R}$ and

intercept $\log_{10} \frac{A_4}{A_5^{\frac{1}{2}}}$

Least squares treatment gave, slope $= -2.18 \pm 0.24$

intercept $= 8.01 \pm 0.13$

$$\therefore \frac{-(E_4 - \frac{1}{2} E_5)}{2.303R} = -2.18 \pm 0.24 \text{ and } \log_{10} \frac{A_4}{A_5^{\frac{1}{2}}} = 8.01 - 4.0$$

$$\therefore E_4 - \frac{1}{2} E_5 = 10.0 \pm 1.0 = 4.01 \pm 0.13$$

Taking the rate of combination of trichloromethyl radicals⁹⁶ to be, $k_5 = 10^{9.7}$ (303 - 673°K) and assuming, $E_5 = 0$ then $E_4 = 10.0 \pm 1.0$ k cal mol⁻¹ and $\log_{10} A_4 = 8.86 \pm 0.13$. This gives a value of $k_4 = 10^{(8.86 \pm 0.13)} \exp(-10,000 \pm 1,000 \text{ cal/RT})$ which is in good agreement with the value of White and Kuntz¹⁷ ($k_4 = 10^{8.79} \exp(-10,700 \text{ cal/RT})$).

$$\text{also} \quad \frac{R_{\text{RCl}}}{R_{\text{R}_2}^{1/2}} = \frac{k_3 [\text{CCl}_4]}{k_7} \quad (\text{E})$$

The function (E) has not been used directly to obtain Arrhenius parameters, since measurable amounts of the combination product bicyclohexyl were not formed over the complete temperature range. However, the rate constant ratio calculated from this function in the high temperature range, $k_3/k_7^{1/2}$ (table II.7), are in excellent agreement with the Arrhenius parameters derived from equation (F) below.

$$\frac{R_{\text{RCl}} \times R_{\text{CHCl}_3}}{R_{\text{RCCl}_3}} = \frac{k_3 k_4}{k_6} [\text{CCl}_4] [\text{RH}] \quad (\text{F})$$

By using the Arrhenius equation in the form $k = A e^{-E/RT}$ and taking logarithms,

$$\log_{10} \frac{R_{\text{RCl}} \times R_{\text{CHCl}_3}}{R_{\text{RCCl}_3} [\text{CCl}_4] [\text{RH}]} = \log_{10} \frac{A_3 A_4}{A_6} - \frac{(E_3 + E_4 - E_6)}{2.303RT}$$

Plotting $4 + \log_{10} \frac{R_{\text{RCl}} \times R_{\text{CHCl}_3}}{R_{\text{RCCl}_3} [\text{CCl}_4] [\text{RH}]}$ against $10^3/T$ (fig. II.4, P.62)

a straight line was obtained of slope $-\frac{(E_3 + E_4 - E_6)}{2.303R}$

and intercept $\log_{10} \frac{A_3 A_4}{A_6}$

Least squares treatment gave, slope = -4.77 ± 0.84

intercept = 12.92 ± 0.36

$$\therefore \frac{-(E_3 + E_4 - E_6)}{2.303R} = -4.77 \pm 0.84 \text{ and } \log_{10} \frac{A_3 A_4}{A_6} = 12.92 - 4.0$$

$$\therefore E_3 + E_4 - E_6 = 21.8 \pm 3.5 = 8.92 \pm 0.36$$

Assuming $E_6 = 0$ and $E_4 = 10.0 \text{ k cal mol}^{-1}$

then $E_3 = 11.8 \pm 3.5 \text{ k cal mol}^{-1}$

and $\log_{10} A_4 = 8.86$

therefore $\log_{10} \frac{A_3}{A_6} = 0.1 \pm 0.5$

Since the rate of combination of cyclohexyl radicals is unknown it is not possible to separate the ratio of pre-exponential factors $\frac{A_3}{A_6}$, however an upper limit can be determined on A_3 . The kinetic parameters for chlorine abstraction from carbon tetrachloride by methyl and ethyl radicals have recently been determined in this laboratory⁹⁶,

$$k_3 (R\cdot = \text{CH}_3\cdot) = 10^{8.6} \exp (-9,100 \text{ cal}/RT) \quad \text{and}$$

$$k_3 (R\cdot = \text{C}_2\text{H}_5\cdot) = 10^{8.4} \exp (-8,900 \text{ cal}/RT).$$

Since cyclohexyl radicals will if anything have more stringent steric requirements than methyl or ethyl radicals we can regard $\log_{10} A_3 = 8.6$ as an upper limit, leading to a value of $\log_{10} k_6 (384 - 475^\circ \text{K}) \leq 8.5$. By using the relationship,

$$\frac{k_6}{(k_5 \cdot k_7)^{1/2}} = 1.8 \quad (\text{table II.7, P.56})$$

a limit can be found for the rate of combination of cyclohexyl radicals.

$$\log_{10} k_7 (384 - 475^\circ\text{K}) \leq 7.0$$

This very low value for the combination of cyclohexyl radicals is consistent with the recent value reported for the combination of t-butyl radicals $\log_{10} k (462^\circ\text{K}) = 5.6$, determined by Benson and co-workers⁹⁷. This low value for combination of cyclohexyl radicals is the reason why hexachloroethane is the only termination product in the gas phase photolysis of carbon tetrachloride in the presence of cyclohexane.

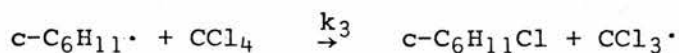
Table II.8 compares the activation energy found in this work with those of other alkanes, for reaction (4).

TABLE II.8 Arrhenius Parameters for the Reaction
 $\text{CCl}_3\cdot + \text{RH} \rightarrow \text{CCl}_3\text{H} + \text{R}\cdot \quad (4)$

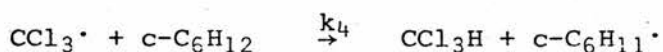
RH	$\log_{10} A$ ($1 \text{ mol}^{-1} \text{ s}^{-1}$)	E (k cal mol^{-1})	Reference
c-C ₅ H ₁₀	9.0	10.7	83
c-C ₆ H ₁₂	8.79	10.7	17
c-C ₆ H ₁₂	8.86	10.0	this work
n-C ₆ H ₁₄	8.81	10.8	83
(CH ₃) ₂ CHCH(CH ₃) ₂	7.88	8.2	83
c-C ₇ H ₁₄	9.07	9.9	83
c-C ₆ H ₁₁ CH ₃	8.75	9.9	83
c-C ₈ H ₁₆	9.11	9.6	83

The solution phase studies gave trichloromethylcyclohexane as the only termination product. This can be explained by considering the chain reactions are occurring within a solvent cage, thus ensuring that termination can only occur between a trichloromethyl and a cyclohexyl radical.

The results from this section have been used to calculate the two rate constants k_3 and k_4 , which were found to be very similar.



$$k_3 = 10^{8.6} \exp(-11,800 \pm 3000 \text{ cal/RT})$$



$$k_4 = 10^{8.86 \pm 0.13} \exp(-10,000 \pm 1000 \text{ cal/RT})$$

These values put in doubt the argument of White and Kuntz and lead one to the more logical conclusion that the slow rate of cyclohexyl combination is the reason why hexachloroethane is the only termination product observed from the photolysis of carbon tetrachloride and cyclohexane.

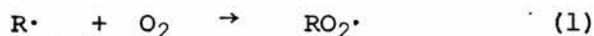
PART III
INTRODUCTION

One of the largest fields of chemical research has been devoted to the study of alkanes with molecular oxygen. The oxidation of hydrocarbons can be considered in three main stages. The first stage involves the slow oxidation of hydrocarbons at low temperatures ($<250^{\circ}\text{C}$). Results from these oxidations indicate that reactions in the gas phase are very similar to reactions in weakly polar solvents.

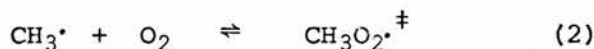
The second stage occurs when the reaction enters the cool flame region ($250\text{--}400^{\circ}\text{C}$), this region is characterised by induction periods and the appearance of pressure peaks. The final stage involves auto-acceleration as the reaction approaches the explosion limit ($>420^{\circ}\text{C}$).

One of the most studied reactions has been that between hydrogen and oxygen to form water⁹⁸. The overall reaction sequence contains ~ 13 steps.

A vast amount of work has been compiled on hydrocarbon oxidation, yet many of the reaction sequences are not understood. The primary step in the oxidation of alkyl radicals has been known for many years. This involves the generation of a peroxy radical^{99,100,101}.

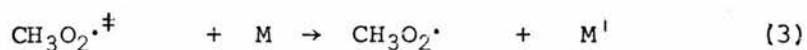


For methyl radicals this process (1) is reversible. Previous workers^{102,103} found that this reaction proceeds with third-order kinetics.



suggesting the establishment of an equilibrium between the energy rich radical $\text{CH}_3\text{O}_2\cdot^{\ddagger}$ and its dissociation products in (2).

Reaction (3) shows how the energy rich $\text{CH}_3\text{O}_2^\cdot$ radical is stabilized through loss of energy by collision.



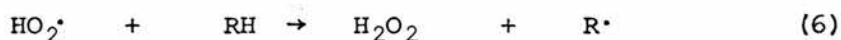
In the case of higher alkyl radicals this third body should not be required. These radicals have adequate modes of freedom to dissipate the excess energy.

For low temperature oxidations in the liquid phase, the main fate of the alkyl peroxy radical will be in hydrogen atom abstraction from the substrate (RH), to give the alkyl hydroperoxide.



Although reaction (4) will only proceed rapidly if the bond that is formed (ROO-H) is at least as strong as the bond that is broken (R-H), other factors can play an important role. Ingold and co-workers¹⁰⁴ have found that steric hindrance and polar effects exhibited by both the attacking radical and substrate can also affect the rate of hydrogen atom abstraction by the alkyl peroxy radical.

For higher temperature oxidations ($>250^\circ\text{C}$), the major product is the conjugate olefin, formed in reaction (5);



with the HO_2^\cdot radical continuing the chain. From the oxidations of ethane¹⁰⁵, propane¹⁰⁶ and isobutane^{107, 108}, about 80% of the initial oxidation product is the conjugate olefin. From the oxidation of higher alkanes, hexane^{109, 110} and 2-methylpentane^{111, 112} only relatively small amounts of the conjugate olefin are produced.

The reactions of the alkyl peroxy radical are not well known, but one reaction that is well characterised in both liquid and gas phases is the formation of alkoxy radicals^{113,114}.



The abstraction of hydrogen atoms by the alkyl peroxy radical is expected to be generally slow in the gas phase, except for weakly bound hydrogen atoms. Benson¹¹⁵ has estimated the bond dissociation energies $D^0(\text{RO}_2\text{-H})$ are about 90 ± 2 k cal. Using this value in conjunction with the bond dissociation energies given in Table III.1, one would expect rapid hydrogen atom abstraction from tertiary C - H bonds, from aldehydes and from H-Br. Abstraction from secondary C-H bonds are expected to be generally slow and very much slower for primary C-H bonds.

TABLE III.1

	D^0 (k cal)
C-H (3°)	91.7
C-H (aldehyde)	86.0
H-Br	87.0
C-H (2°)	94.5
C-H (1°)	98.0

In general, primary and secondary peroxy radicals appear to be more reactive than tertiary peroxy radicals in abstraction reactions^{116,117}.

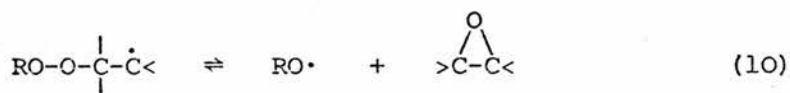
The alkyl peroxy radical can add to olefins.



A vast amount of addition work has been carried out by Mayo and co-workers^{118,119}. They found that the alkyl peroxy radical always adds to the double bond so as to produce the more stable β -peroxy alkyl radical (9). When the double bond

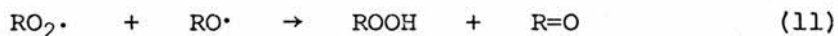


is conjugated with an aromatic carbonyl or another vinyl group, addition is favoured over abstraction of an allylic hydrogen atom. However, even olefins which give mainly hydroperoxides form some addition products¹²⁰. With the free valence on the β -carbon atom of an alkyl peroxy radical, epoxides are usually formed¹²¹.



At higher temperatures ($>350^\circ\text{C}$) these epoxides will readily isomerise to aldehydes.

In the absence of olefins and available hydrogen atoms for abstraction, the only fate of the alkyl peroxy radicals are in radical-radical reactions. This should be especially relevant in low temperature oxidation studies. Since the alkyl peroxy radical is a relatively inert radical^{115,122} it is expected to be an important participant in termination processes. Reaction with another alkyl peroxy radical results in alkoxy radicals (7); reaction with an alkoxy radical will result in the formation of the alkyl hydroperoxide and either an aldehyde or ketone.

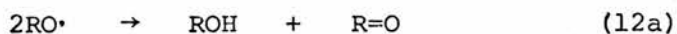


Reaction of alkyl peroxy radicals with alkyl radicals is unlikely since all alkyl radicals in the system will be readily scavenged by oxygen molecules present.

Alkyl peroxy radicals can undergo internal hydrogen atom abstraction¹²²⁻¹²⁵ reactions both in the gas and liquid phases. Recent work¹²⁴ shows that chain branching can suppress intramolecular abstraction through steric hindrance. The intramolecular process is most favourable when a six-membered transition state is involved.

Alkoxy radicals can abstract hydrogen atoms as is demonstrated by the methoxy radical^{127,128}.

Radical-radical reactions of the alkoxy radical have been mentioned previously except for reaction with themselves. This reaction produces an alcohol and either an aldehyde or ketone (12a). It can also give the dialkyl peroxide (12b).

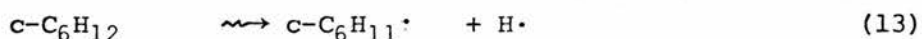


The Oxidation of Cyclohexane

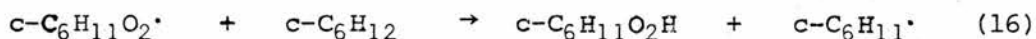
Cyclohexane has been extensively used by workers in the field of hydrocarbon oxidation. The cool flame combustion of cyclohexane^{129,130} involves intramolecular decomposition of the peroxy radical which leads to many open chain aldehydes and ketones, containing from two to six carbon atoms. Also, many of the lower hydrocarbons are observed.

The radiolytic oxidation of liquid cyclohexane has also attracted considerable attention as a simple model system for low temperature hydrocarbon studies¹³¹⁻¹³⁶. The major products of the reaction are cyclohexanol and cyclohexanone, formed in approximately equal amounts, together with smaller quantities of cyclohexyl hydroperoxide and cyclohexene.

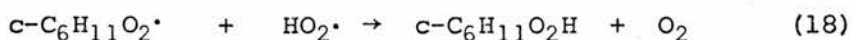
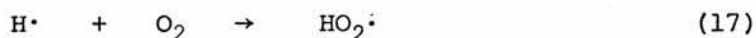
From the gamma or electron radiolysis of cyclohexane very little bicyclohexyl is observed. This confirms that the cyclohexyl radicals formed are efficiently scavenged by molecular oxygen, producing cyclohexyl peroxy radicals. The mutual combination of these radicals is generally assumed to be responsible for the formation of cyclohexanol and cyclohexanone in the overall reaction (15).



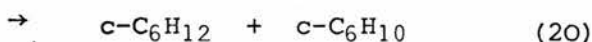
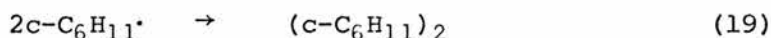
The above mechanism is consistent with the near equal amounts of cyclohexanone and cyclohexanol formed. McCarthy and MacLachlan¹³³ confirmed this mechanism by observing that cyclohexyl peroxy radicals disappeared by a bimolecular process from the radiation-induced reaction between cyclohexane and oxygen. Other workers have found that the relative yield of cyclohexyl hydroperoxide was independent of the radiation intensity, indicating the unimportance of the chain propagating reaction (16).



The hydroperoxide is most likely formed from reactions (17) and (18).



Cyclohexene is probably not formed from the combination of cyclohexyl radicals (20)



since large amounts of cyclohexene remain after the addition of oxygen, while bicyclohexyl formation is almost completely suppressed.

The most likely source of cyclohexene is from reaction (21).



through the reaction of a cyclohexyl radical and the sibling hydrogen atom immediately after their formation within the cage of surrounding molecules.

The absence of cyclohexene in the products from the photo-oxidation of diphenylmercury-cyclohexane mixtures supports this hypothesis, since the system provides a source of cyclohexyl radicals without an associated H-atom¹³⁷.

The present work was initiated in order to study the reaction of cyclohexyl radicals with molecular oxygen from about room temperature to just below the cool flame region. In particular, it was hoped to examine the reactions of cyclohexoxyl radicals produced from the combination of cyclohexyl peroxy radicals.

PART III SECTION I

THE PHOTOLYSIS OF AZOCYCLOHEXANE-OXYGEN MIXTURES

IN THE PRESENCE OF CYCLOHEXANE

PART III SECTION I

EXPERIMENTAL

1. Materials

Oxygen was the research grade of the British Oxygen Co. Ltd. and was used without further purification. Azocyclohexane and cyclohexane were the same materials as described in part I (section I). Cyclohexanone (Fisons Laboratory reagent), cyclohexanol (Fisons Laboratory reagent) and cyclohexene (Fisons laboratory reagent) were used for identification purposes without further purification. Pure samples of cyclohexyl hydroperoxide were prepared by the method of Gunstone and Hammond¹³⁸.

2. Apparatus

The light intensity was varied by placing gauzes of different mesh sizes between the lamp and the reaction vessel. The gauze transmissions had previously been calibrated on a 'Unicam' SP800 ultraviolet spectrometer. The same apparatus was used as described in part I (section I).

3. Procedure

The vacuum line and bulb E were evacuated and a pressure of oxygen introduced into the line. The tap on bulb E was closed and the remaining oxygen in the line pumped away, using the rotary pump. The diffusion pump could be isolated from the rotary pump thus ensuring that the hot silicone oil never came into contact with oxygen. Azocyclohexane and cyclohexane were introduced into the reaction vessel as described in part I (section I). With the liquid nitrogen still surrounding the reaction vessel, the tap on bulb E was opened and a known pressure of oxygen allowed into the

reaction vessel. The reaction vessel tap was closed and the oxygen in the line pumped away as before. The reaction was carried out as described in part I (section I). The reaction vessel was surrounded with liquid nitrogen when the reaction was completed. The excess oxygen and nitrogen (formed in the reaction) were pumped away. The products were distilled into a small tube as described in part I (section I). Cyclohexyl hydroperoxide was trapped and distilled on the line and stored in a darkened tube.

The reaction vessel was coated with potassium chloride by rinsing the vessel with a 15% solution of the salt, leaving it to drain, and drying slowly in an oven ($\sim 100^{\circ}\text{C}$). The reaction vessel was then pumped down on the vacuum line. The boric acid coating was applied by rinsing the vessel with a saturated solution of boric acid in 95% ethanol. The vessel was then dried as before.

4. Analysis

The analysis was carried out as described in part I (section I). The most satisfactory stationary phase for separating the products was 10% by weight diethylene glycol succinate on 100-120 mesh Celite. Unfortunately, this stationary phase decomposed cyclohexyl hydroperoxide. Injecting authentic samples of the hydroperoxide down the column gave equal amounts of cyclohexanol and cyclohexanone. This was repeated several times and was found to be very consistent. Cyclohexyl hydroperoxide could also be quantitatively reduced to cyclohexanol by triphenyl phosphite. Using these two analytical procedures, the products could be quantitatively analysed.

5. Identification of Products

Under normal analytical conditions, three product peaks were observed. Cyclohexanone, cyclohexanol and cyclohexene were identified by comparison of retention times with those for authentic samples. On treating the reaction mixture with triphenyl phosphite the cyclohexanol peak increased, while the cyclohexanone peak decreased in size. This confirms the presence of cyclohexyl hydroperoxide.

Water was qualitatively analysed for by comparison of retention time with that of an authentic sample. The water peak appeared as a negative peak on the chromatogram since it has a lower molecular weight than nitrogen (carrier gas). Water in the samples could not be quantitatively analysed since it formed two layers with the reaction mixture.

To separate and measure the product peaks accurately two sets of chromatograms were required. The column was first operated at 40°C, nitrogen flow rate 60 cm³/min and then at 90°C, nitrogen flow rate 60 cm³/min.

6. Results

The products formed in the gas phase photo-oxidation of azocyclohexane ($\lambda > 300$ nm) in the presence of cyclohexane were cyclohexanone, cyclohexyl hydroperoxide, cyclohexanol, cyclohexene and water. The quantitative analysis of water proved impracticable. The rate data is given relative to cyclohexanone formation in order to present a clearer picture of the results (except table III.6).

Table III.2

Variation of Oxygen Concentration

Series	Reactant Concentrations			Temp °C	$\frac{[c-C_6H_{10}O]_D}{[c-C_6H_{11}OH]_D}$	Rc-C ₆ H ₁₀ O	Rc-C ₆ H ₁₁ O ₂ H	Rc-C ₆ H ₁₁ OH	Rc-C ₆ H ₁₀
	$[(c-C_6H_{11})_2N_2]$	$[c-C_6H_{12}]$	$[O_2]$						
A ₁ ⁵¹	2.47	11.2	1.08	172	2.0	1.0	1.0	0.19	0.059
A ₂ ⁵¹	2.47	11.2	10.8	170	2.7	1.0	1.0	0.05	0.075
A ₃ ⁵¹	2.47	11.2	53.8	171	2.5	1.0	1.0	0.18	0.19
B ₁	1.48	11.2	10.8	108	3.4	1.0	1.0	<0.0	0.020
B ₄	1.48	11.2	53.8	102	3.2	1.0	1.1	<0.0	0.032

Reactant Concentrations [], mol l⁻¹ x 10⁴.

Series A - reaction time 5.4 x 10⁴s.

Series B - reaction time 1.8 x 10³s.

Two separate light sources were used: the source used in series B has approximately ten times the intensity of that used in series A. Within series A the light intensity was further reduced by calibrated filters eg. A⁵¹ = 51% of the full intensity.

$\frac{[c-C_6H_{10}O]_D}{[c-C_6H_{11}OH]_D}$ (See page 101)

$[c-C_6H_{11}OH]_D$

R - rate relative to cyclohexanone formation

Table II.3

Variation of Cyclohexane Concentration

Series	Reactant Concentrations			Temp ° C	$\frac{[c-C_6H_{10}O]}{[c-C_6H_{11}OH]}$	Rc-C ₆ H ₁₀ O	Rc-C ₆ H ₁₁ O ₂ H	Rc-C ₆ H ₁₁ OH	Rc-C ₆ H ₁₀
	$[(c-C_6H_{11})_2N_2]$	$[c-C_6H_{12}]$	$[O_2]$						
B ₅	1.48	0.00	10.8	102	2.9	1.0	1.0	0.08	-
B ₁	1.48	11.2	10.8	108	3.4	1.0	1.0	<0.0	0.020
B ₂	1.48	11.2	10.8	102	3.2	1.0	1.0	<0.0	0.027
B ₆	1.48	16.8	10.8	102	3.1	1.0	1.0	<0.0	0.023
B ₃	1.48	33.5	10.8	103	3.1	1.0	1.0	<0.0	0.022
A ₂ ¹	2.47	11.2	10.8	170	2.7	1.0	1.0	0.05	0.075
A ₄ ¹	2.47	27.9	10.8	172	2.3	1.0	1.0	0.14	0.074

Reactant Concentrations [], mols l⁻¹ × 10⁴.

Series A - reaction time 5.4 × 10⁴ s.

Series B - reaction time 1.8 × 10³ s.

Table III.4 Variation of Temperature

Series	Temp °C	$\frac{[c-C_6H_{10}O]_D}{[c-C_6H_{11}OH]_D}$	Rc-C ₆ H ₁₀ O	Rc-C ₆ H ₁₁ O ₂ H	Rc-C ₆ H ₁₁ OH	Rc-C ₆ H ₁₀
A ₅ ¹⁰⁰	84	3.6	1.0	1.1	< 0.0	0.038
A ₆ ¹⁰⁰	93	3.2	1.0	1.1	< 0.0	0.025
A ₇ ¹⁰⁰	144	3.0	1.0	1.0	< 0.0	0.048
A ₈ ¹⁰⁰	177	3.2	1.0	1.0	< 0.0	0.071

Reactant Concentrations [], mols l⁻¹ x 10⁴

[(c-C₆H₁₁)₂N₂] = 2.47 ; [c-C₆H₁₂] = 11.2 ; [O₂] = 10.8

Series A - reaction time 5.4 x 10⁴s.

Table III.5 Variation of Surface Effects

Series	Cell Coating	Temp °C	$\frac{[c-C_6H_{10}O]_D}{[c-C_6H_{11}OH]_D}$	Rc-C ₆ H ₁₀ O	Rc-C ₆ H ₁₁ O ₂ H	Rc-C ₆ H ₁₁ OH	Rc-C ₆ H ₁₀
A ₉ ¹⁰⁰	Boric Acid	97	3.0	1.0	1.0	<0.0	0.038
A ₁₀ ¹⁰⁰	KCl	95	3.2	1.0	1.1	<0.0	0.025
A ₆ ¹⁰⁰	-	93	3.2	1.0	1.1	<0.0	0.025
A ₁₁ ⁵¹	Boric Acid	175	4.3	1.0	1.2	<0.0	0.069
A ₁₂ ⁵¹	KCl	172	3.0	1.0	1.0	<0.0	0.041
A ₂ ⁵¹	-	170	2.7	1.0	1.0	<0.05	0.075

Reactant Concentrations [], mols l⁻¹ x 10⁴.

[(c-C₆H₁₁)₂N₂] = 2.47 ; [c-C₆H₁₂] = 11.2 ; [O₂] = 10.8

Series A - reaction time 5.4 x 10⁴s.

Table III.6 Variation of Light Intensity

Series	Temp °C	R _{C-C₆H₁₀O}	R _{C-C₆H₁₁O₂H}	R _{C-C₆H₁₁OH}	R _{C-C₆H₁₀}
A ¹⁰⁰ ₈	177	3.8	3.9	<0.00	0.27
A ¹⁰⁰ ₁₃	172	3.5	3.5	<0.00	0.09
A ⁵¹ ₁₄	172	2.2	2.2	<0.00	0.09
A ⁵¹ ₃	171	2.0	2.0	<0.00	0.44
A ⁵¹ ₂	170	1.9	1.9	0.10	0.15
A ³¹ ₁₅	176	1.25	1.25	0.09	0.12

Reactant Concentrations [], mols l⁻¹ x 10⁴

$[(c-C_6H_{11})N_2] = 2.47 ; [c-C_6H_{12}] = 11.2 ; [O_2] = 10.8$

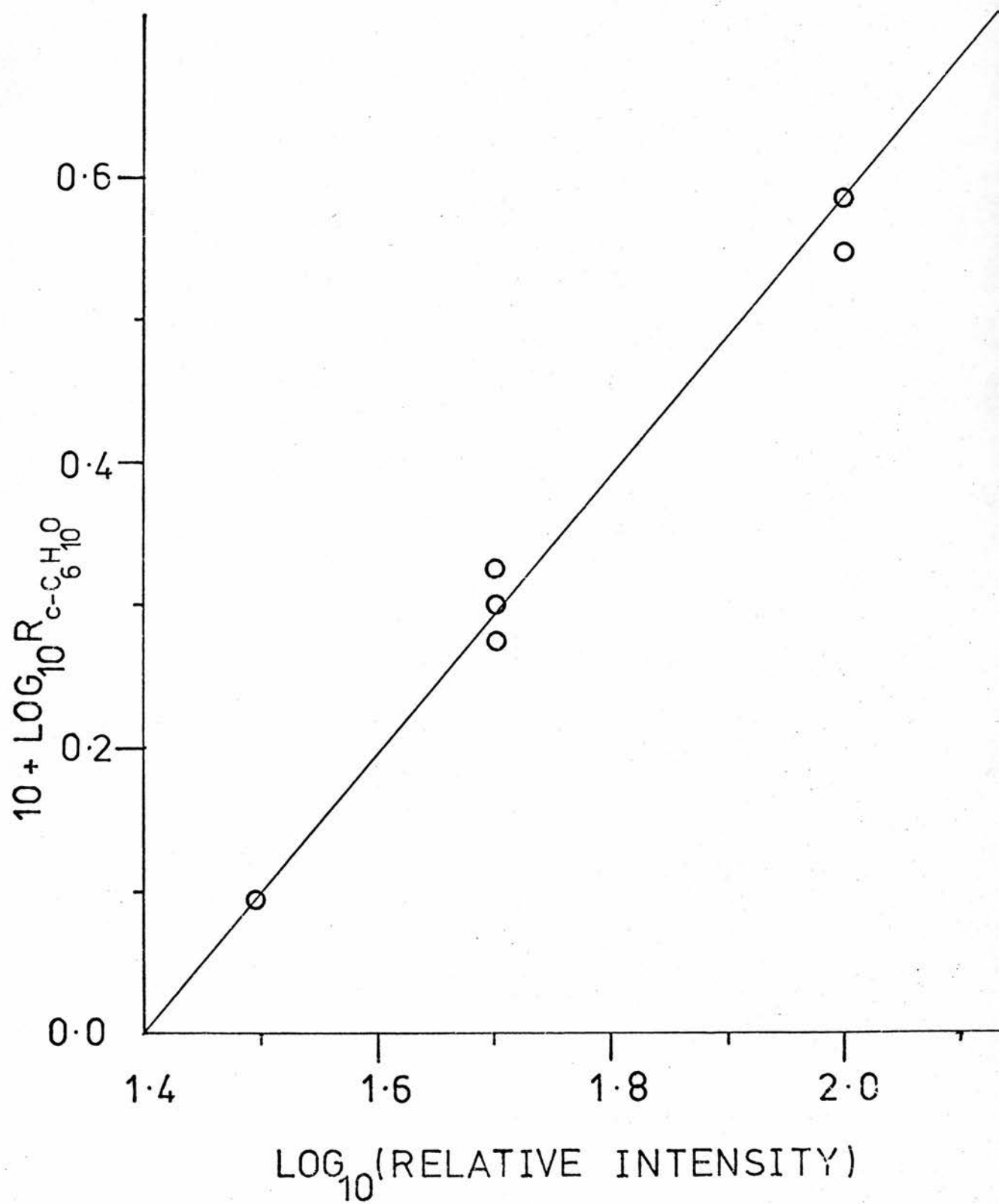
All Rates (R) mol l⁻¹ s⁻¹ x 10⁹

Series A - reaction time 5.4 x 10⁴ s.

A least squares plot of log₁₀ R_{C-C₆H₁₀O} versus log₁₀ (relative intensity), (fig. III.1)

gave a straight line of slope = 0.902 ± 0.11

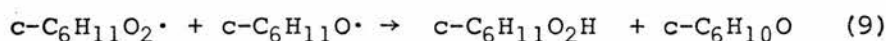
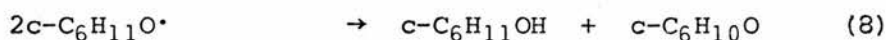
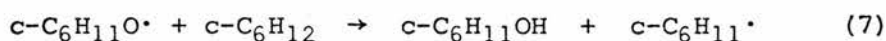
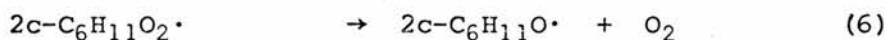
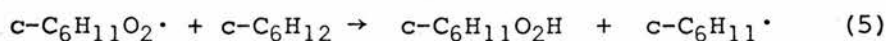
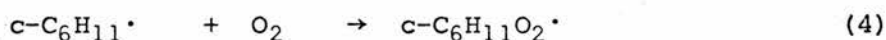
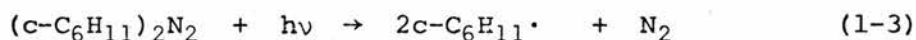
and intercept = -1.24 ± 0.06



PART III SECTION I

DISCUSSION

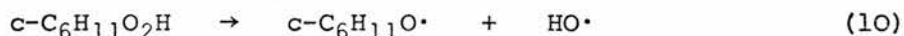
The major products from the photolysis of azocyclohexane in the presence of cyclohexane and excess oxygen are cyclohexanone and cyclohexyl hydroperoxide. In addition smaller amounts of cyclohexanol, cyclohexene and water were detected. The increase of total product yield with a decrease in overall pressure or an increase in reaction temperature is indicative of the participation of excited molecules in the initiation step for the photolysis of azocyclohexane. The following general mechanism will be used to explain the rate data for product formation (tables III.2 - III.6).



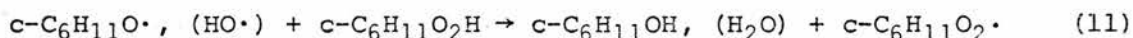
The reaction steps (1-3) have already been discussed in part I (section I) (P. 30).

The stability of cyclohexyl hydroperoxide under the present reaction conditions is of considerable importance and was fully investigated. Samples of the hydroperoxide were unchanged after irradiation at wavelengths >300 nm. Although pure cyclohexyl

hydroperoxide was found to decompose quite rapidly at the highest temperatures used in these studies (177°C), negligible decomposition of the product cyclohexyl hydroperoxide occurred when reaction mixtures were pyrolyzed at temperatures approaching 180°C . Benson¹³⁹ has shown that the direct dissociation into cyclohexoxyl and hydroxyl radicals in reaction (10) contribute negligibly to the observed kinetics of cyclohexyl hydroperoxide decomposition in solution.



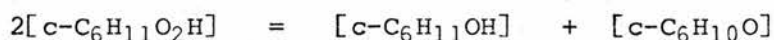
Farkas and Passaglia¹⁴⁰ report the Arrhenius parameters for this reaction as, $A_{10} = 10^{13.1} \text{ s}^{-1}$ and $E_{10} = 34 \text{ k cal mol}^{-1}$. Benson has rationalized these results in terms of a chain reaction involving $\text{c-C}_6\text{H}_{11}\text{O}_2\cdot$ and $\text{c-C}_6\text{H}_{11}\text{O}\cdot$ radicals, for which the important pathways are reactions (10), (11), (6) and (9).



This provides an estimate of the 1st order rate constant for reaction (10) of $k_{10} = 10^{15} \exp(-42,000 \text{ cal}/RT) \text{ s}^{-1}$ ¹³⁹. In the present work involving very low conversions, the reaction mixture contains only small concentrations of cyclohexyl hydroperoxide and the chain mechanism is unimportant. Using the above rate constant, the half-life of cyclohexyl hydroperoxide is approximately 50 hours at 177°C and therefore decomposition of the hydroperoxide can be neglected.

It was mentioned earlier that the direct quantitative analysis of cyclohexyl hydroperoxide proved to be impossible with the present

gas/liquid chromatographic techniques. Decomposition of the hydroperoxide occurred to a greater or lesser extent for all column conditions tested. Therefore, a complete decomposition method was used in all the quantitative experiments. Under the reported gas chromatographic conditions (see experimental) pure samples of cyclohexyl hydroperoxide were found to degrade giving equal amounts of cyclohexanol and cyclohexanone; observing the simple relationship,



Careful checks on the quantitative nature of this decomposition were made on samples of pure hydroperoxide in typical reaction product mixtures. The applicability of this expression to many such control mixtures was rigorously tested. Several analyses were made on each run using this procedure. The remaining sample was then treated with triphenyl phosphite to reduce the hydroperoxide to cyclohexanol. The reduced product was analysed by gas chromatography in the normal way. Experiments on pure samples of cyclohexyl hydroperoxide showed the reduction to be quantitative. The two sets of analysis procedures for each oxidation experiment provides estimates of the cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide concentrations in the reaction mixtures from the following relationships:-

a. Direct Analysis (gas/liquid chromatography)

$$[\text{ROH}]_D = [\text{ROH}]_O + \frac{1}{2}[\text{RO}_2\text{H}]_O$$

$$[\text{R}(-\text{H})=\text{O}]_D = [\text{R}(-\text{H})=\text{O}]_O + \frac{1}{2}[\text{RO}_2\text{H}]_O$$

b. Triphenyl Phosphite Reduction.

$$[\text{ROH}]_{\text{T}} = [\text{ROH}]_{\text{O}} + [\text{RO}_2\text{H}]_{\text{O}}$$

$$[\text{R}(-\text{H})=\text{O}]_{\text{T}} = [\text{R}(-\text{H})=\text{O}]_{\text{O}}$$

Combination of the results from a. and b. gives:-

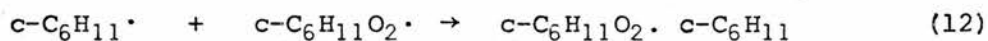
$$[\text{RO}_2\text{H}]_{\text{O}} = 2\{[\text{R}(-\text{H})=\text{O}]_{\text{D}} - [\text{R}(-\text{H})=\text{O}]_{\text{T}}\}$$

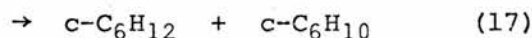
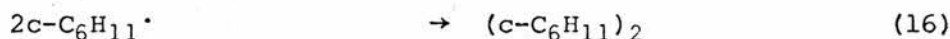
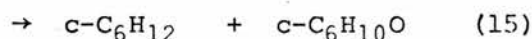
$$[\text{ROH}]_{\text{O}} = [\text{ROH}]_{\text{D}} - \frac{1}{2}[\text{RO}_2\text{H}]_{\text{O}}$$

where $[\text{X}]_{\text{D}}$ and $[\text{X}]_{\text{T}}$ refer to the concentration of species X, as measured by direct gas/liquid chromatographic analysis and analysis following triphenyl phosphite reduction respectively. $[\text{X}]_{\text{O}}$ is the concentration of X in the reaction mixture.

The relatively large excess of oxygen used in these studies would be expected to ensure that cyclohexyl radicals will react predominantly with oxygen to form cyclohexyl peroxy radicals in reaction (4). Support for this argument comes from the rate data in table III.2 (P. 93), where a fifty-fold increase in oxygen concentration has no measurable effect on the major product rate ratios.

Assuming not all alkyl radicals are scavenged by oxygen then they could participate with cyclohexyl peroxy or cyclohexoxyl radicals in one of the following reactions.





The above combinations involving cyclohexyl radicals would be expected to decrease with increasing oxygen concentration. No bicyclohexyl peroxide (12) or bicyclohexyl ether (14) was detected under the lowest oxygen concentrations. It is likely that disproportionation¹⁴¹ would predominate for combination of cyclohexyl radicals with either the alkoxyl or peroxy radicals. The products from these disproportionations, (13) and (15), are also products from the proposed scheme (reactions 1-9, P. 99) and this makes it difficult to test their importance. Since reaction (15) yields cyclohexanone an increase in oxygen concentration would be expected to reduce the product relative to cyclohexyl hydroperoxide. Table III.2 (P. 93) shows that the ratio of cyclohexanone to cyclohexyl hydroperoxide remains constant with increase in oxygen concentration. Similarly, no traces of bicyclohexyl were found in any of the runs, although small amounts of cyclohexene were detected. Compare the results with the photolysis of azocyclohexane in the absence of oxygen, table I.1 (P. 15), where bicyclohexyl and cyclohexene were major products formed in approximately equal amounts from the combination of cyclohexyl radicals, reactions (16) and (17).

The present oxidation results indicate that the source of cyclohexene cannot be associated with this combination. Possible mechanisms for cyclohexene formation are discussed later.

The most obvious fate of cyclohexyl peroxy radicals would at first sight seem to be hydrogen atom abstraction from the excess cyclohexane present, reaction (5). However, this is consistent neither with ratio of the major products, nor with the effect of changes in temperature and cyclohexane concentration (tables III.3 and III.4, P. 94). For runs in both the high light intensity series B and also in the unfiltered experiments of the lower intensity series A, direct gas/liquid chromatographic analysis of the reaction mixtures shows the ratio of cyclohexanone to cyclohexanol concentration to be close to 3. Reduction of the cyclohexyl hydroperoxide in these reaction mixtures by triphenyl phosphite, prior to analysis, results in the formation of equal amounts of cyclohexanone and cyclohexanol. These results can only be interpreted in terms of the formation of equal amounts of cyclohexanone and cyclohexyl hydroperoxide with insignificant quantities of cyclohexanol in the reaction. Only the radical-radical reactions (6) and (9), (P. 99), are consistent with these results. This result is in agreement with the expected slowness of the endothermic hydrogen atom abstraction reaction ($\Delta H_{298}^{\circ} + 4.5 \text{ k cal}$, since $D^{\circ}(\text{RO}_2\text{-H}) = 90 \pm 2 \text{ k cal}$ and $D^{\circ}(\text{c-C}_6\text{H}_{11}\text{-H}) = 94.5 \text{ k cal}$)¹⁴². A recent study of the peroxide-initiated oxidation of isobutane provides an estimate of the activation energy for propagation by the tertiary butyl peroxy radical,



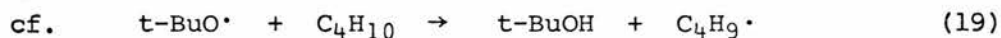
$$E_{18} = 15.8 \text{ k cal mol}^{-1} \quad 143$$

Since the activation energy for the analogous secondary hydrogen atom abstraction by cyclohexyl peroxy radicals is likely

to be similar, reaction (5) (P. 99) is unlikely to provide the route for cyclohexyl hydroperoxide formation even at the highest temperature of the present work.

More surprising is the negligible contribution of the cyclohexoxyl radical hydrogen atom abstraction reaction (7) (P. 99) to the reaction sequence, witnessed by the absence of cyclohexanol in the majority of experiments. However, for the highest temperature runs with reduced light intensity of series A the ratio $[c-C_6H_{10}O]_D/[c-C_6H_{11}OH]_D$ is significantly smaller than 3 suggesting that cyclohexanol is produced in these runs. Further, since the yield of cyclohexanol is greater than that of cyclohexanone following reduction of the final reaction mixtures with triphenyl phosphite, it is reasonable to assume that the major source of the small amounts of cyclohexanol are from reaction (7) and not from the combination of cyclohexoxyl radicals, reaction (8). This latter reaction, although reducing the cyclohexanone to cyclohexanol ratio to below 3 in the direct analysis procedure, would have no effect on the equality of these products in the reduction analysis since both cyclohexanol and cyclohexanone are formed in this radical-radical reaction.

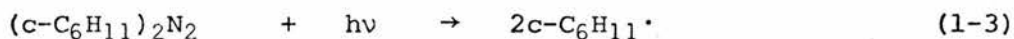
Reaction (7) may be expected to have a relatively low activation energy



$$E_{19} = 6.9 \text{ k cal mol}^{-1} \quad 144$$

and would be expected to dominate over the radical combination reaction (8). Presumably the steady state concentration of cyclohexyl peroxy radicals is sufficiently high at all but the lowest light intensities for reaction (9) to provide the major removal pathway for the cyclohexoxyl radicals.

The principal reaction sequence can now be reduced to the following reactions:-

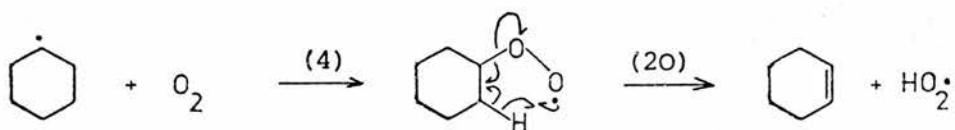


This reaction sequence gives the simple rate law:-

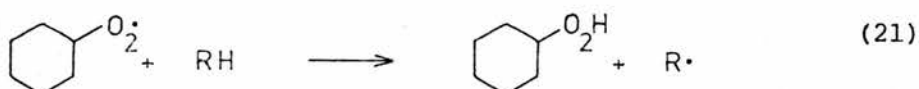
$$R_{c-C_6H_{11}O_2H} = R_{c-C_6H_{10}O} = \phi I_a \quad (A)$$

where I_a is the absorbed light and ϕ is the quantum yield for azocyclohexane decomposition. Figure III.1 (P. 98) shows the results (table III.6, P. 97) from a series of experiments in which calibrated filters were used to vary the incident light intensity. The gradient from a plot of $\log_{10} R_{c-C_6H_{10}O}$ or $\log_{10} R_{c-C_6H_{11}O_2H}$ versus \log_{10} (relative intensity) gives the exponent of the light intensity 0.9 ± 0.1 which is close to the value of 1.0 as required by function (A).

Cyclohexene is a minor product in all the runs. However, the results do not support a definite mechanistic pathway for its formation. Ho and Freeman¹³⁴ have suggested an alternative pathway to the simple association reaction (4) for the reaction of cyclohexyl radicals with oxygen. This involves hydrogen atom abstraction by molecular oxygen, producing cyclohexene and $HO_2\cdot$ radicals. Presumably the reaction involves a five-membered ring transition complex



Although this overall process is exothermic ($\Delta H^0 \sim -9 \text{ kcal mol}^{-1}$) most of the energy is not released until the final step, involving formation of the stable molecule (cyclohexene). The internal abstraction reaction is similar to reaction (21)

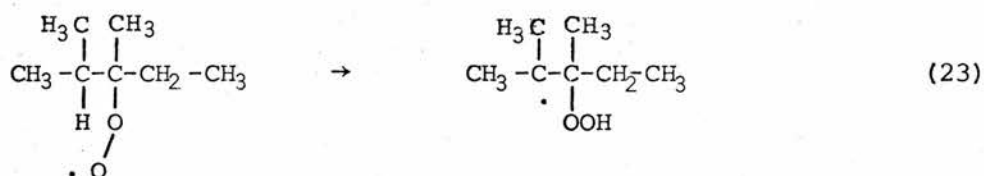
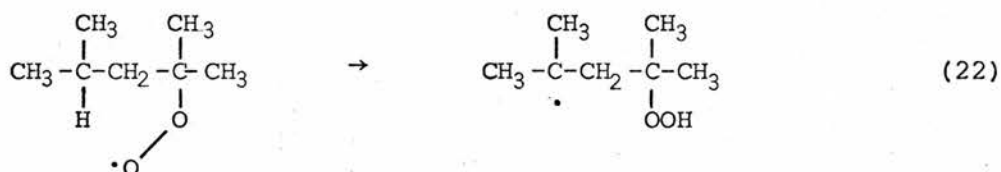


in terms of activation energy i.e. $\sim 16 \text{ kcal}$ although it will have a higher A factor¹⁴⁵. This conclusion is in accord with presently available literature data for the reaction of alkyl radicals with molecular oxygen. In low temperature oxidations ($< 250^\circ\text{C}$) this latter reaction appears to be an association leading to the formation of peroxy radicals, RO_2^{\cdot} ¹¹⁴. At higher temperatures the hydrogen atom abstraction process becomes increasingly important.

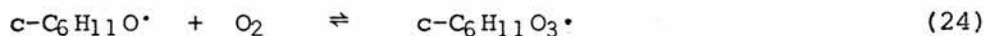
Reaction (20), which is in competition with reaction (4), would be expected to show a strong temperature dependence and be unaffected by oxygen pressure. In fact the proportion of cyclohexene is not greatly influenced by temperature (table III.4 P. 95) and is also dependent on the oxygen concentration (table III.2, P. 93). Apparently the possible reaction pathway (20) has sufficient activation energy so it is unimportant compared to the bimolecular cyclohexyl peroxy radical combination reaction (4), even at the highest temperature runs of this study.

Intramolecular abstraction reactions are not favoured for five membered transition complexes,^{115, 146} i.e. an alkyl peroxy radical, but they are very facile when a six membered ring transition complex is involved (e.g. the Barton reaction). Work by Rust on the oxidation of neat 2,3 and 2,4-dimethylpentanes

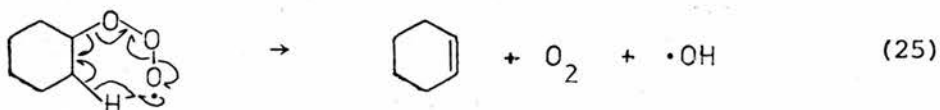
showed that internal hydrogen atom abstraction can proceed through a six membered transition complex in the oxidation of the 2,4-isomer (22) to give the dihydroperoxide. In the case of the 2,3-isomer no dihydroperoxide was observed indicating that a five membered transition complex is not favoured.



A six membered transition complex could be formed by the $\text{c-C}_6\text{H}_{11}\text{O}_3\cdot$ radical. The species although of limited stability, could be present in high steady-state concentration when molecular oxygen is present in large excess.



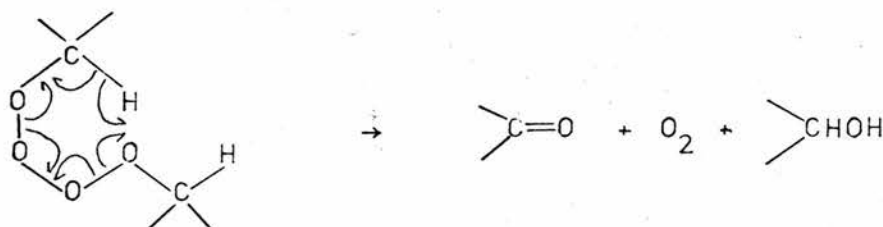
The favoured six membered transition complex leads to the formation of molecular oxygen



(presumably in a singlet state) and hydroxyl radicals as well as cyclohexene. These hydroxyl radicals are the probable source of the observed water, through rapid hydrogen atom abstraction from

cyclohexane¹⁴⁷. The oxygen dependence observed for cyclohexene (table III.2, P. 93) formation appears to be a direct consequence of the equilibrium (24).

The above results must be compared with the solution phase data, where combination of $c\text{-C}_6\text{H}_{11}\text{O}_2\cdot$ radicals is a terminating reaction leading to stable molecular products. The reaction is believed to proceed through a tetroxide intermediate ROOOOR , which rapidly decomposes within the solvent cage to give an alcohol and a ketone either through a cyclic transition state,



or by direct decomposition into alkoxy radicals followed by reaction (8) (p. 99). In the gas phase reaction (6) is non-terminating giving alkoxy radicals ($\text{RO}\cdot$). The present results suggest the major fate of this radical ($\text{RO}\cdot$) is cross-combination with the unreactive alkyl peroxy radical ($\text{RO}_2\cdot$), rather than chain propagation, reaction (7) (P.99). However, in the presence of excess oxygen the alkoxy radical can lead to olefin formation through the formation of the $\text{RO}_3\cdot$ radical followed by an intramolecular abstraction and elimination reaction. The confinement of alkoxy radicals within the solvent cage prevents this reaction pathway in the solution phase.

Finally the possibility of heterogeneous pathways for product formation was investigated. Several oxidations were carried out using boric acid and potassium chloride surface treated reaction

vessels. Consistent results were obtained from both the coated and un-treated vessels, table III.5,(P.96) , suggesting the absence of significant wall effects in these reactions. These cell coatings have been used extensively in gas phase oxidations e.g. the $H_2 + O_2$ reaction¹⁴⁸.

In conclusion, the reaction between cyclohexyl radicals and molecular oxygen involves no ring splitting. The major products are formed by radical-radical reactions involving the $c-C_6H_{11}O_2\cdot$ and $c-C_6H_{11}O\cdot$ radicals. The minor products, cyclohexene and water can be explained by the participation of the $c-C_6H_{11}O_3\cdot$ radical.

PART III SECTION II

THE PHOTOLYSIS OF AZO-n-BUTANE-OXYGEN MIXTURES

PART III SECTION II

EXPERIMENTAL

1. Materials

Oxygen (research grade of the British Oxygen Co. Ltd.) and n-butane (Matheson gas products) were used without further purification. n-Butanol (G.P.R. Hopkin and Williams Ltd.) n-butyraldehyde (Fisons laboratory reagent), propionaldehyde (B.D.H. laboratory reagent), acetaldehyde (Fisons laboratory reagent), n-propanol (Fisons laboratory reagent), n-octane (B.D.H. laboratory reagent) and di-n-butyl ether (Fisons laboratory reagent) were used without further purification for identification purposes. Azo-n-butane was prepared in an identical manner to the preparation of azoisopentane (part I, section II). n-Butyl hydroperoxide ^{149,150} was prepared in two stages. The first stage involved the preparation of n-butyl methane-sulphonate.

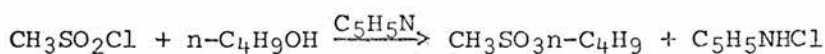
A mixture of 14.8g (0.2 mols) n-butanol and 22.9g (0.2 mols) methanesulphonyl chloride (B.D.H. laboratory reagent) was placed in a 500 cm³ three necked flask, equipped with a mechanical stirrer and a separating funnel, and cooled in an ice-salt bath to 0°C. The stirrer was started and 31.6g (0.4 mols) dry pyridine was added at a temperature of 0-5°C over a period of 3 to 4 hours. The stirring was continued for one-quarter hour; the cream coloured reaction mixture was then poured into 125 cm³ of ice-cold 10% hydrochloric acid and immediately an oil was seen to form. The product was extracted with 75 cm³ of ether. The resulting solution was washed with two 20-cm³ portions of water followed by a 30-cm³ portion of saturated sodium bicarbonate solution.

The solution was dried over anhydrous potassium carbonate, filtered and the ether removed on a rotary evaporator. The reaction mixture at this stage was a yellow oily liquid.

The residue was distilled at reduced pressure to give a colourless liquid with a pungent odour ie. n-butyl methanesulphonate.

An infrared spectrum was taken of the compound and compared with the literature spectrum of n-butyl methanesulphonate.

The two spectrum were identical.



The n-butyl methanesulphonate (6.1g; 0.04 mols) was dissolved in 25cm³ of methanol and the mixture cooled in an ice-bath. Added to this mixture was 27.5% hydrogen peroxide (20.0g; 0.16 mols) and 50% aqueous potassium hydroxide (5.0g; 0.045 mols), in that order. The mixture was then placed in a water bath (23⁰C) for 18 hours. The mixture at this stage consisted of two layers. After the reaction was completed the mixture was cooled in ice and slowly combined with 50% potassium hydroxide (15.0g). The alkaline mixture was extracted with 25cm³ of benzene to remove unreacted alkyl methanesulphonate, alcohol or dialkyl peroxide. The aqueous layer was cooled in ice, neutralised (pH7) with concentrated hydrochloric acid, and extracted with four 15-cm³ portions of benzene. These benzene extracts still contained a small amount of hydrogen peroxide. The combined benzene extracts were extracted with 20g of cold 25% potassium hydroxide. The alkaline solution was cooled in ice, neutralised with concentrated

hydrochloric acid, and then the neutralised mixture extracted with four 10-cm³ portions of benzene. The hydroperoxide solution was dried over anhydrous sodium sulphate and the benzene removed on a rotary evaporator. The hydroperoxide was purified by distillation. Weight = 0.5g; % yield ~ 20.



An infrared spectrum taken of the compound was identical to the spectrum of authentic n-butyl hydroperoxide¹⁵¹.

2. Apparatus

The same apparatus was used as described in part III (section I).

3. Procedure

n-Butane was trap to trap distilled and stored in bulb A. The vapour pressure of azo-n-butane was allowed to fill bulb D. The contents of the bulb were then distilled into the reaction vessel. A known pressure of oxygen was allowed into the vessel. The same procedure was then followed as described in part III (section I).

4. Analysis

A Pye 104 series gas/liquid chromatograph employing a flame ionisation detector was used for analysis. Columns (7' glass) packed with 20% by weight dinonyl phthalate on 60-80 mesh 'Embacel' were used for separating the components of the reaction mixtures. But-1-ene and n-Butane were separated

using a 20% squalene column.

With the column operating at 60°C pure samples of n-butyl hydroperoxide could be injected without any decomposition occurring. It was found however that the retention times of azo-n-butane and n-butyl hydroperoxide were almost identical. Since azo-n-butane was in such large excess in all the runs the n-butyl hydroperoxide could not be analysed directly. Reduction of n-butyl hydroperoxide with triphenyl phosphite was found to give quantitative amounts of n-butanol. Using this technique the n-butyl hydroperoxide could be analysed indirectly.

The peak areas were measured using a fixed arm planimeter.

5. Identification of Products

The main products from low temperature runs were, n-butyraldehyde, n-butanol and n-butyl hydroperoxide. At higher temperatures (~150°C) the main products were propionaldehyde, n-butyraldehyde, but-1-ene, n-butanol and n-butyl hydroperoxide. In most runs small amounts of n-octane, n-butane, n-propanol and acetaldehyde were present.

All the above product peaks were identified by mass spectra recorded on an A.E.I. MS 902 mass spectrometer with g.l.c. inlet from a Pye 104 series gas/liquid chromatograph. Samples for mass spectra analysis were photolysed for ~3 hours. Because of this long photolysis time other products were formed which were not observed in kinetic runs. From such samples n-propane, ethanol, di-n-butyl ether, n-butyric acid

and n-butyl-n-butanate were identified. For complete mass spectra analysis three columns were used. All were, 7' glass columns with solid support 60-80 mesh 'Embacel'. The stationary phases were 20% dinonyl phthalate, 20% silicone oil and 20% squalene.

Mass Spectra of Products Formed in the Oxidation of Azo-n-Butane.

Table III.7

n-Propane		But-1-ene	
Product	Authentic	Product	Authentic
m/e %	m/e %	m/e %	m/e %
29 100	29 100	41 100	41 100
28 60	28 58	56 37	56 41
27 37	27 31	39 35	39 31
43 31	43 27	28 29	28 26
44 29	44 25	27 25	27 23
41 21	39 14	55 18	55 19
39 20	41 14	29 14	29 12
26 11	26 5	26 8	26 7

n-Butane		acetaldehyde	
Product	Authentic	Product	Authentic
m/e %	m/e %	m/e %	m/e %
43 100	43 100	29 100	29 100
29 47	29 45	44 69	44 89
27 35	27 38	43 50	43 47
28 34	28 33	41 13	15 34
41 34	41 28	15 13	28 26
42 15	39 13	28 12	42 13
58 12	58 13	27 11	14 11
39 12	42 12	26 6	41 5

propionaldehyde

ethanol

Product		Authentic		Product		Authentic	
m/e	%	m/e	%	m/e	%	m/e	%
29	100	29	100	31	100	31	100
58	87	58	83	45	43	45	35
27	73	28	82	29	24	29	27
28	70	27	57	27	24	27	24
57	32	57	26	46	16	46	15
18	25	18	8	26	13	43	8
31	24	41	7	28	10	28	7
26	22	31	7	30	5	30	6

n-butyraldehyde

n-Propanol

Product		Authentic		Product		Authentic	
m/e	%	m/e	%	m/e	%	m/e	%
27	100	27	100	31	100	31	100
29	89	29	96	27	20	27	17
44	86	44	88	29	18	29	16
43	85	43	81	42	7	59	9
41	69	41	62	59	5	42	7
72	44	72	45	28	5	28	6
39	30	39	35	41	4	41	6
28	29	28	27	60	3	60	6

n-butanol

n-octane

Product		Authentic		Product		Authentic	
m/e	%	m/e	%	m/e	%	m/e	%
56	100	31	100	43	100	43	100
31	98	56	91	41	52	41	38
41	91	41	74	27	39	29	35
43	78	43	64	29	37	57	34
27	60	27	63	57	33	85	30
42	38	29	37	85	24	27	29
29	27	42	36	56	22	71	23
28	24	28	25	71	20	56	18

di-n-butyl ether

n-butyric acid

Product		Authentic		Product		Authentic	
m/e	%	m/e	%	m/e	%	m/e	%
57	100	57	100	60	100	60	100
41	48	41	20	41	41	73	30
29	27	87	19	73	37	41	17
87	19	56	15	27	31	27	16
56	19	29	15	43	27	42	16
27	17	58	5	29	23	43	15
55	17	27	5	39	20	45	13
58	5	55	4	45	14	29	9

n-butyl-n-butanoate

Product		Authentic	
m/e	%	m/e	%
71	100	71	100
56	57	89	79
89	53	56	77
43	52	43	63
41	47	41	41
29	30	29	23
27	28	57	21
57	23	27	17

6. Results

The products formed in the gas phase photo-oxidation of azo-n-butane ($\lambda > 300\text{nm}$) were n-butanol, n-butyraldehyde, n-butyl hydroperoxide, n-butane, but-1-ene, n-octane, n-propanol, propionaldehyde and acetaldehyde. The rate data is given relative to n-butanol formation.

Table III.8
Variation of Oxygen Concentration

Series	$[(n-C_4H_9)_2N_2]$	$[O_2]$	$Rn-C_4H_9OH$	$Rn-C_4H_8O$	$Rn-C_4H_9O_2H$	$Rn-C_4H_{10} + n-C_4H_8$	$Rn-C_8H_{18}$	$Rn-C_3H_7OH$	$Rn-C_3H_6O$
B ₁ ³⁷	5.4	1.08	1.00	2.81	0.62	0.08	0.10	a	a
B ₂ ³⁷	5.4	5.4	1.00	2.03	0.31	0.11	0.15	a	a
B ₃ ³⁷	5.4	21.6	1.00	2.66	0.40	0.12	0.17	a	a
B ₇ ³⁷	2.7	53.8	1.00	3.12	1.41	0.16	0.22	0.09	0.50
B ₁₂ ³⁷	5.4	5.4	1.00	2.43	0.80	b	0.17	a	a
B ₅ ⁵⁹	5.4	5.4	1.00	3.74	1.08	0.11	0.11	b	0.19
B ₆ ⁵⁹	2.7	21.6	1.00	1.53	b	0.11	0.08	0.10	b

a - product not determined because it was below the limit necessary for accurate analysis

b - product not determined because of analytical failure.

* Run B₁₂³⁷ had in addition $\underline{n-C_4H_{10}}$

Reactant concentration $[]$, $\text{mol l}^{-1} \times 10^4$ $[n-C_4H_{10}] = 5.4$

Series B - reaction time 1.8×10^3 s.

B₃₇ = 37% and B₅₉ = 59% of full light intensity

Reaction Temperature = 60°C.

Table III.9

Variation of Temperature

Series	Reaction Time	Temp (°C)	Rn-C ₄ H ₉ OH	Rn-C ₄ H ₈ O	Rn-C ₄ H ₉ O ₂ H	Rn-C ₄ H ₁₀ + n-C ₄ H ₈	Rn-C ₈ H ₁₈	Rn-C ₃ H ₇ OH	Rn-C ₃ H ₆ O	Rn-C ₂ H ₄ O
B ₂ ³⁷	1.8	60	1.00	2.03	0.31	0.11	0.15	a	a	a
B ₈ ³⁷	1.8	100	1.00	2.29	0.61	0.14	0.06	0.27	0.55	0.08
B ₉ ³⁷	1.2	158	1.00	3.08	0.97	1.80	0.19	0.55	4.37	0.57
B ₁₀ ³⁷	0.9	200	1.00	13.66	0.90	8.53	0.80	1.86	22.64	13.94

Reactant Concentration [], mol⁻¹ x 10⁴[(n-C₄H₉)₂N₂] = 5.4; [O₂] = 5.4Reaction Time, s x 10⁻³

Table III.10 Variation of Light Intensity

Series	Reaction Time	Rn-C ₄ H ₉ OH	Rn-C ₄ H ₈ O	Rn-C ₄ H ₉ O ₂ H	Rn-C ₄ H ₁₀ + n-C ₄ H ₈	Rn-C ₈ H ₁₈	Rn-C ₃ H ₆ O	Rn-C ₂ H ₄ O
B ₂ ³⁷	1.3	1.00	2.03	0.31	0.11	0.15	a	a
B ₃ ⁵⁹	1.8	1.00	3.74	1.08	0.11	0.11	0.19	a
B ₁ ⁰⁰	1.2	1.00	3.01	1.03	0.08	0.08	0.12	0.03

Reactant Concentrations [], mols l⁻¹ x 10⁴

[(n-C₄H₉)₂N₂] = 5.4; [O₂] = 5.4

Reaction Time, s x 10⁻³

Reaction Temperature = 60° C

The ratio of alkene to alkane

Series	$[(n-C_4H_9)_2N_2]$	$[O_2]$	Temp. (°C)	Rn-C ₄ H ₉ OH	Rn-C ₄ H ₈ O	Rn-C ₄ H ₉ O ₂ H	Rn-C ₄ H ₁₀ + n-C ₄ H ₈	Rn-C ₈ H ₁₈	Rn-C ₃ H ₇ OH	Rn-C ₃ H ₆ O	Rn-C ₂ H ₄ O	$\frac{Rn-C_4H_8}{Rn-C_4H_{10}}$
B ⁵⁹	5.4	5.4	60	1.00	3.74	1.08	0.11	0.11	a	0.19	a	1.0
B ⁵⁹	2.7	21.6	60	1.00	1.53	b	0.11	0.08	0.10	a	a	1.5
B ⁵⁹	2.7	53.8	60	1.00	b	b	b	0.06	b	b	b	1.0
B ³⁷	5.4	5.4	100	1.00	2.29	0.61	0.14	0.06	0.27	0.55	0.08	6.43

Reactant Concentrations [], mols l⁻¹ × 10⁴.Reaction Time = 1.8 × 10³s.

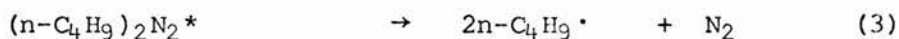
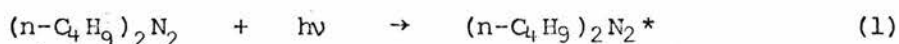
PART III SECTION II

DISCUSSION

From the observed products it is quite evident that the photo-oxidation of azo-n-butane is more complex than the previous study involving azocyclohexane. In that study cyclohexanone and cyclohexyl hydroperoxide were the principal products, cyclohexanol and cyclohexene minor products. In the present work n-butanol is a major product. Furthermore, fragmentation of the carbon chain was negligible with cyclohexyl radicals over the temperature range studied (84-177°C). Even at the lowest temperatures studied (60°C), propionaldehyde was formed in the present work.

Attempts to find carboxylic acids i.e. acetic, propanoic and n-butyric, and bifunctional alcohols and ketones, cyclic ethers and epoxides proved negative. n-Butyric acid was observed in some high conversion runs.

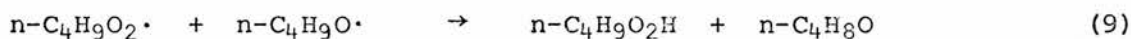
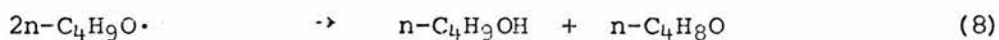
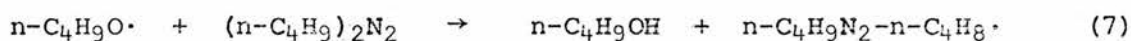
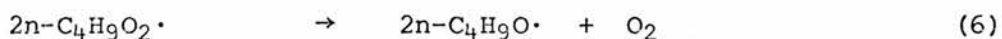
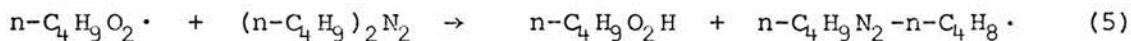
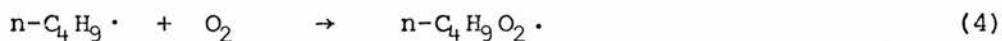
The photolysis of azo-n-butane has been studied by Morganroth and Calvert³⁰ and they established the following mechanism.



The possible extrusion of nitrogen to form n-octane was considered by these workers and dismissed as unimportant. This third primary process, which accounts for about 1% in the photolysis of azomethane is considered to be less important for the higher azo-alkanes.

Considering the results at temperatures below 100°C and using an identical mechanism as used for the photolysis of azocyclohexane-oxygen mixtures, then



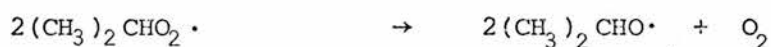
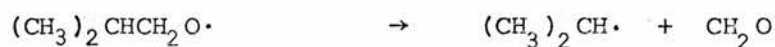


Although this mechanism predicts the observed major products, it does not account for their distribution. *n*-Butyraldehyde is the major product in all low temperature (<100°C) runs, but the mechanism (1-9) does not account for this.

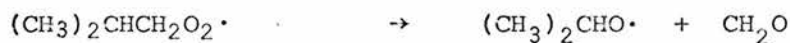
A large amount of work has been carried out on *n*-butane^{152,153} oxidations but very little attention has been focussed on the reactions of *n*-butyl radicals with oxygen. The former system generates predominantly *sec*-butyl radicals. The main products from this system are, *sec*-butyl hydroperoxide, *sec*-butanol, ethanol, acetaldehyde, methyl ethyl ketone and trace amounts of *n*-butanol.

Calvert and Slater¹⁵⁴ studied the photo-oxidation of azoisobutane (35-132°C) and found that the major products did not contain the isobutyl group. The major products were, acetone and isopropanol with smaller amounts of isobutanol, isobutyraldehyde and isobutyl hydroperoxide. From their data it was not possible to postulate a mechanism for acetone or isopropanol formation although the authors

mentioned two possible paths.



and

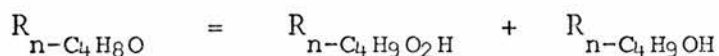


Mayo et al¹⁴³ studied the low temperature oxidation of isobutane in both the gas (100-155°C) and liquid (50-100°C) phases. This study differs from the work of Calvert and co-workers since the initiation step generates t-butyl radicals which then undergo oxidation. The effect of phase changes were found to be surprisingly small and the major products all contained the t-butyl group i.e. t-butyl hydroperoxide, t-butanol, acetone and methanol, and at higher temperatures isobutene.

The results from the present investigation suggest that at moderate temperatures (~100°C) the n-butyl peroxy and/or n-butoxy radicals do not decompose very readily. This agrees with structural considerations, since a branched chain radical (isobutyl peroxy, isobutoxy) is more likely to undergo C-C cleavage than a straight chain radical (n-butyl peroxy, n-butoxy).

Studying the results in table III.8 (p.120) chain propagation does not seem to be very evident. The addition of n-butane (run B₁₂³⁷) does not affect the distribution of the major products. This is in agreement with Calvert and co-workers¹⁵⁵ who found that the main products from the photo-oxidation of 2,2'-azoisobutane originated from radical-radical disproportionation reactions; not from hydrogen abstraction from azoisobutane or hydrogen containing products. The main products from this system were, acetone, formaldehyde, t-butyl hydroperoxide and t-butanol.

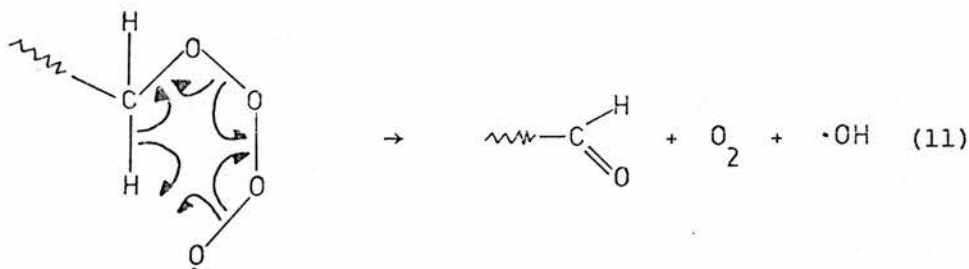
If reactions (8) and (9), (P.125), were the only source of n-butyraldehyde, n-butanol and n-butyl hydroperoxide, then



Results from table III.8 (p.120) show that this relationship is not observed. In all runs there is an excess of n-butyraldehyde.

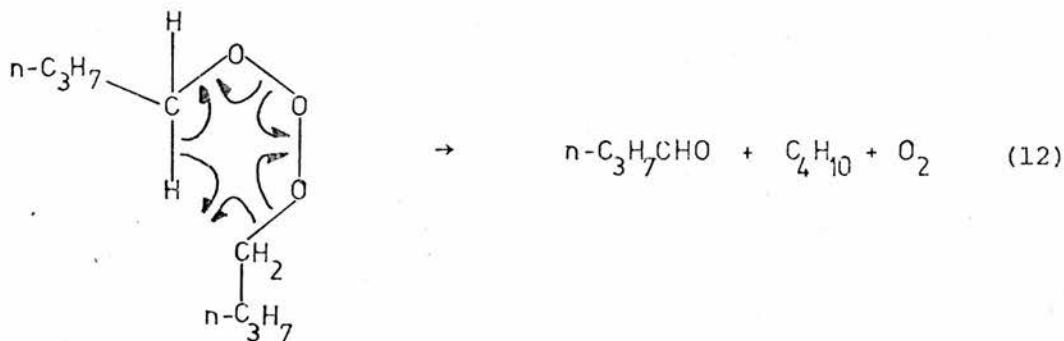
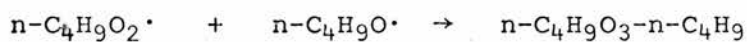
Since the simple mechanism (1-9) does not explain the formation of the wide variety of products formed in this study, other routes must be investigated. The majority of the products formed in the photo-oxidation of azo-n-butane (60-200°C) are even observed at the lowest temperature of the study (60°C). This indicates that the processes involved must have low activation energies. The species must also have a reasonable life-time in the presence of a large excess of molecular oxygen. In the azocyclohexane study, formation of cyclohexene was suggested to occur via an alkyl trioxyl radical (P.108). If the species RO₃• is important the analogous RO₄• is more likely since RO₂• is a secondary radical and RO• is a tertiary radical. This species can lead to n-butyraldehyde by an intra-

molecular process.



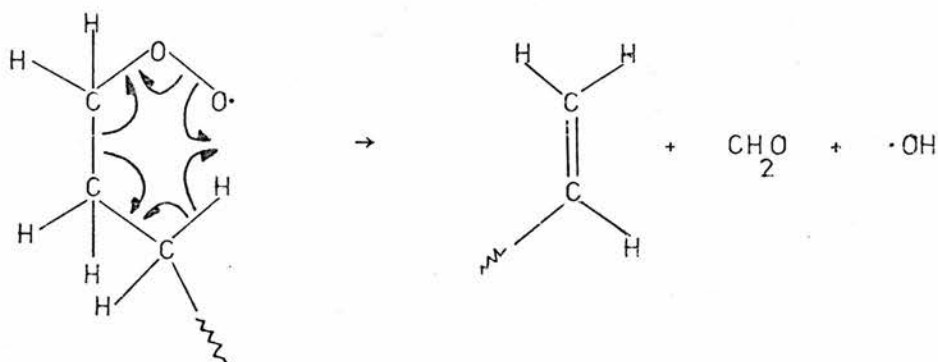
The above reaction involves the favourable six-membered transition state.

Another product which is not predicted by the general mechanism (P.125) is n-butane. This product can also be accounted for via an intramolecular process.



Calvert and Slater¹⁵⁴ found small amounts of isobutane from the photolysis of azoisobutane-oxygen mixtures, but could not deduce a reaction path for its formation.

At high temperatures the alkyl peroxy radicals themselves could undergo decomposition to propene and formaldehyde



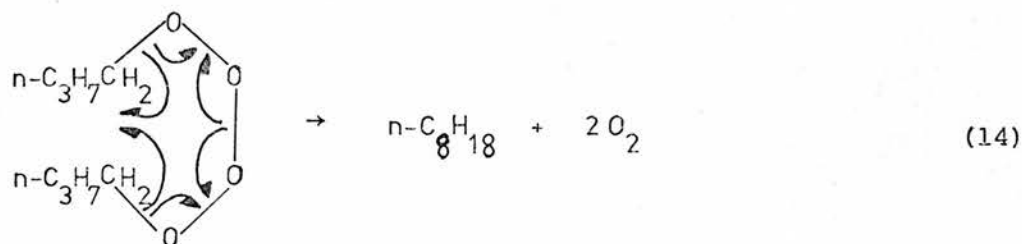
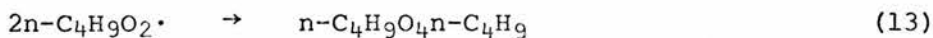
No attempt was made to analyse for formaldehyde in the present work.

Small amounts of n-octane were observed in all reaction mixtures. Neglecting the possibility that n-octane could be formed from the combination of two n-butyl radicals, (table III.8, (P.120) increase in oxygen concentration does not decrease n-octane formation) a probable source is the direct extrusion from excited azo-n-butane.

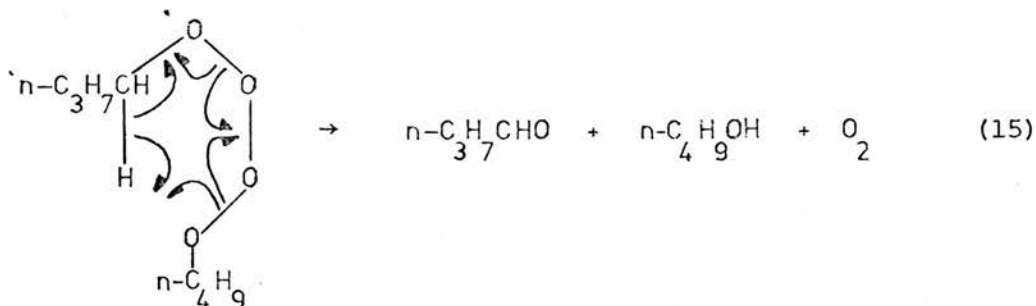


From runs in the presence and absence of oxygen the extrusion process, if operating, was estimated to be contributing about 5% to the total n-octane product formation from the photolysis of azo-n-butane. Examination of table III.8 (P.120) shows that the yield of n-octane increases with increasing oxygen concentration. This rules out the possibility of the extrusion process being the source of n-octane.

An alternative path involves the combination of n-butyl peroxy radicals.



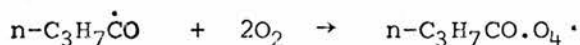
The combination of two n-butyl peroxy radicals could also yield n-butyraldehyde and n-butanol. This reaction has previously been postulated by Russell¹⁵⁶ for 1-phenylethylperoxy radicals in solution.



The Russell mechanism has recently been confirmed by Howard and Ingold¹⁵⁷. This was achieved by considering the Wigner spin-conversion rule. If the rule is not to be violated the oxygen must be eliminated in the singlet state, either $^1\Sigma_g^+$ or $^1\Delta_g$. The

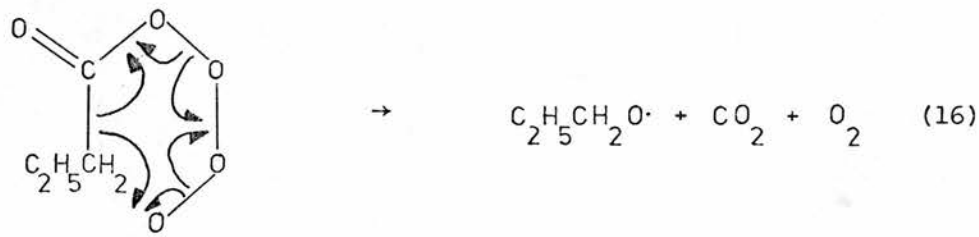
oxygen could also be eliminated in its triplet ground state $^3\Sigma^-$, if the ketone is also formed in its excited triplet state. The authors identified singlet oxygen in the self-reaction of sec-butyl peroxy radicals and therefore have obtained experimental support for the Russell mechanism. Further evidence was presented by Kellogg¹⁵⁸ from chemiluminescence experiments by showing that the carbonyl group was initially eliminated in the triplet state, which then in solvent cage yields triplet oxygen by energy transfer. Howard and Ingold¹⁵⁹ also observed a primary isotope effect when α -hydrogen atoms in the alkyl group were replaced by deuterium. The Russell mechanism requires that the α -hydrogen on one peroxy radical is transferred to the second peroxy radical in one of the rate controlling steps of the reaction. The replacement of the α -hydrogen by deuterium reduced the rate constant for the chain termination of secondary peroxy radicals thus confirming the mechanism.

An interesting feature of the high temperature (100-200°C) results is the emergence of propionaldehyde and acetaldehyde as the major products. The formation of these products can also be accommodated in the cyclic peroxide hypothesis. Propionaldehyde is most likely formed from n-butyraldehyde (table III.9, P.121) with the first step involving hydrogen abstraction from n-butyraldehyde to yield the butyroyl radical. The butyroyl radical can then combine with two molecules of oxygen to form a tetroxyl radical.



where $\text{X}\cdot = n\text{-C}_4\text{H}_9\cdot$ or $n\text{-C}_4\text{H}_9\text{O}_2\cdot$ or $n\text{-C}_4\text{H}_9\text{O}\cdot$

This tetroxyl radical can then undergo intramolecular reaction to form propoxyl radicals.

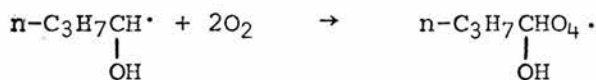


The propoxyl radical will be converted into propionaldehyde by hydrogen abstraction (disproportionation reaction analogous to reaction (8) or (9), (P.125)).

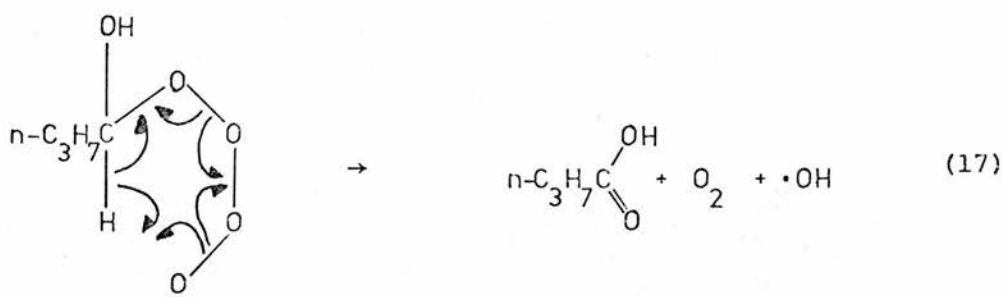


Acetaldehyde can be formed in a similar manner by hydrogen abstraction from propionaldehyde.

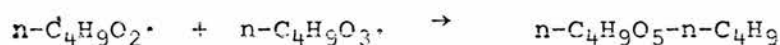
A minor product in high conversion runs is n-butyric acid; the most probable precursor is n-butanol again via a cyclic intermediate.



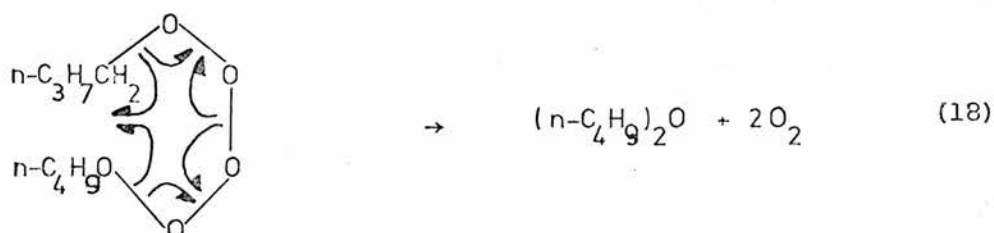
where $\text{X}\cdot = \text{n-C}_4\text{H}_9\cdot$ or $\text{n-C}_4\text{H}_9\text{O}_2\cdot$ or $\text{n-C}_4\text{H}_9\text{O}\cdot$.



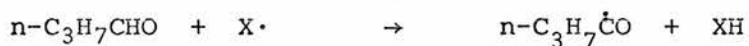
Another product which is found in high conversion runs is di-n-butyl ether. This product can also be accounted for in terms of a cyclic intermediate. The combination of either an n-butyl tetroxyl radical and an n-butoxyl radical, or the combination of an n-butyl peroxy with an n-butyl trioxyl radical leads to a penta-oxygen intermediate.



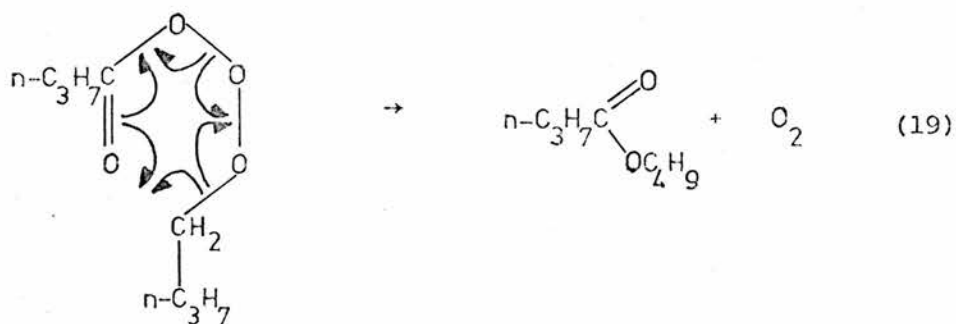
This intermediate leads to di-n-butyl ether via intramolecular reaction.



The other minor product which could be formed via a cyclic intermediate is n-butyl-n-butanoate. It was previously mentioned that n-butyroyl radicals are formed in the production of propionaldehyde (16) (P.132). The ester might be formed by the combination of this radical and an n-butoxyl radical

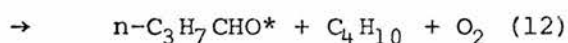
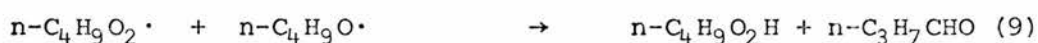
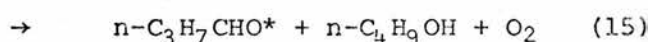


However, it is unlikely that a radical as reactive as the butyroyl radical could exist long enough to react with a tertiary radical unless it can be stabilized in some way. The radical could be stabilized by reaction with oxygen to give the much less reactive butyroyl peroxy radical. This radical will be more likely to react with the butoxyl radical.



From the azocyclohexane-oxygen study the formation of cyclohexene was explained by the formation of an alkyl trioxyl radical. From the present results the proportion of but-1-ene is greater and a similar mechanism can be invoked.

A general mechanism for the photolysis of azo-n-butane-oxygen mixtures is summarised as follows:-



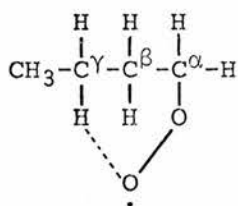
where * indicates electronically excited species.

The relative rates of formation of the major products requires that reaction (15) rather than reaction (6) to be the principal fate of n-butyl peroxy radicals. This does not agree with the fate of cyclohexyl peroxy radicals where reaction (6) was the main reaction. The difference between the two systems can be accounted for in the structures of the two radicals. The n-butyl chain is flexible while the cyclohexyl ring is

quite rigid. This rigidity in the cyclohexyl ring makes it very difficult to form a cyclic intermediate required for reaction (15).

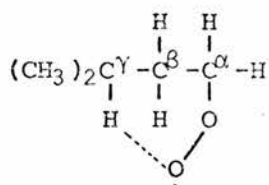
The involvement of these cyclic intermediates in oxidation processes cannot as yet be specifically assessed. Only more detailed experiments will determine the true importance of these intermediates. For the present it is suffice to say that these intermediates may be one of a number of processes involved in oxidations at low and at moderate temperatures.

The specific reason for studying the reactions of n-butyl radicals with molecular oxygen was to discover whether intramolecular hydrogen abstraction was taking place within the n-butyl peroxy radical.



The most likely site of attack is the γ -carbon atom. This involves the favourable six-membered transition state. The absence of bifunctional alcohols or ketones indicates that intramolecular hydrogen abstraction does not take place.

The next stage in this work was to investigate an alkyl peroxy radical, with one more carbon atom than the n-butyl peroxy radical, and with an easily abstractable hydrogen atom. The isopentyl peroxy radical (3-methylbutyl peroxy) fits these requirements. The most likely site of attack, for intramolecular hydrogen abstraction, is again the γ -carbon atom.



This radical should undergo intramolecular hydrogen abstraction more readily than the n-butyl peroxy radical.

A number of preliminary experiments were carried out to determine the reaction products from the photolysis of azoisopentane-oxygen mixtures. The sample for analysis was taken from a reaction mixture that had been photolysed for one hour at 100⁰ C. Thirteen peaks were observed from mass spectra g.l.c. although only nine were positively identified. These were: propene, ethylene oxide, 2-methyl propene, 3-methyl but-1-ene, acetone, propan-2-ol, 2-methyl propionaldehyde, 3-methyl butyraldehyde and 3-methyl butan-1-ol.

The major peak in low conversion runs (~1%) was 3-methyl butyraldehyde. Although 3-methyl butyl hydroperoxide was not identified from mass spectra data, the addition of triphenyl phosphite to samples from low conversion runs increased the amounts of 3-methyl butan-1-ol. It seems likely that the 3 main products from the photolysis of azoisopentane-oxygen mixtures, at low temperatures (<100⁰ C), are 3-methyl butyraldehyde, 3-methyl butan-1-ol and 3-methyl butyl hydroperoxide. This shows that the major products all contain the isopentyl group. The observed products are also in agreement with the azocyclohexane and azo-n-butane studies.

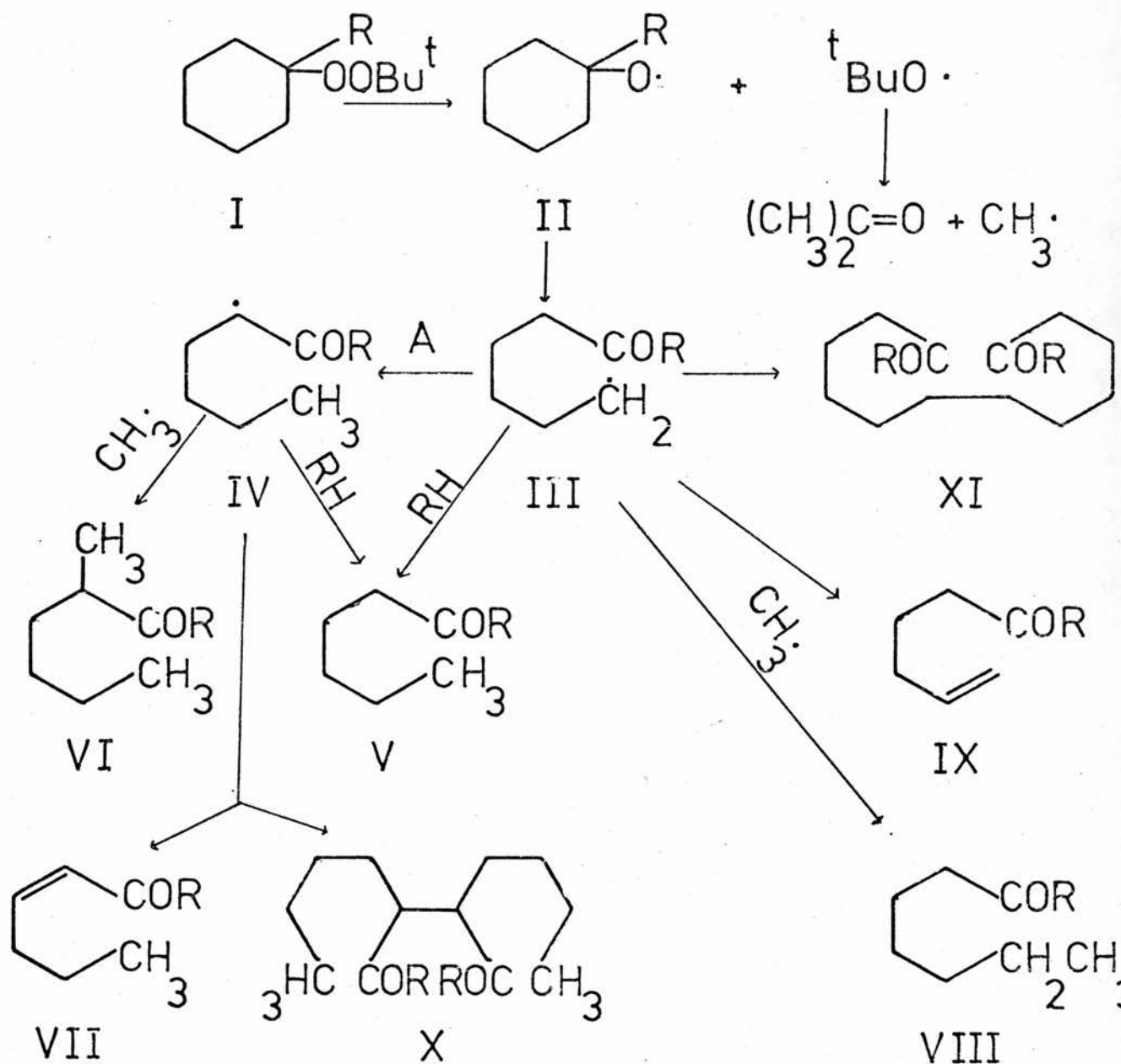
PART IV

THE DECOMPOSITIONS OF DIALKYL HYDROPEROXIDES AND
DIALKYL *t*-BUTYL PEROXIDES

PART IV
INTRODUCTION

Work by Milas and Perry ¹⁶⁰ on the decomposition of t-butyl-1-methylcyclohexyl peroxide (I) first observed the following rearrangement.

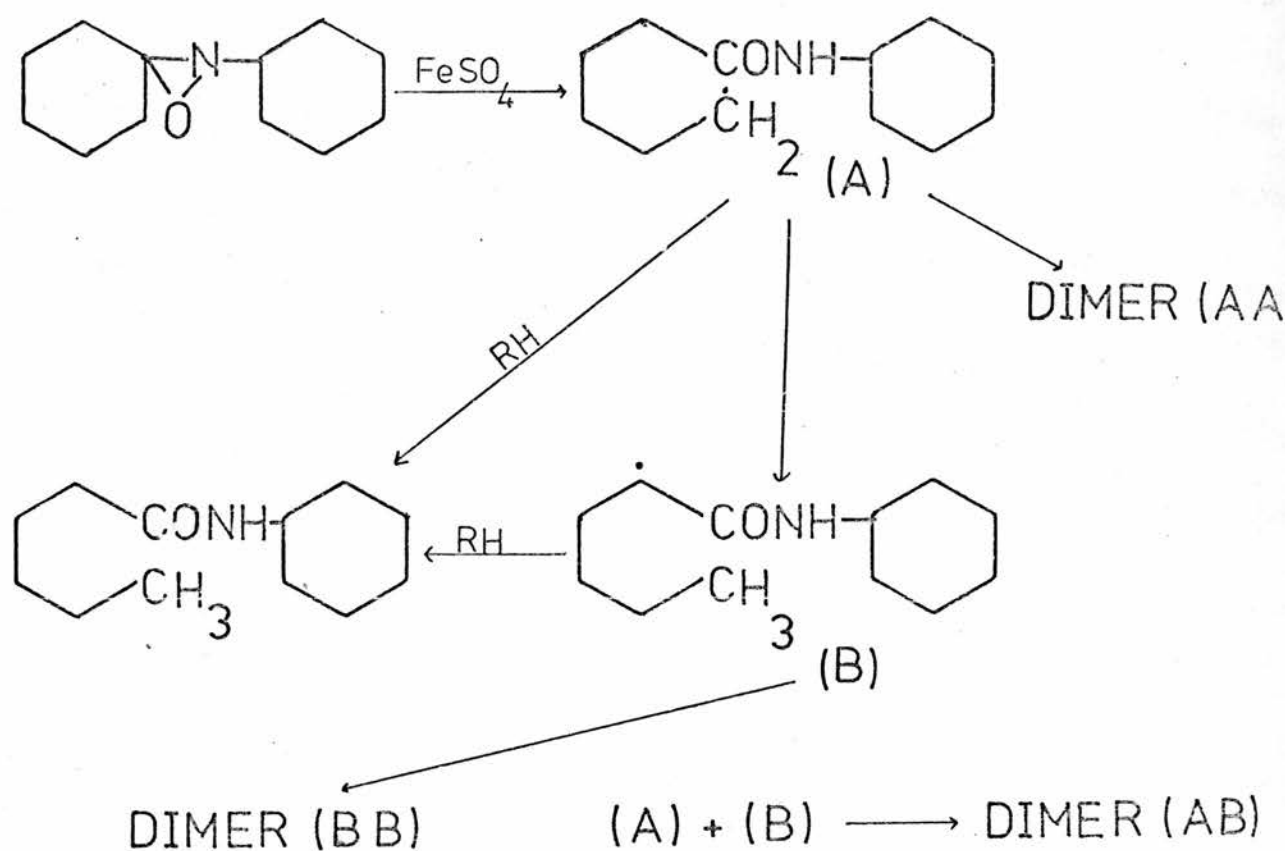
R = methyl. Step A is the 1,5-rearrangement (see page 140)



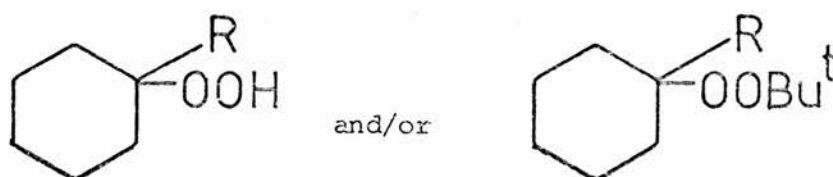
The products formed from this reaction were acetone,

3-methylheptan-2-one (VI), 3,4-di-n-butyl hexanedione-2,5 (X) and ethane.

Hawkins did some work on similar radicals and also found the 1,5-rearrangement was operating. This work used ferrous sulphate to decompose oxaziridines.

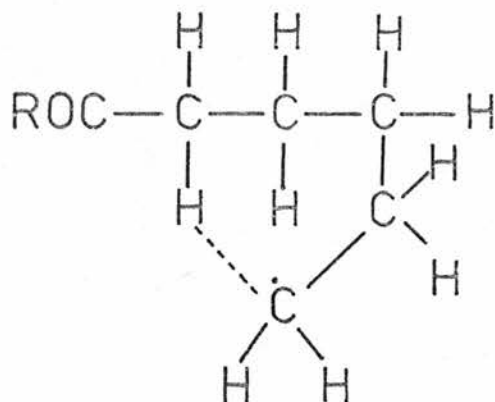


This present work was started in the hope of finding which factors influence the 1,5-rearrangement. The first factor looked into was the gem grouping, R.



R = Me, Et, i-Pr, n-Hexyl, Cyclohexyl and Phenyl.

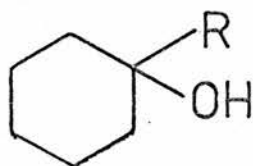
An interesting feature of the 1,5-rearrangement is that it must involve a 6 membered transition state; which as we have seen previously is very common for this type of interchange.



PART IV
EXPERIMENTAL

1. Materials

The tertiary alcohols were prepared by the general method of ketone and Grignard reagent¹⁶¹.



R = Me, Et, i-Pr, n-C₆H₁₃, c-C₆H₁₁, Ph.

The 1-isopropylcyclohexanol contained cyclohexanol (50%) as an impurity and could be purified no further. Attempted preparation of 1-phenylcyclohexanol yielded 1-phenylcyclohexene¹⁶² with a small alcohol impurity. The methyl- and ethyl- alcohols contained small amounts of cyclohexanol while the n-hexyl- and cyclohexyl- alcohols contained some cyclohexenylcyclohexanone.

Preparation of 1-Methylcyclohexyl Hydroperoxide¹⁶⁰

To avoid explosions the preparation was carried out in three separate flasks.

1-Methylcyclohexanol (6.72g; 0.06 mols) was added dropwise to a mixture of hydrogen peroxide (80-90%; 10 cm³) and concentrated sulphuric acid (0.08 cm³) with stirring between 10-15°C. The solution was allowed to come to room temperature, stirred for 1 hour and left overnight. The solution was stirred for 1 hour and some water added. The solution was extracted with ether, washed with water and dried over anhydrous magnesium sulphate. The combined extracts were distilled under reduced pressure.

B.Pt. 39-42°/0.2 mm (Lit¹⁶³ 38°/0.03 mm)

Wt = 17.2g. % Yield = 75%

Peroxide Equivalent (C) = 135.5 .'. %Purity = 95% (see P.145)

Analysis by I.R. N.M.R. and M.S. showed no appreciable impurities.

Preparation of 1-Ethylcyclohexyl Hydroperoxide

The same procedure was used as above.

B.Pt. 47.5-48.5°/0.35 mm (Lit¹⁶³ 39°/0.01 mm)

Wt = 17.4g. % Yield = 67.8%

Peroxide Equivalent (C) = 156.7 .'. % Purity = 92%

Analysis by I.R. N.M.R. and M.S. showed no appreciable impurities.

Preparation of 1-Isopropylcyclohexyl Hydroperoxide

The same procedure as above was used. Two fractions were obtained from distillation.

1st Fraction B.Pt 45-52°/0.15 mm Wt = 4.1g. Peroxide Eq(C) = 232.7

2nd Fraction B.Pt 53-54°/0.15 mm Wt = 0.96 g. Peroxide Eq(C) = 197.8

(Lit¹⁶³ 52°/0.01mm)

% Purity = 80%

Results from N.M.R. on fraction 2 indicate that the 1-isopropylcyclohexyl hydroperoxide in the sample amounts to a small component only as the signal due to

$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH-} \\ \diagup \\ \text{CH}_3 \end{array}$
 is very weak (could also be due to starting material).

The major absorption is due to cyclic structure and there is evidence for -OOH.

Preparation of 1-Phenylcyclohexyl Hydroperoxide¹⁶⁴

The preparation of the hydroperoxide was attempted from 1-phenylcyclohexene because the alcohol could not be prepared.

1-Phenylcyclohexene (6.55g) in ether (10 cm³) was added dropwise with stirring to a solution of concentrated sulphuric acid (0.04 cm³) in 80-90% hydrogen peroxide at room temperature. After the addition the mixture was stirred at room temperature for 6 hours and stored overnight. Water (50 cm³) was added and the solution was extracted with ether. The extract was washed with NaHCO₃ solution and water, dried, and evaporated at room temperature. Attempted recrystallisation of the hydroperoxide from light petroleum gave no product. The hydroperoxide should be a white solid (Lit¹⁶⁴ M.Pt. 60°C). A different method was then attempted.

80-90% Hydrogen peroxide (4g) in ether (35 cm³) was stirred with some magnesium sulphate for a short time. The solution was filtered and to it was added 1-phenylcyclohexene (8g) in ether. The solution was cooled slightly, a few drops of thionyl chloride added and the solution allowed to come to room temperature. Stirring is not required since there is only one phase. Work up and subsequent crystallisation gave no product.

Attempts at using concentrated sulphuric acid instead of thionyl chloride in the method above again yielded no product.

Preparation of 1-Cyclohexylcyclohexyl Hydroperoxide

The procedure for the preparation of 1-methylcyclohexyl hydroperoxide was again followed.

The majority of the residue obtained was unreacted alcohol.

Residue weight = 7.8g Peroxide Equivalent (C) = 459.2

Distillation at reduced pressure gave a fraction of 1-cyclohexyl-cyclohexanol.

residue (colourless liq) Weight = 0.7g Peroxide Equivalent (C) = 245.0

% Purity = 80.8% (Lit¹⁶⁵)

Another procedure was attempted. The alcohol was dissolved in ether and then added to the solution of peroxide and concentrated acid. Again the majority of the residue obtained was unreacted alcohol.

Residue Weight=(6.9g). Peroxide Equivalent (C) = 1000

Preparation of 1-n-Hexylcyclohexyl Hydroperoxide

The procedure for the preparation of 1-methylcyclohexyl hydroperoxide was again followed. The residue obtained was distilled at reduced pressure.

Fraction: B.Pt. 66-69°/0.2 mm. Weight = 6.0g.

Residue: Weight = 2.0g. Peroxide Equivalent (C) = 3330

% Purity = 6%

Residue decomposed on attempted distillation.

The following methods are used to determine the purity of peroxides and hydroperoxides.

Methods for Unreactive Peroxides

A. To a 100 cm³ conical flask was added sodium iodide, sodium bicarbonate, glacial acetic acid (25 cm³), concentrated hydrochloric acid (5 cm³) and the peroxide (~0.1g). After heating on a water

bath for 10 mins, more sodium bicarbonate was added and the flask heated for a further 10 mins. The flask was cooled quickly to room temperature and some distilled water added ($\sim 30 \text{ cm}^3$). The contents of the flask are then titrated with 0.1M sodium thiosulphate. A blank solution was run simultaneously.

$$\text{Peroxide Equivalent} = \frac{\text{Weight of Peroxide} \times 20,000}{\text{Titre}}$$

$$\% \text{ Purity} = \frac{\text{Molecular Weight} \times 100}{\text{Peroxide Equivalent}}$$

B. This method is more applicable to dialkyl peroxides^{166'167}

Reflux glacial acetic acid (50 cm^3) for a few mins. Cool and add 6g of sodium iodide. Add an aliquot of the sample (up to 2.5 m. eq.) in acetic acid or xylene. (For di-tert-alkyl peroxides add 37% hydrochloric acid (2 cm^3) and put on to boil immediately. Reflux for 50 mins, add 100 cm^3 of distilled water and titrate with 0.1M sodium thiosulphate. A blank solution was run simultaneously. The peroxide equivalent was calculated as before.

C. For Reactive Peroxides and Hydroperoxides

To a 100 cm^3 conical flask was added, saturated potassium iodide (5 cm^3), sodium bicarbonate, glacial acetic acid (25 cm^3) and the hydroperoxide ($\sim 0.1\text{g}$). The flask was heated on a steam bath for 5 mins and then quickly cooled to room temperature. A small amount of distilled water was added and the solution titrated with 0.1M sodium thiosulphate solution. The peroxide equivalent was calculated as before.

Preparation of t-Butyl-1-Methylcyclohexyl-1-Peroxide¹⁶⁰

To 1-methylcyclohexanol (70g) was added dropwise with stirring 65% by weight concentrated sulphuric acid (100g). This solution was then cooled to 0°C and t-butylhydroperoxide (70%; 100g) was added dropwise with stirring, the temperature being kept at 0-5°C. After all the hydroperoxide had been added, the solution was gradually allowed to come to room temperature over 2 hours. The mixture was stored at room temperature overnight and then stirred at 30-35°C for 1 hour. The upper layer was separated with ether, washed with water, dried over magnesium sulphate and distilled under reduced pressure in an atmosphere of nitrogen. Note 1.

B.Pt 75-80°/15 mm (Lit¹⁶⁰ 28-29°/2.5 mm)

Weight obtained = 22g. ∴ % Yield = 17.3%

Peroxide Equivalent (A) = 258.3 Peroxide Equivalent (B) = 217.4

∴ % Purity = 72.8%

∴ % Purity = 85.6%

Note 1

When distilling peroxides protective shields should be used and the distillation should be carried out under nitrogen. In the above preparation and subsequent preparations a first distillation under reduced pressure and nitrogen was carried out to remove any ether, di-t-butylperoxide (impurity in t-butylhydroperoxide) unreacted t-butylhydroperoxide and 1-methylcyclohexanol.

Analysis by N.M.R., I.R. and M.S. showed the sample to contain a very small amount of the starting alcohol. Attempts to remove this impurity by column chromatography and fractionation were unsuccessful.

Preparation of t-Butyl-1-Ethylcyclohexyl-1-Peroxide

The procedure for the preparation of t-butyl-1-methylcyclohexyl-1-peroxide was again followed.

B.Pt 45-55⁰/0.7 mm

Weight obtained = 40g % Yield = 29.5%

Peroxide Equivalent (A) = 252.2 Peroxide Equivalent (B) = 219.4

% Purity = 79.3%

% Purity = 91.2%

Analysis by N.M.R., I.R. and M.S. showed the peroxide contained a very small amount of the starting alcohol.

Preparation of t-Butyl-1-Isopropylcyclohexyl-1-Peroxide

The procedure used for the preparation of t-butyl-1-methylcyclohexyl-1-peroxide was again followed. A colourless liquid distilled over.

B.Pt 55-62⁰/0.5 mm

Weight = 11.25g. Peroxide Equivalent (A) = 277.5

Residue Weight = 7g. Peroxide Equivalent = 201.4

The peroxide equivalent of the residue is too low and is probably a mixture of the required peroxide and a peroxide with a lower molecular weight. This is quite possible since the starting alcohol was very impure. Another method was then used.

Concentrated sulphuric acid (1 cm³) was added slowly to a solution of isopropylcyclohexanol (8.2g) and t-butylhydroperoxide (7.9g) in acetic acid (30 cm³). The temperature during the addition was kept between 15-20⁰C. The solution was then stirred at room temperature for ~3 hours and left overnight. After usual work up no peroxide was present in the distillate.

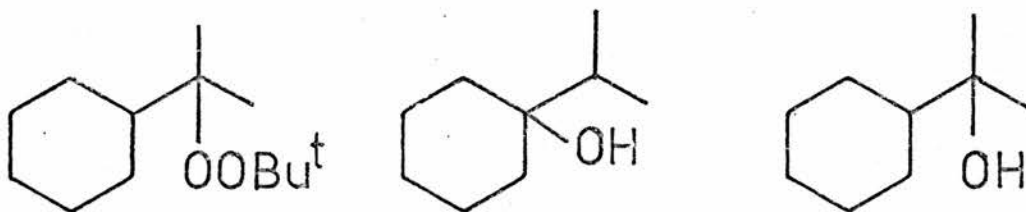
The 1-isopropylcyclohexanol was purified to a certain degree by fractionation and then used in the preparation as before.

B.Pt 49-52°/0.15 mm weight = 1.91g

Peroxide Equivalent = 229.7

% Purity = 93.2%

Analysis by N.M.R. and I.R. showed that the sample contained about 50% of the peroxide, ~10% of the alcohol and 40% unknown. From M.S. analysis the sample could contain the required peroxide together with:-



Preparation of t-Butyl-1-Phenylcyclohexyl-1-Peroxide^{168,169}

The same procedure was followed as before except the 1-phenylcyclohexene was used instead of the alcohol. No product was obtained. Another method was then tried.

Concentrated sulphuric acid (2 cm³) was added very slowly to a solution of 1-phenylcyclohexene (18g) and t-butylhydroperoxide (10g) in acetic acid (60 cm³), cooled in water. The solution went very dark. After leaving overnight the solution was poured into water (~100 cm³). The organic layer was washed with dilute sodium hydroxide solution and with saturated potassium carbonate solution and dried over potassium carbonate. Distillation under

reduced pressure gave a colourless liquid.

B.Pt 55° /0.15 mm Weight = 6.0g

Peroxide Equivalent proved negative.

Preparation of t-Butyl-1-Cyclohexylcyclohexyl-1-Peroxide

The procedure for the preparation of t-butyl-1-methylcyclohexyl-1-peroxide was again followed.

- i. Distillation under reduced pressure.

B.Pt $43-59^{\circ}$ C/0.15mm Peroxide Equivalent (A) = 394.4

Bath temp = 74° C. Residue: Peroxide Equivalent (A) = 293.8

Analysis by N.M.R., I.R. and M.S. on the residue showed evidence for the peroxide but also ~20% of the starting alcohol and appreciable amounts of C=O (at least 3 types, probably ketone, ester and lactone). Also evidence for -C=C-.

- ii. Same procedure as before.

B.Pt $46-50^{\circ}$ C/0.15mm. Bath Temp kept below 63° C.

Residue : Peroxide Equivalent = 339.9.

Analysis showed similar spectrum to (i) but slightly fewer impurities.

Preparation of t-Butyl-1-n-Hexylcyclohexyl-1-Peroxide

The same procedure was again used.

- i. Distillation under reduced pressure gave a colourless liquid.

B.Pt $46-50^{\circ}$ C/0.15mm Residue: Peroxide Equivalent (A) = 503.2.

Bath Temperature never exceeded 62° C.

ii. Same procedure as above.

B.Pt $60-72^{\circ}/0.2\text{mm}$ Peroxide Equivalent (A) = 1028

Residue: Peroxide Equivalent (A) = 550.4

Peroxide Equivalent (B) = 225.5

Bath Temperature 82°C .

- i. Analysis showed sample contained ~30% of the starting alcohol and also evidence for unsaturation $-\text{CH}_2-\text{C}=\text{C}$ and/or $-\text{CH}_2-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-$
- ii. Very similar results from analysis.

2. Apparatus and Procedure

The Pyrolysis of t-Butyl-Dialkyl Peroxides at 300°C .

The pyrolysis equipment consisted of a hollow glass tube filled with glass beads and surrounded by a cylindrical oven. Nitrogen slowly passed through the system and the pyrolysis was carried out at atmospheric pressure. The peroxide was dropped slowly through the apparatus and the decomposition products formed, pass through a distillation column into a receiving vessel which was cooled in a cardice-acetone bath. A side arm on the receiving vessel lead into a cold trap cooled by another cardice-acetone bath. The products were distilled into a number of fractions.

t-Butyl-1-alkylcyclohexyl -1-Peroxide	Weight of Peroxide used (g)	Weight of Material Recovered (g)
-methyl-	10.0	9.1
-ethyl-	10.0	8.94
-cyclohexyl- (i)	10.0	8.83
-cyclohexyl- (ii)	7.6	6.0
-n-Hexyl- (i)	10.0	8.92
-n-Hexyl- (ii)	10.0	9.20

Decomposition of Hydroperoxides by Ferrous Sulphate

To a solution of ferrous sulphate (26.73g in 50³cm water; 25% excess) was added concentrated sulphuric acid (4.5g; excess) and methanol (40 cm³). The solution was cooled to ~0°C and the hydroperoxide (10g) in methanol (10 cm³) was added dropwise with stirring, the temperature being kept between 0-5°C. During the addition nitrogen was bubbled through the solution. After all the hydroperoxide had been added the solution was brought to room temperature and stirred for 0.5 hr. The solution was then diluted with water and extracted with ether. The ether extract was washed with water and dried over magnesium sulphate. The bulk of the ether was removed at atmospheric pressure and the remainder under reduced pressure. At this point a sample was taken for analysis. The solution was then distilled under reduced pressure and certain fractions were taken of the distillate.

1-alkylcyclohexyl hydroperoxide	weight of hydroperoxide used (g)	weight recovered (g)
methyl-	10	7.92
ethyl-	10	7.84

The Photo-Decomposition of t-Butyl-Dialkyl Peroxides

The photo-decompositions were carried out in the apparatus shown (fig. IV.1). All the reactions were carried out using benzene as solvent. It was also found necessary to use an initiator to speed up the decompositions. Initially benzophenone was used but tetraphenylporphin proved more successful. At varying intervals during photolysis aliquots of the reaction mixture were taken and their peroxide content found by method A.

t-Butyl-1-alkylcyclohexyl- 1-peroxide	Photolysis time	Peroxide at start	Contents at finish
-methyl-	11 hrs	0.0167mols	0.004mols
-ethyl-	14½ hrs	0.03 mols	0.0022mols

In both experiments 10g of peroxide was used in 220 cm³ benzene. The photolyses were carried out in a quartz reactor at room temperature. After photolysis was completed the bulk of the benzene was removed by distillation at atmospheric pressure. The remaining benzene was distilled over under reduced pressure. The products were then distilled under reduced pressure into certain fractions for analysis.

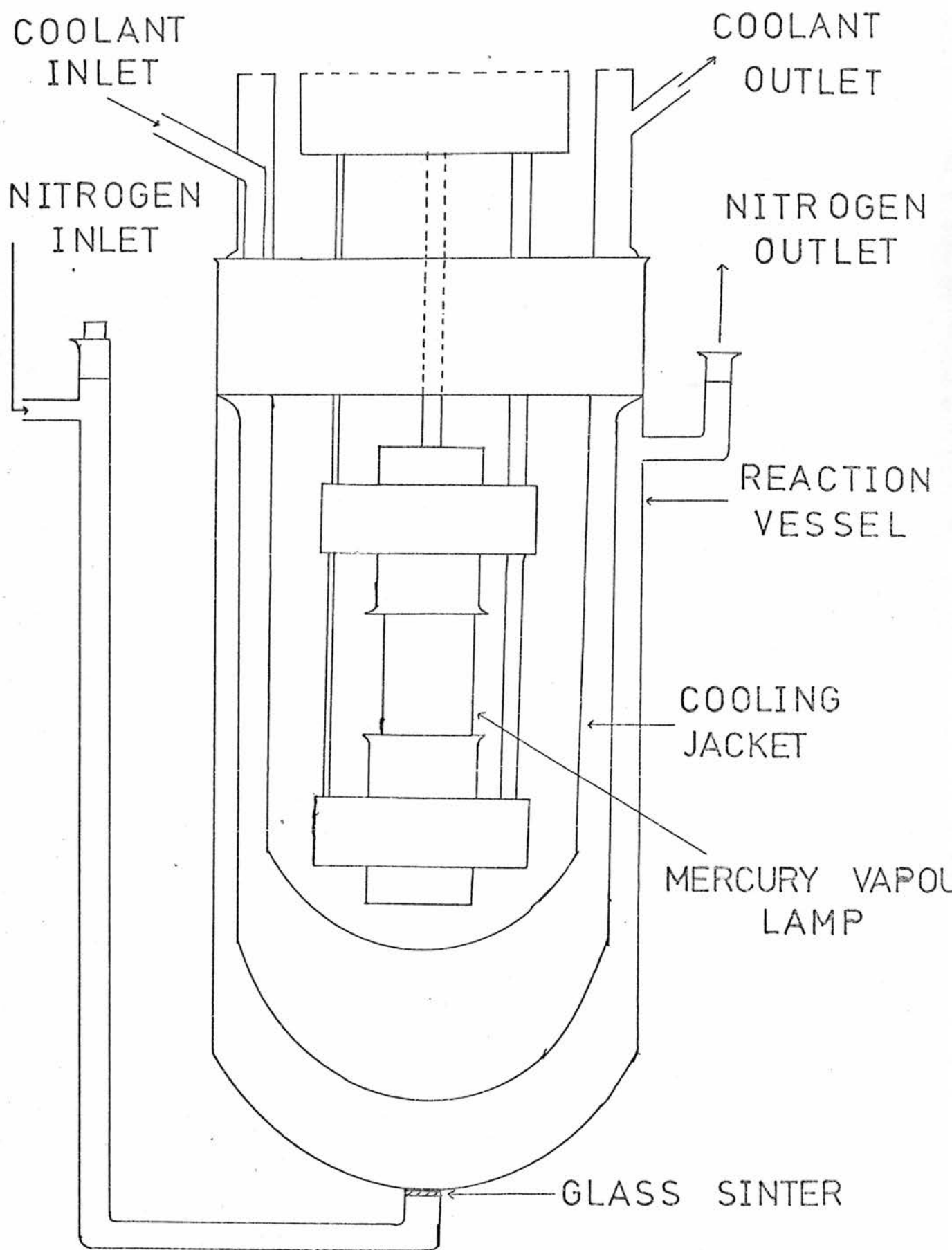


FIGURE IV.1

3. ResultsTABLE IV.1 The Ferrous Sulphate Decomposition of
1-Methylcyclohexyl Hydroperoxide

Product	%
Heptan-2-one ($\text{CH}_3\text{CO}^n\text{C}_5\text{H}_{11}$)	63.6
1-Methylcyclohexanol	22.1
1-Methylcyclohexanol (geometrical isomers)	2.1 4.3
not identified - probably	0.6
$\text{C}_{14}\text{H}_{26}\text{O}$ but fragmentation	1.7
not correct for diketones	2.5
6 small unidentified peaks	2.9

TABLE IV.2 The Ferrous Sulphate Decomposition of
1-Ethylcyclohexyl Hydroperoxide

Product	%
Octan-3-one ($\text{C}_2\text{H}_5\text{CO}^n\text{C}_5\text{H}_{11}$)	60.9
Cyclohexanone *	16.6
1-Ethylcyclohexanol	6.4
Cyclohexanol *	2.4
not identified - probably $\text{C}_{16}\text{H}_{30}\text{O}_2$	0.6
but fragmentation not as expected	0.8
for the anticipated diketones	1.8
not identified	2.4
4 small unidentified peaks	5.4

* Mainly these products but traces of other compounds.

TABLE IV.3 The Pyrolysis of t-butyl-1-methylcyclohexyl-1-peroxide

Product	%
3-methyl heptan-2-one (ⁿ C ₄ H ₉ CHCOCH ₃) CH ₃	36.2
Acetone	34.9
C ₁₄ H ₂₆ O ₂ (probably not diketones)	5.6 5.4
C ₃ H ₆ + C ₄ H ₈	3.7
unsaturated ketone (C ₅ H ₉ COCH ₃)	3.2
C ₁₄ H ₂₆ O ₂ (possibly a diketone)	1.9
octan-2-one (ⁿ C ₆ H ₁₃ COCH ₃)	1.5
heptan-2-one (ⁿ C ₅ H ₁₁ COCH ₃)	1.4
2 unidentified peaks	1.9 1.1

TABLE IV.4 The Pyrolysis of t-butyl-1-ethylcyclohexyl-1-peroxide

Product	%
acetone	30.8
4-methyl octan-3-one ($\text{CH}_3\text{CH}_2\text{COCH}^{\text{n}}\underset{\text{CH}_3}{\text{C}}_4\text{H}_9$) + trace ($\text{CH}_3\text{CH}_2\text{CO}^{\text{n}}\text{C}_5\text{H}_{11}$)	29.3
Cyclohexanone + trace ($\text{CH}_3\text{CH}_2\text{CO}^{\text{n}}\text{C}_6\text{H}_{13}$)	13.7
1-Ethylcyclohexene	3.6
$\text{C}_{16}\text{H}_{30}\text{O}_2$	2.8
(probably not diketones)	2.6
Cyclohexanol + trace (unknown compound)	2.5
$\text{C}_{16}\text{H}_{30}\text{O}_2$	1.2
(possibly a diketone)	
8 unidentified peaks	8.0

TABLE IV.5 The Pyrolysis of t-butyl-1-cyclohexylcyclohexyl-1-peroxide

Product i	%	Product ii	%
t-butanol	19.4	1-cyclohexylcyclohexene	26.8
acetone	18.9	acetone	15.0
1-cyclohexylcyclohexene	15.3	t-butanol	14.2
isobutene	9.5	isobutene	10.1
cyclohexanone	8.0	cyclohexanone	9.2
phenylcyclohexane	1.4	9 unidentified peaks	17.0
cyclohexylcyclohexanone	2.9		
8 unidentified peaks	14.0		

TABLE IV.6 The Pyrolysis of t-butyl-1-n-hexylcyclohexyl-1-peroxide

Product i	%	Product ii	%
1-n-hexylcyclohexene	57.8	1-n-hexylcyclohexene	51.6
cyclohexanone	10.7	t-butanol	8.7
t-butanol	6.0	cyclohexanone	7.4
1-n-hexylcyclohexanol	5.6	n-pentyl-n-hexyl ketone	6.9
n-pentyl-n-hexyl ketone $\text{}^{\text{n}}\text{C}_5\text{H}_{11}\text{CO}^{\text{n}}\text{C}_6\text{H}_{13}$ $+ \text{}^{\text{n}}\text{C}_4\text{H}_9\text{CHCO}^{\text{n}}\text{C}_6\text{H}_{13}$ $\quad \quad \quad \text{CH}_3$	5.3		
acetone	3.4	isobutene	5.7
isobutene	3.2	acetone	5.5
n-dodecane	1.1	1-n-hexylcyclohexanol	3.5
unidentified peak	1.9	n-dodecane	1.4
19 small peaks	3.0	unidentified peak	2.3
		20 small peaks	3.1

TABLE IV.7 The Photolysis of t-butyl-1-methylcyclohexyl-1-peroxide

Product	%
heptan-2-one ($\text{CH}_3\text{CO}^{\text{n}}\text{C}_5\text{H}_{11}$)	5.0
1-methylcyclohexanol	5.6

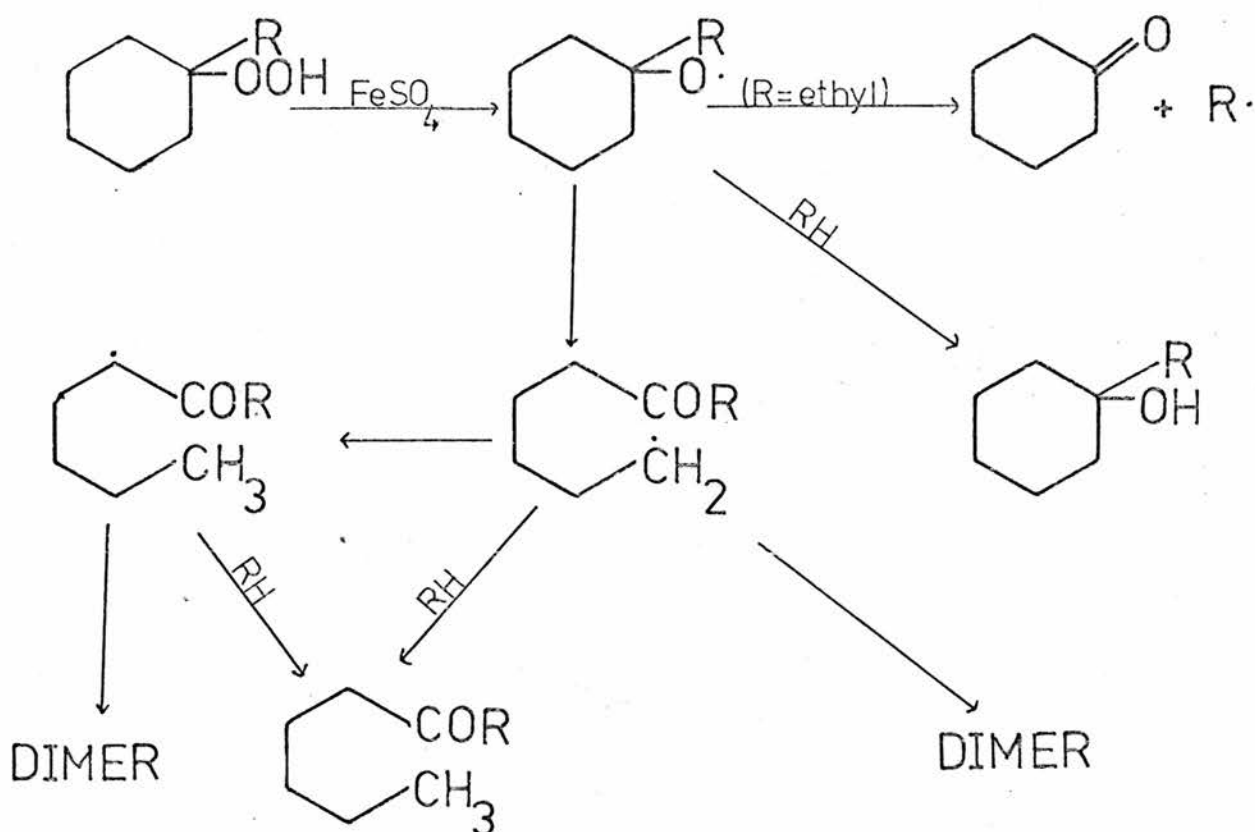
TABLE IV.8 The Photolysis of t-butyl-1-ethylcyclohexyl-1-peroxide

Product	%
1-ethylcyclohexanol	16.8

PART IV
DISCUSSION

Comparing the results from tables IV.1 and IV.2 the only noticeable difference between the two decompositions is the formation of cyclohexanone and cyclohexanol from the 1-ethylcyclohexyl hydroperoxide decomposition.

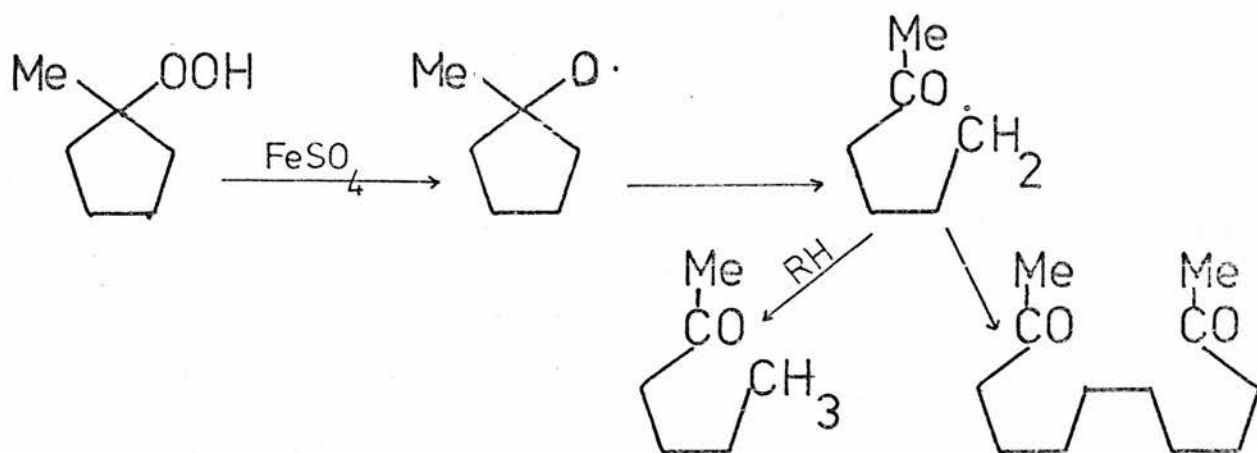
R = methyl or ethyl.



This would indicate that although ring scission of the 1-ethylcyclohexyl-oxy radical is still the major path, a certain amount of elimination is now taking place. Why there should be elimination with ethyl- and none with methyl- is not readily apparent.

Hawkins ¹⁷⁰ studied the ferrous sulphate decomposition of 1-methylcyclohexyl hydroperoxide and found the main products to be

heptan-2-one, tetradecane -2:13-dione (~12%) and an unidentified alcohol. The thermal decomposition of this product gave mainly a mixture of heptan-2-one and 1-methylcyclohexanol. Hawkins and Young ¹⁷¹ studied the ferrous sulphate decomposition of 1-methylcyclopentyl hydroperoxide and found the main product to be dodecane-2:1-dione (up to 60%) and some methyl butyl ketone.



Although the preparation of 1-phenyl-cyclohexyl hydroperoxide was unsuccessful this compound has been studied previously ¹⁶⁴. The thermal decomposition of the hydroperoxide in chlorobenzene yielded n-pentyl phenyl ketone (v), (R=Ph) whereas the ferrous sulphate decomposition gave 1:10 dibenzoyldecane XI, (R=Ph, P.138) (22%). No cyclohexanone was formed from any of these decompositions which points to the absence of cleavage of the bond between the aromatic nucleus and the cyclohexane ring. The authors explain the preferential cleavage of the alicyclic ring as due to the considerable loss of the resonance energy arising from the conjugation of the carbonyl group with the aromatic nucleus which would be involved in the disruption of the radical (II), (R=Ph, P.138).

From the work on hydroperoxides the results show that there is

an alternative reaction to ring scission i.e. elimination ($R=Et$).

The decompositions of the substituted t-butyl-cyclohexyl peroxides should lead to more information concerning the 1,5-rearrangement. The results from the pyrolysis of t-butyl-1-methylcyclohexyl-1-peroxide and t-butyl-1-ethylcyclohexyl-1-peroxide are shown in tables IV.3 and IV.4 (P.155) respectively.

The pyrolysis of t-butyl-1-methylcyclohexyl-1-peroxide shows all the products consistent with the 1,5-rearrangement operating. Even the disproportionation product from the combination of radical (IV) ($R=Me$, P.138) the unsaturated ketone was identified. The combination products i.e. diketones, were found to a lesser extent, but were not positively identified. The difference observed when R is changed from methyl to ethyl is negligible since both sets of results have approximately the same relative percentage of the methyl addition compound (VI), (P.138). Again, in the case of the ethyl-compound a certain amount of elimination is apparent, with the formation of cyclohexanone. 1-Ethylcyclohexene is probably formed from dehydration of the alcohol which is most likely present as a small impurity in the starting material.

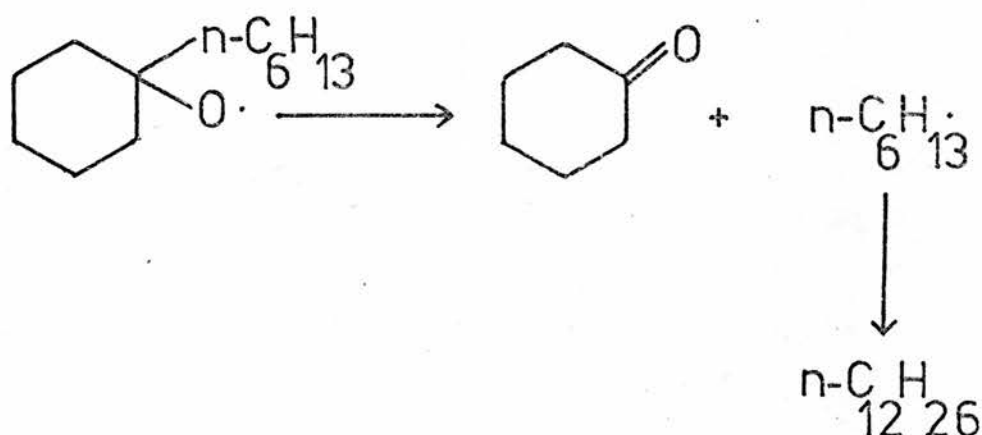
The t-butyl-1-cyclohexylcyclohexyl-1-peroxide and t-butyl-1-n-hexylcyclohexyl-1-peroxide on preparation were found to be very impure. The cyclohexyl-compound contains about 20% of the starting alcohol as well as a small amount of a carboxylic acid and a compound with the grouping $CH_2-C=C$ or $\begin{array}{c} C-CH_2 \\ || \\ O \end{array}$. A large quantity of water was found after completion of the pyrolysis which most likely comes from dehydration of the alcohol.

The n-hexyl-compound contains similar impurities i.e. ~10% of the starting alcohol and a compound with the grouping $-CH=CH-$.

Two samples of each of the above compounds were pyrolysed. The

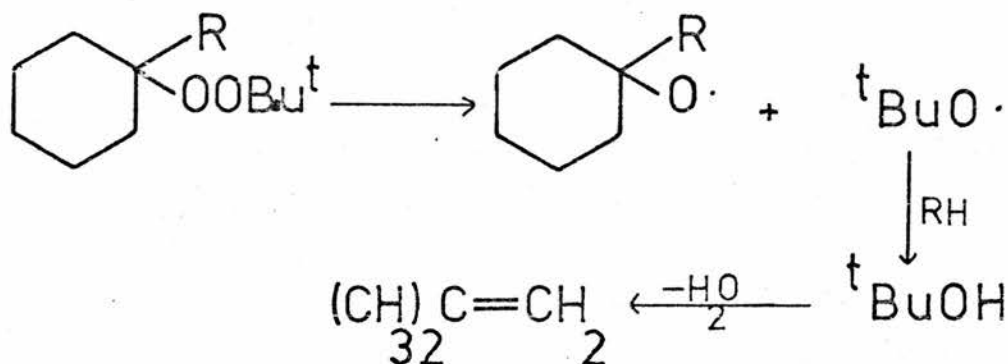
only difference in the preparation of the two samples was the temperature of their final distillation. The results are shown in tables IV.5 and IV.6 (P.156).

The presence of cyclohexanone and n-dodecane from the pyrolysis of the n-hexyl- compound proves that elimination is definitely taking place.



The results from the pyrolysis of the n-hexyl- compound confirm that the 1,5-rearrangement is biased towards the secondary radical (IV) in relation to the primary radical (III), (P.138). In the cyclohexyl- case no ring scission was observed and the main fate of the radical (II, R=cyclohexyl, P.138) appears to be elimination. 1-Cyclohexylcyclohexene probably comes from dehydration of the starting alcohol and this would also account for the water formed in this reaction.

The isobutene formed in both reactions (tables IV.5 and IV.6 P.156) is most likely formed from dehydration of t-butanol.



The final decompositions carried out were the photolyses of *t*-butyl-1-methylcyclohexyl-1-peroxide and *t*-butyl-1-ethylcyclohexyl-1-peroxide in benzene. Since the decompositions were very slow an initiator was used. The results are shown in tables IV.7 and IV.8, (P.157). From the results no deductions can be made concerning the 1,5-rearrangement.

Although the photolysis experiments gave limited results the pyrolysis experiments furnished results which confirmed the 1,5-rearrangement was operating. From the results no general factor influencing the rearrangement was observed although it seems certain that it must proceed through a six-membered transition state. This can be seen more clearly by considering the 1-methylcyclopentyl hydroperoxide decomposition (P. 159) where no rearrangement occurs because a five-membered transition state would be involved.

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