

THE KINETICS AND MECHANISM OF THE THERMAL
DECOMPOSITION OF BIS DIPHENYL METHYL AND
RELATED PEROXIDES IN LIQUID PHASE

BY

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1. ABSTRACT

Rates and products have been determined for the thermal decomposition of bis diphenyl methyl peroxide and diphenyl methyl tert. butyl peroxide at 110°-145°C.

The decomposition was uniformly unimolecular with activation energies for the bis diphenyl methyl peroxide in tetrachloroethylene, toluene and nitrobenzene 26.6, 28.3, and 27 Kcals/mole respectively. Diphenyl methyl tert. butyl peroxide showed an activation energy of 38.6 Kcals/mole.

About 80-90% of the products in the case of diphenyl methyl peroxide could be explained by the concerted process, this coupled with the negative entropies of activation obtained is a conclusive evidence for the reaction adopting a major concerted path.

All the products in the case of diphenyl methyl peroxide could be explained by known reactions of alkoxy radicals. About 80-85% of tert butanol and benzophenone formed suggested far greater cage disproportionation than diffusing apart.

Rates of bis triphenyl methyl peroxide have been determined in tetrachloroethylene at 100-120°C. The activation energy was found to be 31 Kcals/mole.

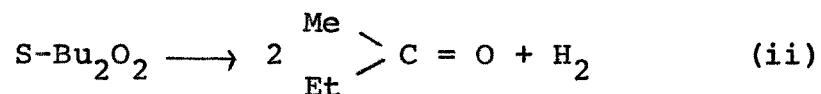
2. INTRODUCTION

2.1 Dialkyl peroxides are supposed to cleave on heating at the -O-O- bond almost exclusively ^{by} a homolytic process, little complicated by other decompositions of a radical or molecular nature.



However, most of the evidence for this belief is based upon the studies of one member of the species, tert-butyl peroxide.

Recent studies indicated that the decomposition of dissecondary alkyl peroxides are more complicated. Thus while Pryor et al (1) found that sec.-butyl peroxide initiated the polymerisation of styrene at the same rate that tert-butyl peroxide did, Hiatt, et.al. (2) found that the former underwent thermal decomposition about four times as fast as the latter. Above all, Hiatt, et.al. (2) found that molecular hydrogen formed a significant product from the decomposition of sec.-butyl peroxide.



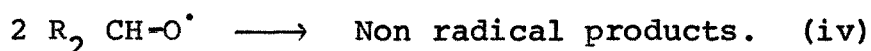
This project has been concerned with the decomposition of secondary alkyl peroxides where the substituent groups are aromatic, (phenyl), the mechanism of hydrogen formation, and the behaviour of the two secondary alkoxy radicals

generated in the solvent cage.

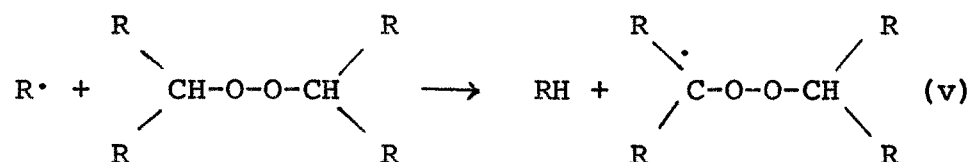
A secondary alkyl peroxide can undergo homolytic or molecular decomposition by at least three ways. The first mechanism is a unimolecular scission of the peroxidic -O-O- bond.

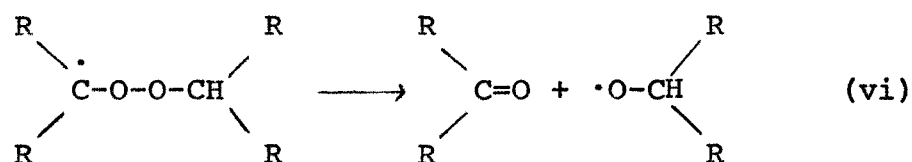


The radicals produced by this mechanism can either attack other molecules present in the system, initiating the radical chain process or can disproportionate giving non radical products.

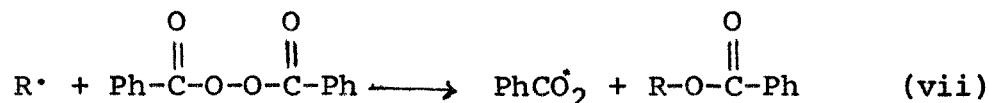


The second homolytic decomposition is by a bimolecular mechanism known as "induced decomposition". The mechanism of "induced" decomposition depends on the structure of the peroxide. For simple alkyl peroxides it is believed to be hydrogen abstraction from the α carbon atom to produce an intermediate radical which undergoes β scission, represented in a simpler form as shown below.





For benzoyl peroxide it is an attack on the peroxidic -O-O- bond.

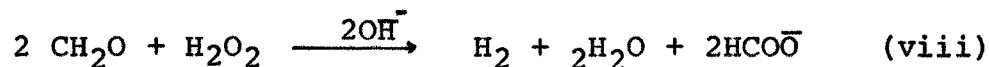


When peroxides are used to initiate radical reactions, the attacking radical $\text{R}\cdot$ can be formed from the peroxide itself.

The third mechanism is the one that yields hydrogen.

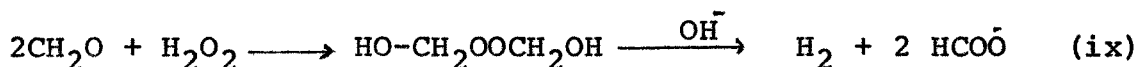
2.2 The Generation of Molecular H_2 from Peroxides

The evolution of hydrogen by the ^{re}action of formaldehyde with hydrogen peroxide in basic medium (sodium hydroxide) was first detected by Blank and Finkenbeiner (3).

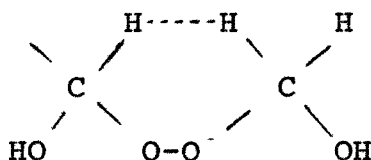


The evolution of hydrogen in presence of an oxidising agent like hydrogen peroxide is quite surprising. The Blank Finkenbeiner reaction was thought to proceed by a hydroxymethyl peroxide intermediate (4, 5).

Wieland and Wingler (5) isolated and synthesised the intermediate hydroxymethyl peroxide and it was found to yield the same products as Blank-Finkenbeiner reaction did under the same conditions.



They proposed a concerted mechanism for this reaction involving a six membered transition state



The photochemical reaction of formaldehyde and oxygen was studied by Style and Summers (6a) at 103°C in a quartz tube using mercury light below 2800 Å. Carbon monoxide, carbon-dioxide, formic acid, water and hydrogen were obtained as products of the reaction. They proposed that the reaction goes through a radical HO_2^\bullet as the essential intermediate. However, they suggested that at temperatures above 150°C the reaction goes through a different path, with a bis hydro xymethyl peroxide as the intermediate.

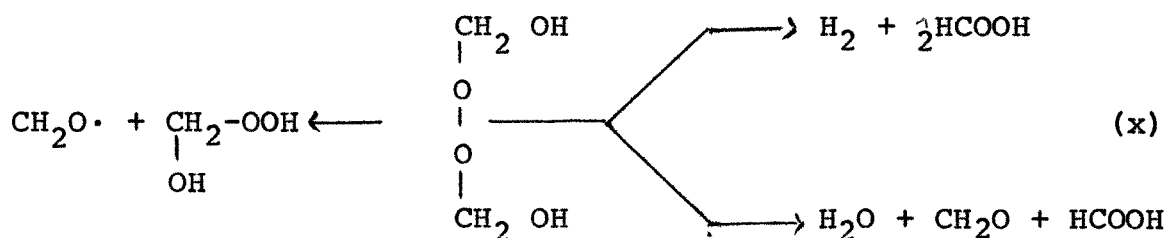
The vapour phase decomposition of bis hydroxymethyl peroxide was studied by Style and Jenkins (6b). The products of decomposition leaving the reaction chamber were passed through a length of narrow bore tubing and a tap into two traps. The first trap removed undecomposed peroxide and the second was cooled in liquid air to trap all condensable materials other than carbon monoxide and hydrogen which were collected for conventional gas analysis. The condensed materials were analysed for each product. They found that at temperatures between 100 and 200°C the products were

hydrogen, water, formaldehyde, formic acid, carbon monoxide and a peroxide material suspected to be $\text{HO}-\text{CH}_2-\text{OOH}$.

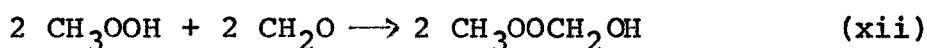
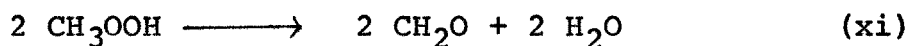
With the increase of temperature from 100°C to 200°C the yields of hydrogen, CO , H_2O , and HCOOH increased; the formation of formaldehyde was increased only slightly and

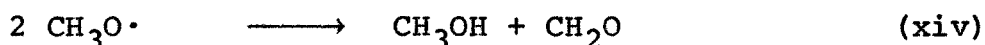
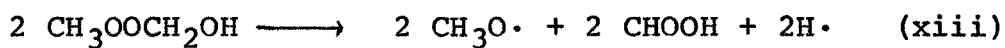
the peroxide yield was suppressed. However, the yield of hydrogen was only 1-4% which is much lower than the yield in condensed phase.

Without specifying a mechanism they simply stated (6a) that the peroxide could decompose in three ways.



Rieche and Hitz (7) found that methyl hydroperoxide decomposed explosively on heating and rapidly in alkaline solution yielding hydrogen. They pointed the similarity of this to the Blank-Finkelbeiner reaction, but rejected the concerted mechanism proposed by Wieland and Wingler in favour of the radical mechanism, based on the observation that the decomposition mixture decolourised methyleneblue-interpreted as the presence of active or atomic hydrogen.



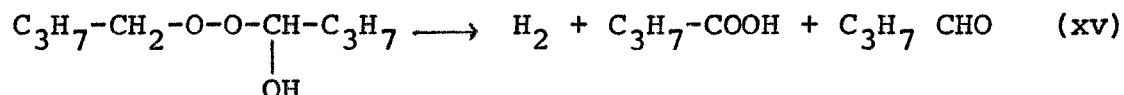


Rieche also studied (13) the decomposition of ethyl hydroperoxide on heating in the presence of alkali. He found very little gaseous products were formed unless formaldehyde was added, in which case hydrogen was formed. Rieche postulated that ethyl hydroxymethyl peroxide was the intermediate and that the decomposition proceeded by the same sequence as eg. (xii, xiii, and xiv) except that the ethyl group replaced the methyl group.

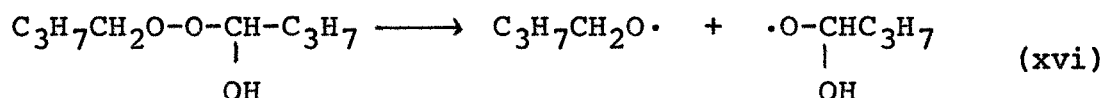
Wurster and Mosher (8) undertook a detailed investigation into the mechanism of decomposition of n-butyl 1-hydroxybutyl peroxide and the relationship of this compound to the decomposition of n-butyl hydroperoxide. The major products of decomposition of n-butyl-1-hydroxybutyl peroxide at 86°C decomposed as a neat liquid were hydrogen, butyric acid, butyraldehyde, butyl alcohol and butyl butyrate and the minor products were propane, CO, butyl formate, butyl propionate and propyl butyrate presumably resulting from radical decompositions. The products obtained by the decomposition of n-butyl hydroperoxide was found to be identical qualitatively and quantitatively with that of n-butyl-1 hydroxybutyl peroxide. They found that the reaction of n-butyl hydroperoxide was autocatalytic due to the formation of butyraldehyde, and were able to isolate the intermediate, the peroxy

hemiacetal. This presumably decomposed in two competitive ways.

(a) The major pathway producing hydrogen and butyraldehyde.

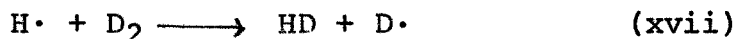


(b) By the radical pathway.



The fact that n-butyl deuteroperoxide (n-BuO₂D) gives no HD or D₂ on decomposition (9) and that there is no HD or D₂ formed when the Blank-Finkenbeiner reaction is conducted in D₂O (10), is added evidence that only the hydrogens attached to the peroxidic carbon atoms are involved in the hydrogen evolution process.

Wurster and Mosher tested more specifically for atomic hydrogen by hydrogen-deuterium exchange reaction (8). The reaction of hydrogen atoms with deuterium gas has a rather

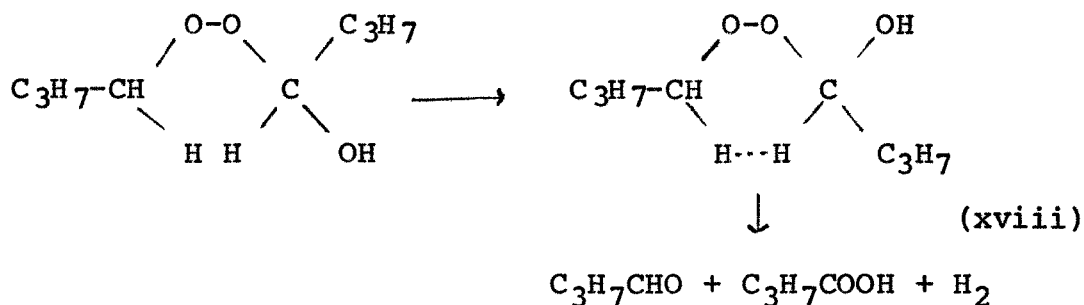


low energy of activation, about 7 kcals. per mole (11) yet molecular hydrogen and deuterium do not exchange appreciably under ordinary circumstances. Accordingly, the decompositions of n-butyl hydroperoxide and n-butyl-1-hydroxybutyl peroxide were conducted under standardised conditions in an atmosphere of deuterium. These results were compared to a blank of

hydrogen, deuterium and tertiary-butyl hydroperoxide, which is known to evolve no hydrogen on decomposition (12) and a control containing cobaltocyanide ion which almost certainly reacts with water to evolve hydrogen in atomic form.*

During the reaction of potassium cobaltocyanide with water there was fifty times more exchanges with Deuterium than that of the peroxides. Furthermore there was approximately the same amount of exchange in the blank containing the tertiary-butyl hydroperoxide. Thus Wurster et al discarded the idea of the atomic hydrogen path as suggested by Rieche and Hitz (13).

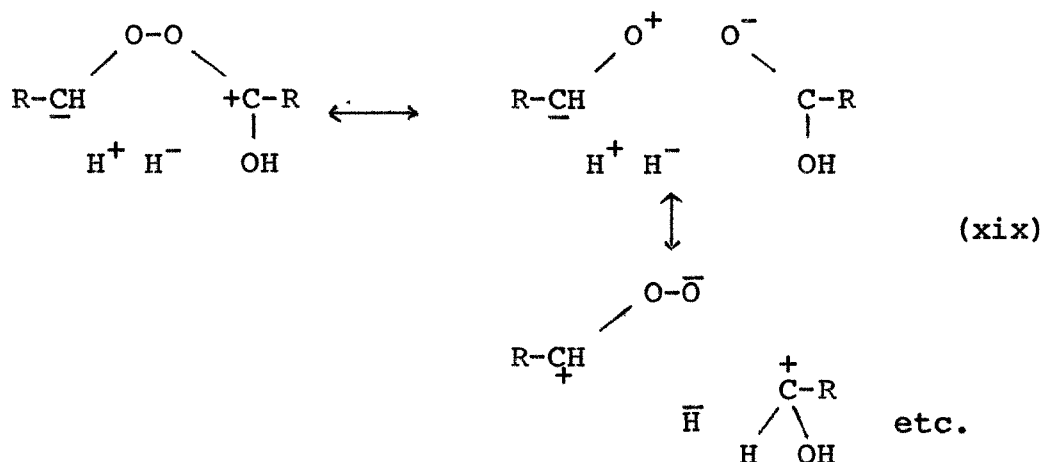
They proposed a concerted mechanism in agreement with the earlier suggestion of Wieland and Wingler.



The transition state in the concerted process can afford lower energy of activation than the homolytic cleavage of the peroxide bond. This results also from the fact that this transition state is stabilised by various hyperconjugated

*Note: The hexacyano cobaltate (II) ion has a total of 37 electrons, the stable arrangement being 36, has a strong tendency to lose one electron in a reaction with water or a proton to give hydrogen atom and stable hexacyano cobaltate (III) ion $\text{Co}(\text{CN})_6^{-4} + \text{H}^+ \longrightarrow \text{H}\cdot + \text{Co}(\text{CN})_6^{-3}$.

forms.



This proposed mechanism requires that the reaction follow first order kinetics. A detailed investigation of the kinetics of this reaction and of deuterium isotope effects of suitably deuterated derivatives was done by Durham and Mosher (14).

They measured the rate of hydrogen evolution from 1-hydroxy-n-butyl n-butyl peroxide and 1-hydroxyisobutyl isobutyl peroxide in ϕ methylstyrene which served as an unusually satisfactory inhibitor and as a good solvent. The overall rate constants of this reaction differed from the rate constants for hydrogen evolution. Both hydrogen yields and rate constants depended on the initial concentration of peroxides indicating the presence of some induced decomposition. An "induced decomposition" is possible in the absence of inhibitors, but it does not appear likely in the presence of inhibitors especially when the solvent itself is an inhibitor.

Using the rate constants of hydrogen formation at

different temperatures the activation parameters were calculated.

The activation energies, A factors and entropies of activation for 1-hydroxy-n-butyl n-butyl peroxide and 1-hydroxyisobutyl isobutyl peroxide obtained by them in α -methylstyrene are summarised below.

Table I (14)

Peroxide	Activation energy Kcals/mole	'A' Factor $\times \text{sec}^{-1}$	Entropy of activation Cals/mole
1-hydroxy-n-butyl n-butyl peroxide	24.6	1.5×10^{10}	-15.7
1-hydroxyisobutyl isobutyl peroxide	21.2	2×10^9	-22.

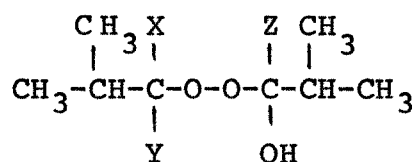
Since the reaction producing hydrogen proceeds unhindered by the presence of radical inhibitors, radical induced mechanisms are unlikely. The quite low 'A' factors and large and negative entropy of activation suggested considerable steric constraint in the transition state as expected for a concerted reaction. But the validity of these numbers are questionable since the reactions had shown deviations from unimolecularity.

Durham and Mosher (15) have also studied the deuterium kinetic isotope effects of the deuterated peroxy hemiacetals. The decompositions of 1-hydroxyisobutyl-1-d isobutyl-1, 1-d₂ peroxide and the related deuterated compounds were carried out also in α -methylstyrene. A part of the

decomposition data are shown in table II.

Table II

Decompositions of Deuterated 1-hydroxyalkyl alkyl peroxides in α methyl styrene. Ref. (6b)



Temp°C	X	Y	Z	Conc[M]	H ₂ yield %	a K _r x10 ⁴	b K _H x10 ⁴
109.9	H	H	H	.505	40	4.39	1.7
109.6	D	D	H	.480	23	3.32	0.76
109.8	D	D	D	.473	27	2.24	0.61

(a) Rate constants for overall decomposition

(b) Rate constants for evolution of hydrogen (H₂ + HD + D₂)

From the above data they calculated isotope rate effects, K_H/K_D , of 3.2-3.9. However, the peroxides they used were not isotopically pure, nor did the H-H, H-D, D-D ratios obtained (determined mass spectrographically) correspond at all well to those calculated from composition of the peroxides and an assumed isotopic rate effect of 4.0. It is to be noted that K_H for the D-D-D compound is only 1.95, and the K_H (H-H-H)/ K_H (D-D-D) is 2.87. Comparison of the D-D-H compound with the D-D-D compound shows that the rates are only slightly higher and that the yield of hydrogen is actually less.

The formation of hydrogen from secondary butyl

peroxide decomposition was first observed by Hiatt and co-workers (2b) and they then proposed a concerted mechanism similar to that of Wieland and Wingler without further experiments.

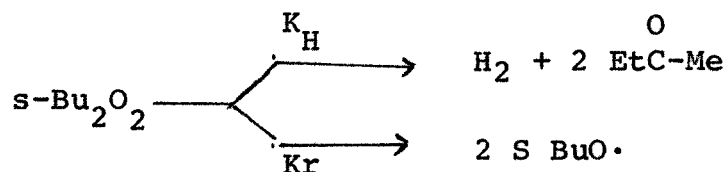
Hiatt and Szilagyi (16) later conducted a detailed investigation on the undeuterated and deuterated sec.-butyl peroxide. They treated the decomposition as the sum of two separate reactions $K_d = K_H + K_r$ (where K_H is hydrogen evolution rate and K_r is homolytic scission). They found

$$K_H = 10^{12} e^{-31.0/RT} \quad \text{and}$$

$$K_r = 10^{15} e^{-35.2/RT}$$

Though the activation energy for hydrogen evolution is lower than the homolysis reaction and the 'A' factor is lower by 10^3 , this is barely below the range of normal 'A' factors for unimolecular reactions. These evidences are not convincing for a concerted mechanism.

α, α -Dideuterated peroxide decomposed slower than the non-deuterated species and the yield of D_2 produced differed little from the non-deuterated compound. Again treating the decomposition as two separate reactions.



they found at 135°C in toluene

$$K_r (H) = 7.32 \times 10^{-3} \text{ min}^{-1}$$

$$K_H (H) = 1.95 \times 10^{-3} \text{ min}^{-1}$$

$$K_r (D) = 5.95 \times 10^{-3} \text{ min}^{-1}$$

$$K_H (D) = 1.16 \times 10^{-3} \text{ min}^{-1}$$

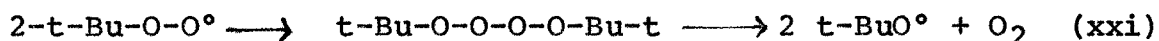
(where (H) and (D) refer to non deuterated and deuterated species)

If K_r is simple homolysis its isotope rate effect is "secondary" and if K_H is concerted its effect would be "primary". Thus "secondary" isotope effect was found to be 1.47 and the primary to be 1.68. The primary effect obtained is quite low to correlate with a concerted mechanism. Thus neither the isotope effect nor the 'A' factors gave a convincing support for a concerted mechanism.

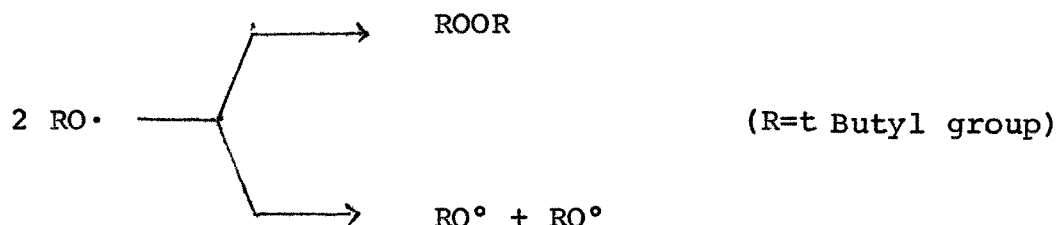
To make matters worse, the yield of hydrogen diminished drastically when the reaction was conducted in the vapour phase, which should not have been the case if the reaction proceeded by concerted mechanism. A cage mechanism was ruled out since the reaction produced the same amount of hydrogen in mineral oil which is of higher viscosity and the secondary isotope effect found was too large to attribute as secondary isotope effect. A polar mechanism was discarded on the grounds that the reaction produced the same amount of hydrogen in acetonitrile as in toluene or benzene. Thus their work disqualified all possible mechanisms, casting some doubt on the concerted mechanism.

2.3 Reactions of Alkoxy Radicals with Each Other

The studies of induced decomposition on tert.-butyl hydroperoxide (17, 18) and the product studies on tert-butyl peroxide at 250 to 300°C (which mainly yielded t-butanol, acetone and ethane) (19) strongly suggests the formation of tertiary alkoxy radicals in two ways: eg. tert-butoxy radicals are formed in the following two ways.



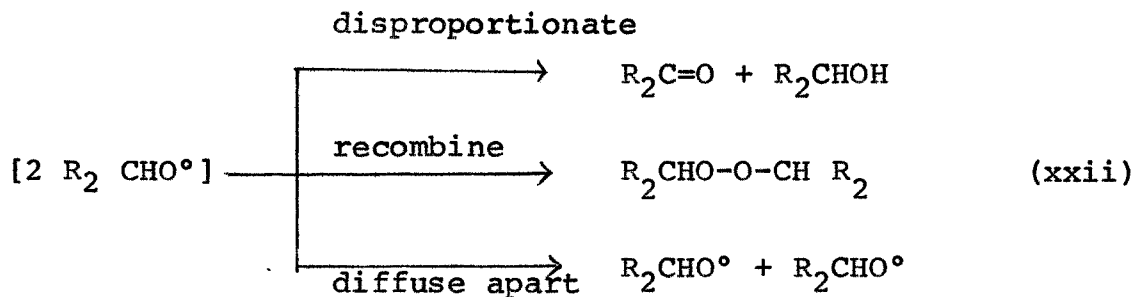
Also it is shown that the t-butoxy radicals produced in the solvent cage adopt the following reaction path.



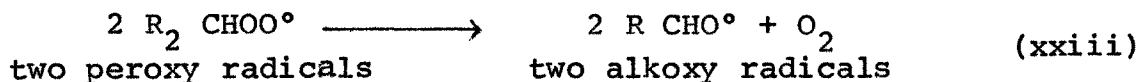
Reaction (xxi) indicates the two possibilities open to tert, alkoxy radicals produced within the solvent 'cage' ie. either they can react with each other giving non radical products or can diffuse out of the solvent cage to initiate new radical process. Because radical-radical coupling is collision controlled ($E_a=0$) diffusion apart controls the number of alkoxy radicals which become free. It is shown that 90% of t-butoxy radicals diffuse apart in benzene at 30°C and greater than 95% diffuse apart at 100°C, in a rough

correlation with solvent viscosity.

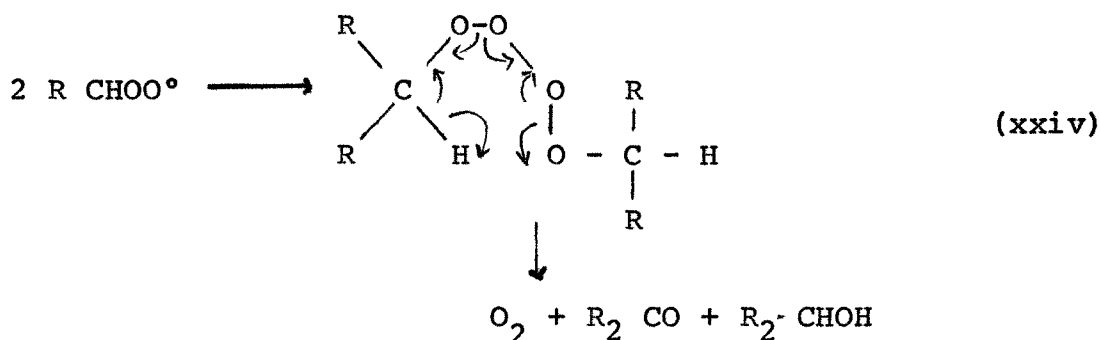
The situation is more complex in the case of secondary alkoxy radicals. Two secondary alkoxy radicals generated in the solvent cage can undergo one of the three reactions mentioned below.



The situation is not clear since most of the reactions studied to generate the secondary alkoxy radicals used the secondary peroxy radical intermediate, which could undergo decomposition via the tetroxide as suggested by Russell (20) and later proved by J. A. Carlsson and K. U. Ingold (21), rather than splitting first to the alkoxy radicals.

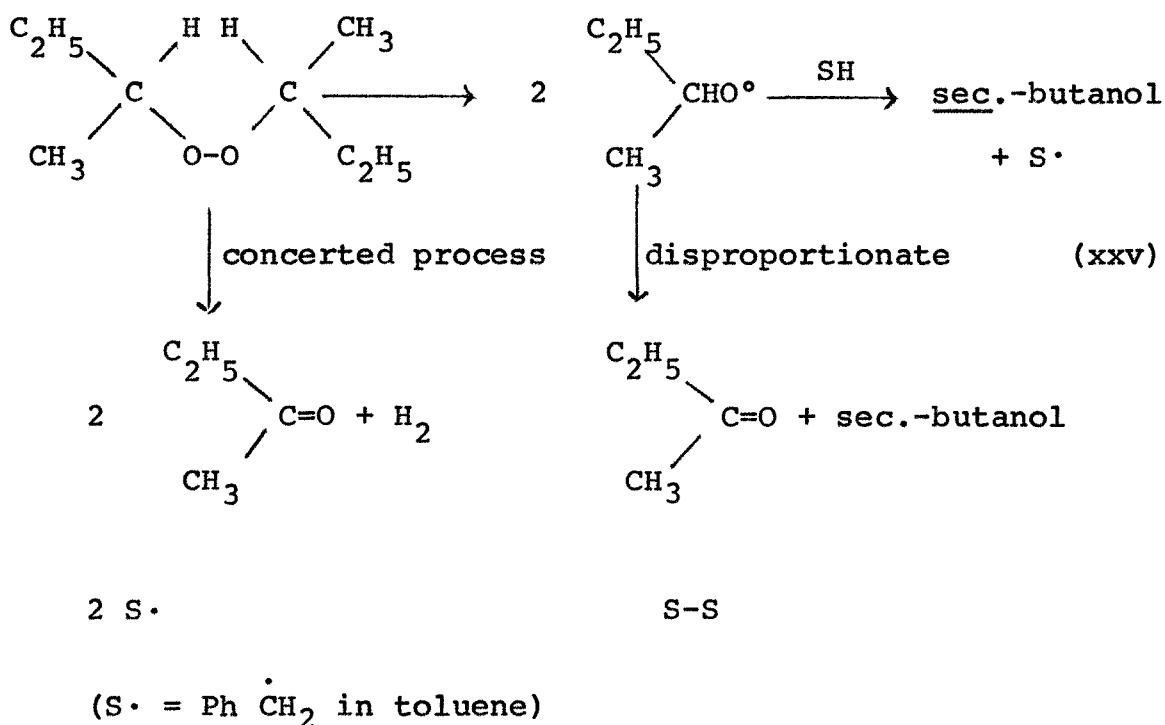


Russell's mechanism



Such a path as shown by Russell cannot occur with tertiary peroxy radicals (21).

The only study on secondary alkoxy radicals in solution generated from a secondary alkyl peroxide appears to be that of Hiatt and Szilagyi (16). Their results showed that the diffusion of the sec.-butyl peroxide radicals far exceeds that of cage disproportionation. Their conclusion however, was based both on the yields of bibenzyl and on the methyl ethyl ketone, obtained through the radical pathway minus the yield of hydrogen, the formation of which is attributed to a concerted process. The following are the reaction pathways for sec.-butyl peroxide explained by them.



2.4 The Peroxides Used In This Work

J. I. G. Cadogan, et.al. (22) found that bis diphenylmethyl peroxide decomposed almost quantitatively to benzophenone in isopropyl benzene, nitrobenzene and other solvents.

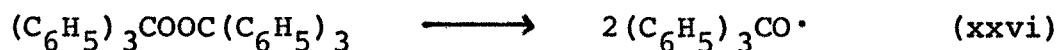
These results indicated to us that it might yield hydrogen as well. However, Cadogan, et.al., (22) explained the reaction adopting a radical path on the mere basis that the reaction in isopropyl benzene yielded a 12% of di-*tert*-cumyl. Our main aim was to correlate the benzophenone yield to hydrogen and to suggest a possible mechanism for the decomposition.

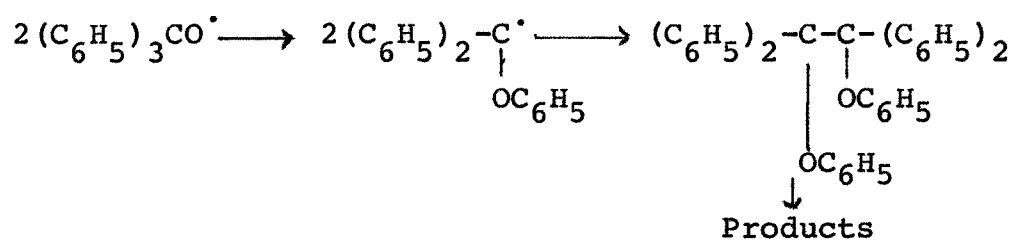
The decomposition of diphenylmethyl tertiary butyl peroxide in toluene was also studied to see whether it produced any hydrogen and also to evaluate the competition between cage disproportionation and diffusion apart.

This peroxide cannot give hydrogen by the concerted mechanism, so that if hydrogen was produced it would be strong evidence against a concerted pathway. If the decomposition proved to be mainly by homolysis more information could be gained on the behaviour of the sec. alkoxy radicals.

Bis triphenylmethyl peroxide

This peroxide has been shown to yield (23) tetraphenyl ethylene, diphenyldiphenoxyethane, benzophenone and phenol possibly through an intermediate tetraphenylsym diphenoxyethane presumably formed by the homolytic scission of the peroxide, rearrangement and recombination.





We thought of investigating these chances, and more over to study the rate of decomposition since it has been never done.

3. EXPERIMENTAL

3.1 Preparation of bis-diphenylmethyl peroxide

Bis-diphenylmethyl peroxide was best prepared by heating benzhydrol and diphenylmethyl hydroperoxide in acetic acid at 80°C by using p-toluenesulphonic acid as the catalyst (22).

3.1.1 Preparation of diphenylmethyl hydroperoxide

Diphenylmethyl hydroperoxide was prepared by a method similar to that of Cadogan, et. al. (22). To 25 ml of 98% hydrogen peroxide 0.1 ml concentrated sulphuric acid and 20 ml ether were added. 30 grams (.163 moles) benzhydrol (Eastman Kodak Co.) recrystallised from n-hexane was added to the above mixture and stirred magnetically for 12 to 14 hours at room temperature. 50 ml water was added and the mixture was separated. The aqueous layer was extracted thrice with 20 ml portions of ether. The ether solution was washed with sodium bicarbonate solution and water; was dried by using anhydrous sodium sulphate. The ether was evaporated and the crude sample was recrystallised by dissolving it in the minimum quantity of benzene and by adding normal hexane.

Yield after recrystallisation = 18 grams = 55%.

3.1.2 Percentage purity of the hydroperoxide

The recrystallised sample was titrated as follows.

A known weight of the sample was taken in a conical

flask. It was dissolved in about 20 ml of 1:10 acetic acid isopropanol mixture. About 3 grams of sodium iodide was added and the mixture was refluxed for fifteen minutes and titrated against 0.1 normal sodium thiosulphate solution. A blank was conducted at the same time. The hydroperoxide was found to be 96% pure (Table III).

3.1.3 Bis-diphenylmethyl peroxide

Benzhydrol (Eastman Kodak) recrystallised from n-hexane 15 grams (0.82 moles) Diphenylmethyl hydroperoxide 5 grams (0.025 moles) and p-toluenesulphonic acid 0.026 grams were taken in 15 ml of glacial acetic acid. The mixture was heated at 80°C for 1 hour, cooled and 60 mls of ethanol was added, and kept in ice for ten hours. The crystals were filtered and recrystallised from chloroform and ethanol.

Yield = 4 grams = 44%

The purity of the peroxide was of much concern here, the peroxide thus prepared is most often found to be contaminated by bis diphenylmethyl ether.

The similarity in the melting points of the peroxide and that of the ether (112 to 113 and 110 to 111° respectively) and similarity in their solubilities made it difficult to separate them. To make matters worse, appreciable quantities of bis diphenylmethyl ether could be present in the peroxide without producing much change in their melting points.

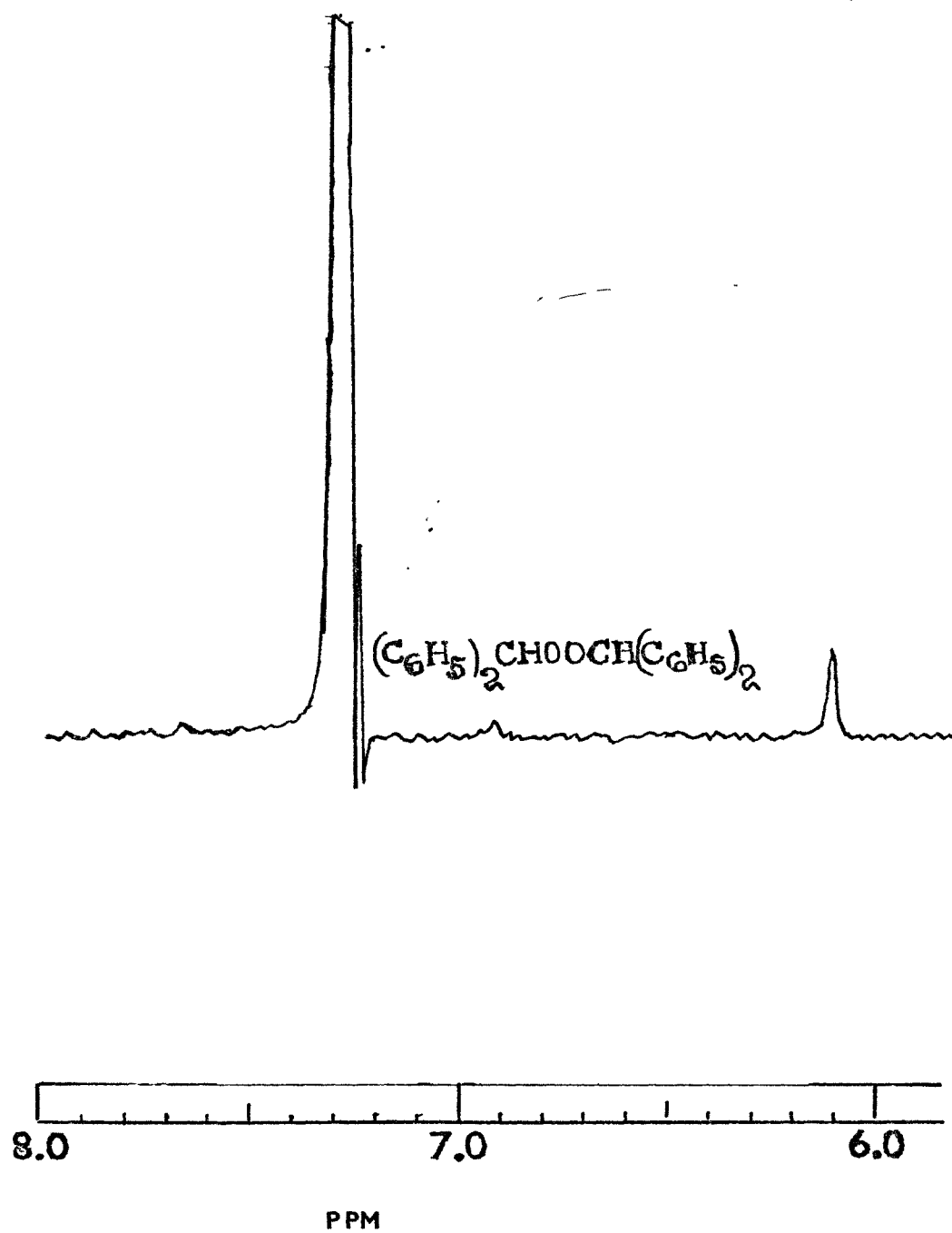
The peroxide and the ether could not be separated by t.l.c.; the usual solvents alcohol, acetone, isopropanol, benzene, n-hexane, mixtures of the above solvents were tried with thin layer plates of silica or alumina. G.l.c. of pure ether using silicone fluoro QF-1 10% on gas chrome gave no peaks.

However, the n.m.r. analysis gave a singlet corresponding to the peroxide at 6.1 PPM (Fig. 1) downfield from TMS, and the ether peak appeared further upfield at 5.45 PPM.

3.1.4 Estimation of bis diphenylmethyl peroxide

The specific estimation of the peroxide was found to be difficult. Titrating the mixture by the iodometric method of Mair and Graupner (24) always gave inconsistent results. Another method using iron resinate as the catalyst (2a) (by dissolving 1.5 gms of iron resinate on 15 mls of glacial acetic acid) was tried. Four drops of the iron resinate was added to a weighed amount of the peroxide in 9:1 isopropanol acetic acid mixture. About 3 grams of sodium iodide was added and the mixture was refluxed for twenty minutes. A blank was conducted at the same time. This method also gave inconsistent results. Therefore, the best method appeared to be the calculation of purity from the n.m.r. peak of the peroxide relative to that of the ether peak (Table IV). The peroxides prepared at different times were labelled 'A', 'B', 'C' and 'D'. Most of the reactions were done using 'C' and 'D'. Though 'A' was found to be

Figure 1



almost completely pure, it was obtained in very low yield, and used up in the analyses. The microanalysis of peroxide 'D' was done and it gave 83.23% of carbon and 6.05% of hydrogen. The microanalysis of ether gave 89.3% of carbon and 3.1% of hydrogen. Thus the microanalysis of peroxide and ether gave theoretical results which are C=85.25%, H=6.01% for the peroxide and C=89.14%, H=6.28% for the ether.

Table III

Estimation of the diphenyl methyl hydroperoxide

Weight of the peroxide taken	= 0.1 gm.
Volume of 0.1 N thiosulphate used	= 10.6 mls.
Blank of 0.1 N thiosulphate used	= 1 ml
Volume of thiosulphate used by peroxide	= 9.6 mls.
Weight calculated	= 0.096 gm.
% Purity	= 96

Table IV

Assessment of Purity of Bis-Diphenylmethyl Peroxide

Peroxide ^a	Titration Mair and Graupner Method	Titration Using Iron Catalyst	NMR Peroxide Peak Impurity Peak	Percentage Purity by NMR	Thermal Decompo- sition	Micro Analysis
A	97%	-	3/ 43	93%	88%	-
B	-	-	9/ 23	60.8%	59%	-
C	48.8%	47.7%	5/ 16	68.8%	68%	-
D	60%	55.7%	6.5/ 42	84.5%	84%	C=85.23% H= 6.05%

^aPeroxide A, B, C and D are samples prepared at different times.

3.2 Preparation of Diphenylmethyl Tertiary Butyl Peroxide

15 grams of benzhydrol (0.0815 moles) (Eastman Kodak) and 15 grams of tertiary butyl hydroperoxide (.166 moles) (Lucidol) were taken in a round bottomed flask. 15 ml acetic acid and 0.05 grams p-toluenesulphonic acid were added. The mixture was heated at 80°C for 1 hour, cooled and washed with sodium hydroxide. The aqueous layer was extracted thrice with 20 ml portions of ether. The extract was washed several times with water and dried by using anhydrous sodium sulphate. Ether was evaporated and the peroxide was obtained as a thick oily liquid.

Yield = 16.5 grams, 79%

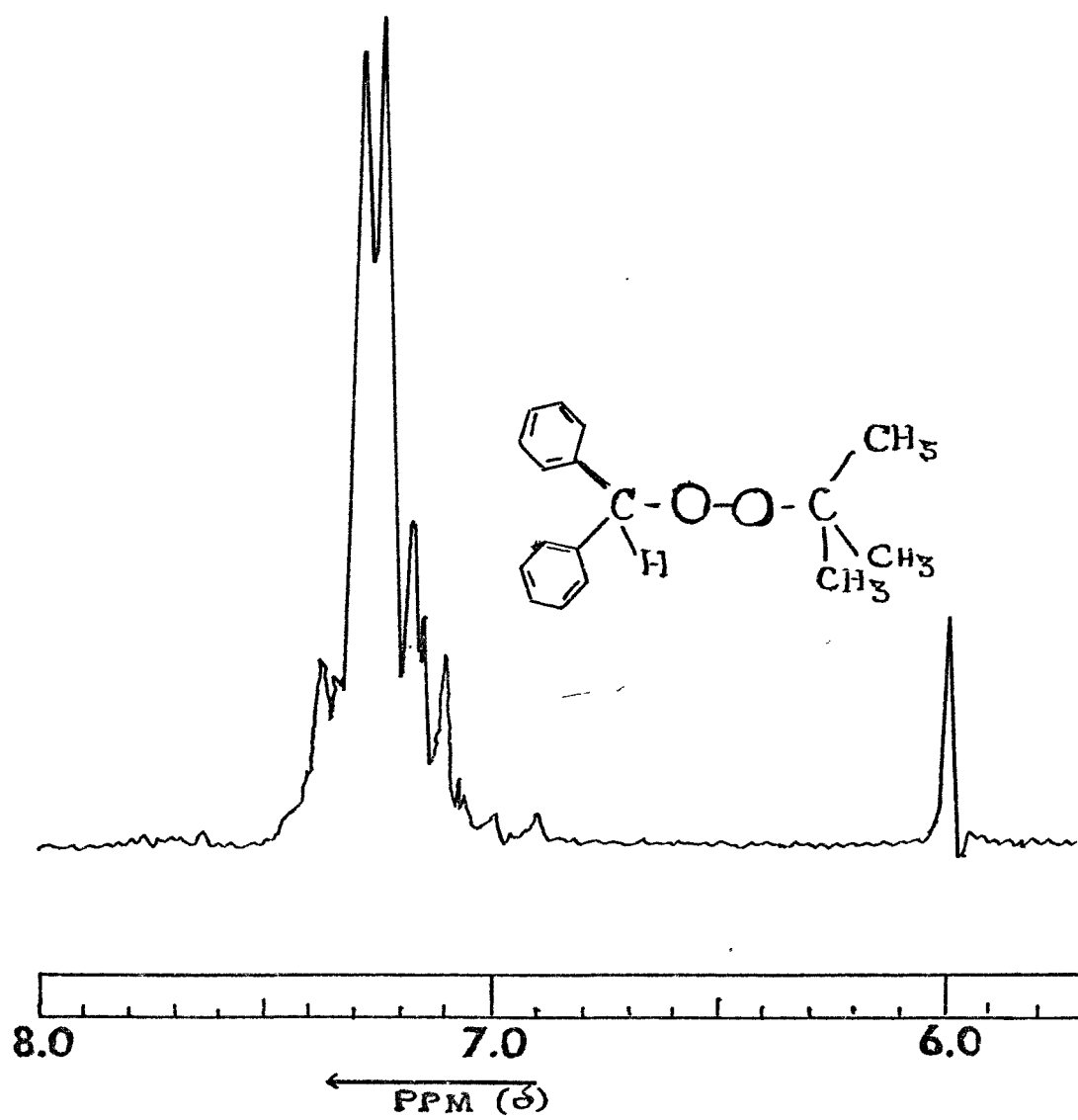
n.m.r. analysis gave the $\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{O}-\text{O}- \end{array}$ singlet at 6 PPM. fig. 2, and the methyl proton singlet at 1.25 PPM., in an integrated area ratio of 1 : 9.5. No extraneous peaks were found.

3.3 Preparation of Bis-triphenyl Methyl Peroxide

Trityl peroxide was prepared by the classical method; i.e., stirring trityl chloride with zinc dust in presence of air at room temperature for about 24 hours. The trityl peroxide formed was then recrystallised from benzene.

Infra red Spectra. Spectra of the peroxides prepared were taken on a Perkin Elmer model 237-B instrument, and are shown in the Appendix.

Figure 2



3.4 Rate Measurements

Rates of decomposition were measured by using u.v. and n.m.r. analysis.

3.4.1 Rate measurements by u.v.

An Hitchi-Perkin-Elmer double beam spectrophotometer was used to measure the increase in benzophenone concentration by its absorption at 287 m μ in the u.v. Bis diphenylmethyl peroxide and trityl peroxide were found to decompose yielding benzophenone.

Tetrachloroethylene was selected as the solvent since it shows negligible absorption in this region. Studies were conducted in sealed u.v. cells.

The u.v. cell fitted with a 14/35 adapter to suit the vacuum line was filled with a dilute solution (1×10^{-4} to 7×10^{-4} molar) of the peroxide, and was connected to the vacuum line. The solution was cooled in dry ice acetone mixture till it became a solid. Air was then pumped out using the pump. This process of degassing was repeated at least three times to ensure perfect degassing. After degassing the u.v. cell was then sealed. The spectrum of the sample at zero time was taken, with pure tetrachloroethylene as the reference. The cell with the contents was then immersed in a constant temperature bath and was withdrawn at every half an hour or every hour, and the spectrum at each time was taken. This is done for about six hours and the cell with the contents was kept in the constant temperature bath till

the reaction was complete. The final spectrum was taken, the height of which represents the product height at infinity. By subtracting the product height at each interval from the product height at infinity gives the peroxide height at each interval.

The calculation of the rate constant was made by graphic methods, plotting $\log [P_{\infty} - P_t]$ versus time.

3.4.2 By n.m.r.

An A-60 varian n.m.r. was used. This method required fairly concentrated solutions, (i.e., greater than 0.3M) but could be used to measure the rate constants for decomposition in toluene and nitrobenzene as solvents. Peroxide concentration was followed by the area of the 6.1 PPM peak relative to an added standard.

An n.m.r. tube fitted with a 14/35 adapter to suit the vacuum line was half filled with a solution of the peroxide. It was then connected to the vacuum line, cooled in liquid nitrogen till the contents became solid. It is then degassed using the pump. The degassing was repeated at least three times. The n.m.r. tube was then sealed. The n.m.r. spectrum of the peroxide at zero time was taken. The tube was then immersed in a constant temperature bath and was withdrawn at suitable intervals for n.m.r. measurements. The peak area at each interval was calculated by the method of triangulation (because of the inconsistency shown by the integrator). As an internal standard the peak area was taken

relative to the peak area of the methyl group of toluene when the experiment was done in toluene, and relative to the added T.M.S. peak when it was done in nitrobenzene.

Plots of the log of relative peroxide areas against time gave straight lines from the slopes of which first order rate constants were calculated.

3.5 Product Studies

The product studies were carried out in sealed pyrex bulbs equipped with break seals.

Bis diphenylmethyl peroxide solutions of known concentrations were degassed using the procedure mentioned before. They were kept in a constant temperature bath for two to three days to make sure complete decomposition. The opening of the bulb was carried out on a vacuum system which is connected to a manometer to notice the pressure change. The evolved gases were collected in a sampling flask.

3.6 Analyses

All analyses except the gases were carried out by using an Aerograph A-90-P₃ gas chromatograph equipped with a disc integrator.

To avoid the large experimental error, each determination was done in triplicate. The calibration was done using internal standards for each series. To minimise the errors due to the injection, the ratios of the peak areas of the products to the solvents, were taken in calculations.

3.6. 1 Analysis of benzophenone

The break seal bulbs from the constant temperature bath were first opened to the vacuumline to study the gaseous products. The solution was then analysed for other products by g.l.c. The g.l.c. column was made of 1/4" diameter 3' long copper tubing packed with silicone QF-1 (Fluoro) 10% on gas chrom. The column temperature was maintained at 180°C with 55 ml helium per minute flow rate. The retention times of toluene and benzophenone are as follows.

Toluene	1/2 minute
Benzophenone	6-7 minutes

3.6.2 Analysis of benzhydrol

Although several columns like carbowax, silicone rubber, FFAP, silicone SE 20 , silicone SE 30 , silicone QF-1 were tried under various conditions, benzhydrol did not elute.

However, it was found that benzhydrol could be nicely eluted and separated as the trimethylsilyl ether, made using Bis-(trimethylsilyl)-acetamide, (BSA) (25). The silylation was a very simple technique. "BSA"

is a very powerful trimethylsilyl donor that will silylate many usually intractable compounds. To 5 to 10 mls of the sample to be analysed, .5 ml of BSA was added, shaken well for three minutes and analysed after keeping 5 to 10 minutes. It was important to condition the column by the first two injections and repeating till the

benzhydrol silyl ether peak levels off. Retention time of the ether on the silicone Qf-1 column (See 3.6.1) was 3 minutes.

3.6.3 Analysis of bibenzyl

The column described above could be used for bibenzyl too, produced when peroxide decompositions were done in toluene. A difficulty due to the close retention time of benzhydrol trimethylsilyl ether was partly solved by estimating the bibenzyl before silylating the mixture. Accurate estimation of the benzhydrol yield was still difficult, however.

3.6.4 Analysis of gaseous products: -

Analysis of hydrogen. The analysis of gaseous products was uncomplicated since bis diphenylmethyl peroxide on decomposition should yield only hydrogen as the gaseous products. This was verified by mass spectrometric analysis.

The break seal bulb containing the liquid and gaseous products were attached to a vacuum line. The contents were then cooled in liquid nitrogen till it became a solid. The break seal is then broken by a magnet hammer. The gaseous products then collected in a sampling flask, and the pressure change in the manometer is noted. The gaseous products were then analysed mass spectrographically and were found to contain only hydrogen.

The total volume of the vacuum system including the sampling flask and the reaction flask was calibrated. The

amount of hydrogen produced is then calculated by using the equation $PV = nRT$, taking the part of the line immersed in liquid nitrogen to be at 77°K and the remainder to be at room temperature. This assumption was not entirely accurate, but the volume of the line at intermediate temperatures was small fraction of the total volume and the results obtained seemed reasonable.

As a further check on this, the analysis was also performed by the following method. The solution in the break seal bulb was sealed and degassed at least ten times to assure complete degassing. It was then sealed and heated in the thermostat to complete the reaction. The bulb with the contents was then attached to the vacuumline and opened without cooling. The pressure change was noted. The hydrogen was then pumped out of the system and the bulb was again opened to the line. The pressure change which was due to the vapour pressure of the solution, was subtracted from the pressure obtained during the first opening and by using the equation $Pv = nRT$, the amount of hydrogen was calculated. The amount of hydrogen calculated by this method and that calculated after applying the correction for cooling under liquid nitrogen were found to agree well.

3.6.5 Experiments on diphenylmethyl tertiary butyl peroxide

(a) Rate measurements. Rate measurements were done by n.m.r. (in toluene) following the decrease in the peroxide peak area at regular intervals of time as described previously.

(b) Analysis of products. Product analysis was done by using break seal bulbs. A solution of known concentration was taken in the break seal bulb, degassed by the procedure described above, sealed and kept in the thermostat for sufficient time to complete the reaction. The break seal bulb with the contents was then opened to the vacuum line to study the gaseous products and afterwards the solution was analysed by g.l.c. for various other products. Benzophenone, benzhydrol and bibenzyl were separated by using silicone QF-1 (Fluoro) 10% on gas chrom column, at the same conditions as in the case of bis diphenyl methyl peroxide.

However, acetone and tertiary butanol were analysed by using the column 1/4" diameter, 6 feet long copper tubing packed with carbowax 1500 on crushed fire brick at a column temperature of 70°C. The retention times and the flow rate are given below.

Helium flow rate	55 mls/min.
Acetone retention time	3-1/2 minutes
Tertiary butanol retention time	6-1/2 minutes
Toluene retention time	13 minutes

(c) Analysis of gaseous products. The gaseous products were collected in a sampling flask and analysed by mass spectrometry. It was found to contain only methane and no hydrogen. The amount of methane was then found by pressure change calculations.

3.6.6 Experiments on Trityl Peroxide

(a) Rate measurements. Rate measurements were done by u.v. following the benzophenone peak as described in the case of bis-diphenylmethyl peroxide.

(b) Product studies. Not much work was done on the products of decomposition. However, benzophenone was detected by g.l.c. using the same column as in the cases mentioned before. Its carbonyl peak at 5.9 microns was detected by i.r. analysis of the product.

4. RESULTS

4.1 Rates of Decomposition of Bis-diphenylmethyl Peroxide

Thermal decompositions of bis-diphenylmethyl peroxide were carried out at temperatures 111°C, 120°C and 130°C in three solvents viz., toluene, tetrachloroethylene and nitrobenzene at initial peroxide concentrations ranging from 0.72[M] to 0.0003[M].

Rates were measured by n.m.r. in the case of toluene and nitrobenzene by following the disappearance of the -C-H peak of the peroxide at 6.1 PPM and in the case of tetrachloroethylene by noting the increase in benzophenone peak at 287 $m\mu$ by u.v. Plots of $\log [\text{Ph}_2 \text{CHOOCHPh}_2]$ versus time were uniformly linear (Fig. 3 and 4) as were plots of $\log [P_0 - P_t]$ against time (where P refers to benzophenone peak) (Fig. 5). First order rate constants determined from the slopes of these lines are shown in tables 5, 6 and 7. The rate constants are not dependent on the initial concentration of the peroxide (Table 6) showing that the reaction was truly unimolecular and not complicated to any great extent by induced decomposition.

The possible errors in the rate determinations are given below.

(a) Errors in tetrachloroethylene. The large scatter at 111°C (see Appendix) was random, independent of $[P]_0$ and most determinations fall within $\pm 20\%$ of the average. The reasons for the error are presumably the 287 $m\mu$ being the

Figure 3

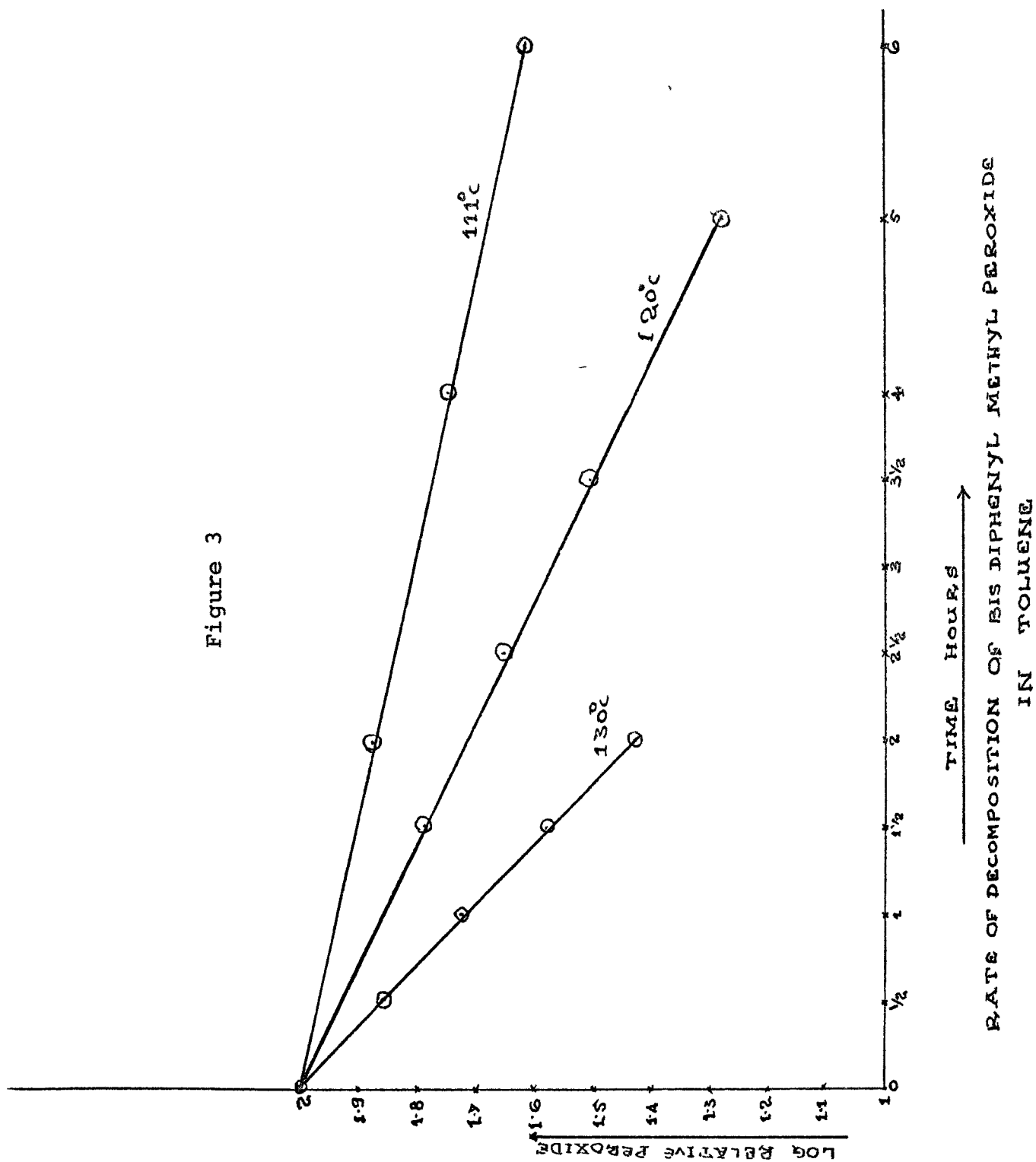
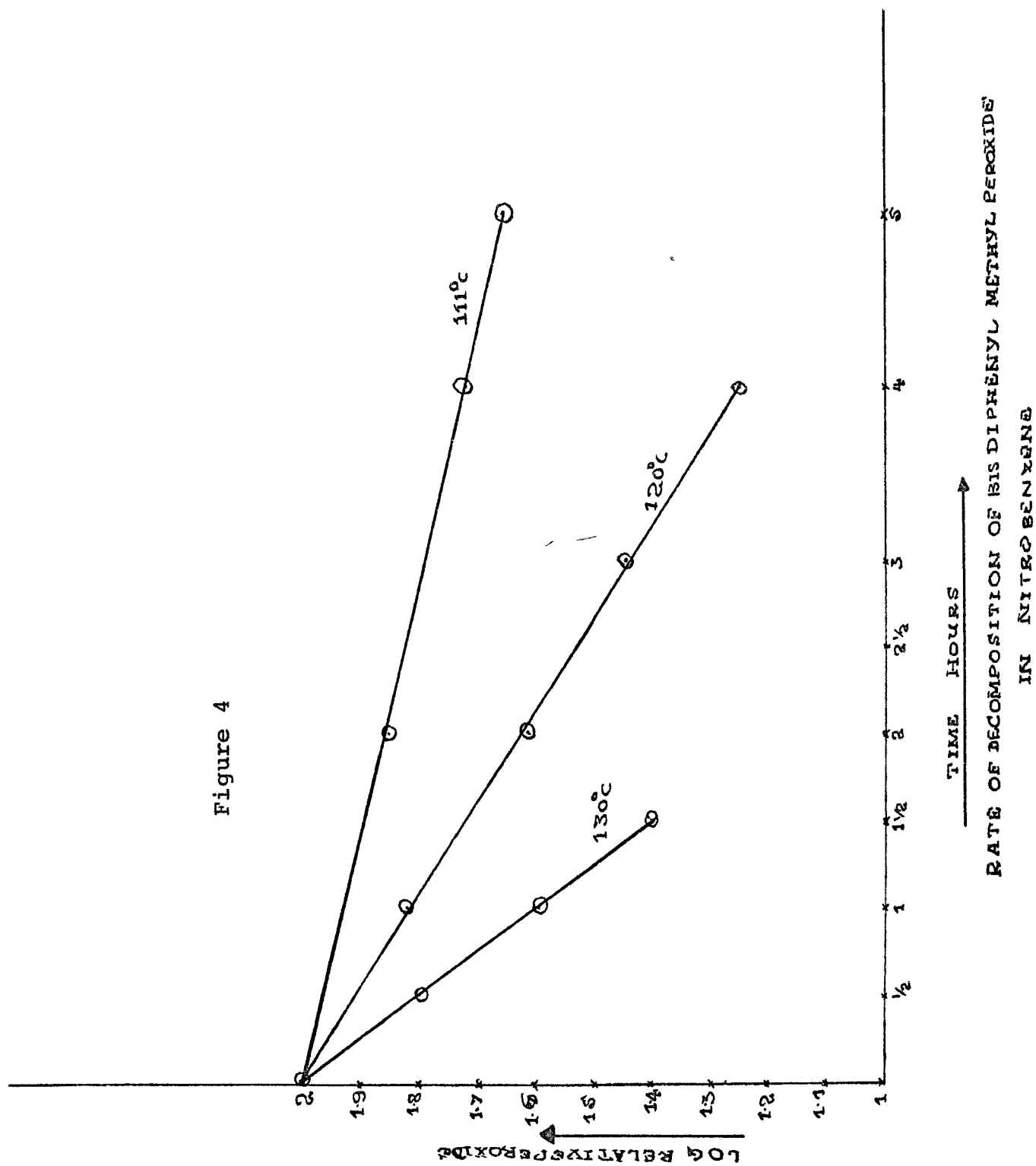
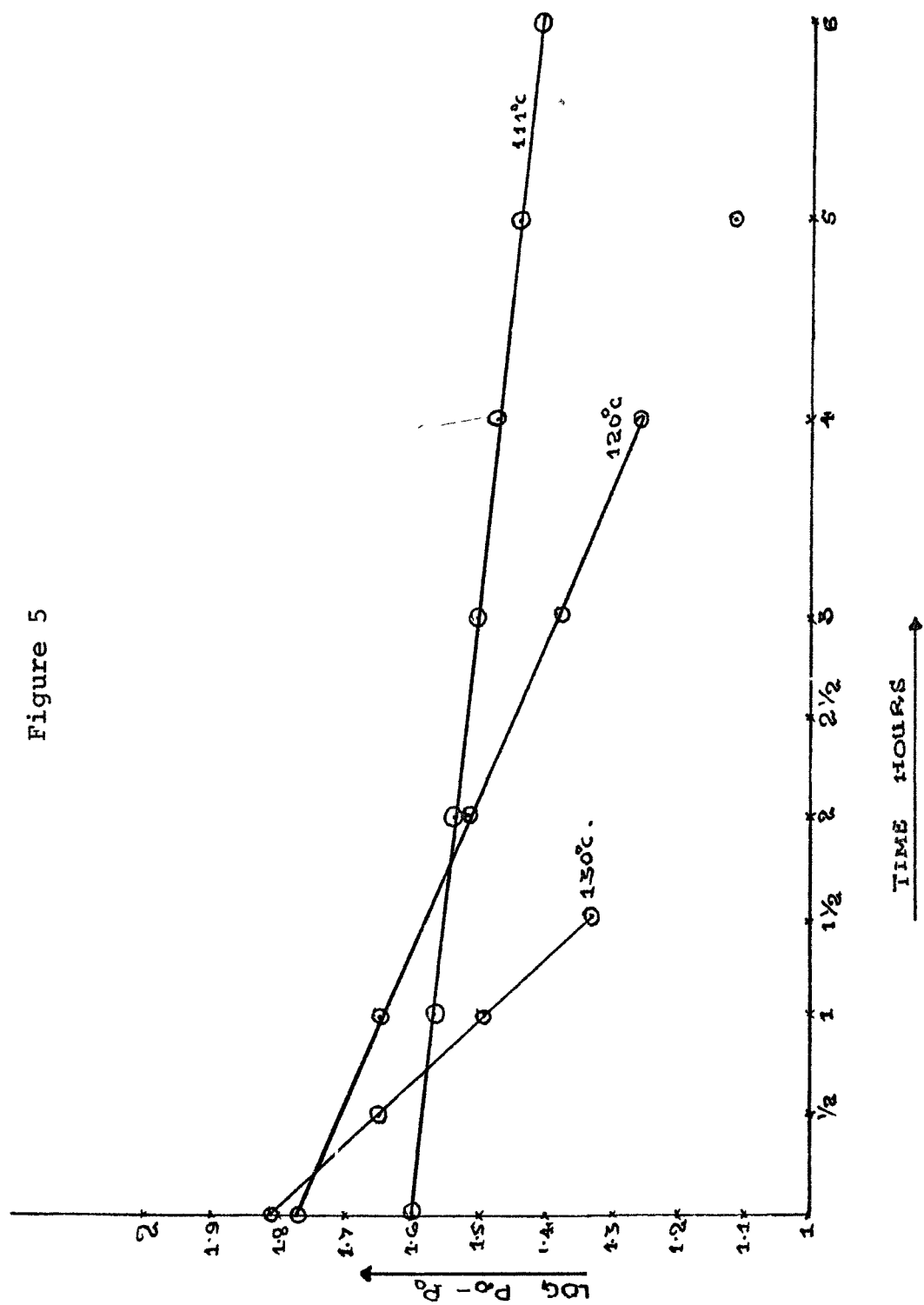


Figure 4



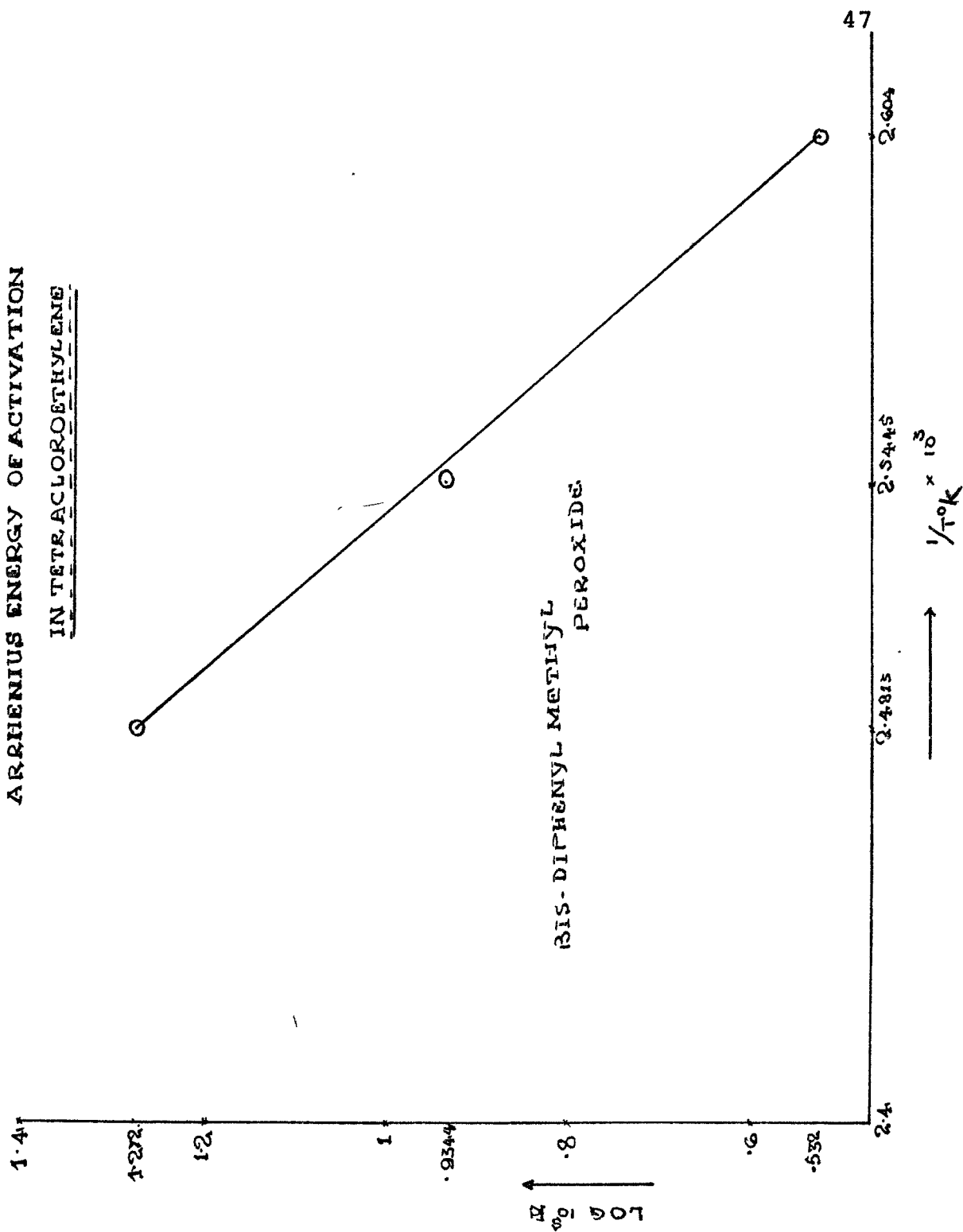
RATE OF DECOMPOSITION OF BIS(DIPHENYL METHYL PEROXIDE)
IN NITROBENZENE

Figure 5



RATE OF DECOMPOSITION OF BIS DIPHENYL METHYL
PEROXIDE IN TETRACHLORO ETHYLENE

Figure 6
 ARRHENIUS ENERGY OF ACTIVATION
IN TETRACHLOROETHYLENE



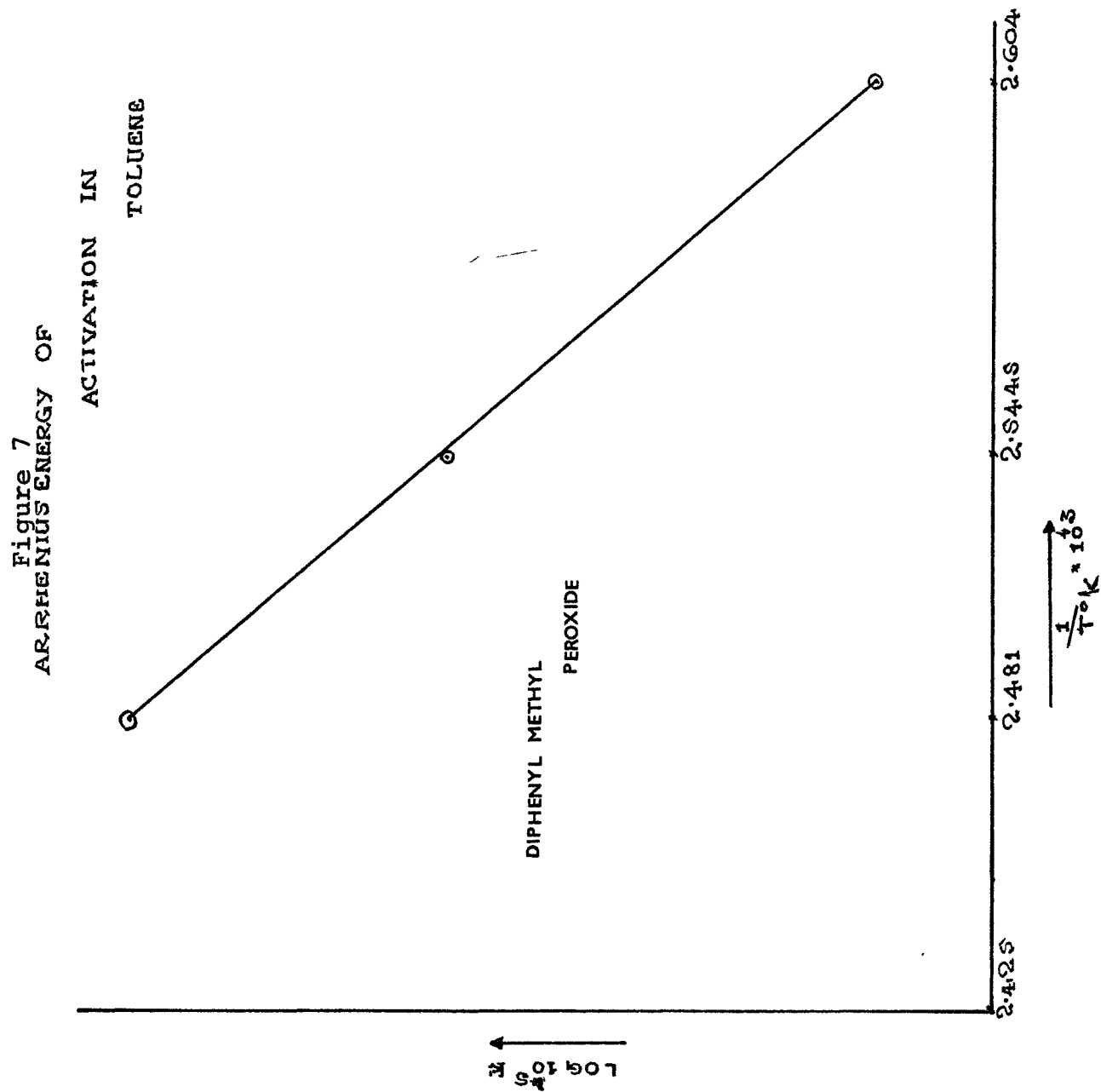


Figure 8

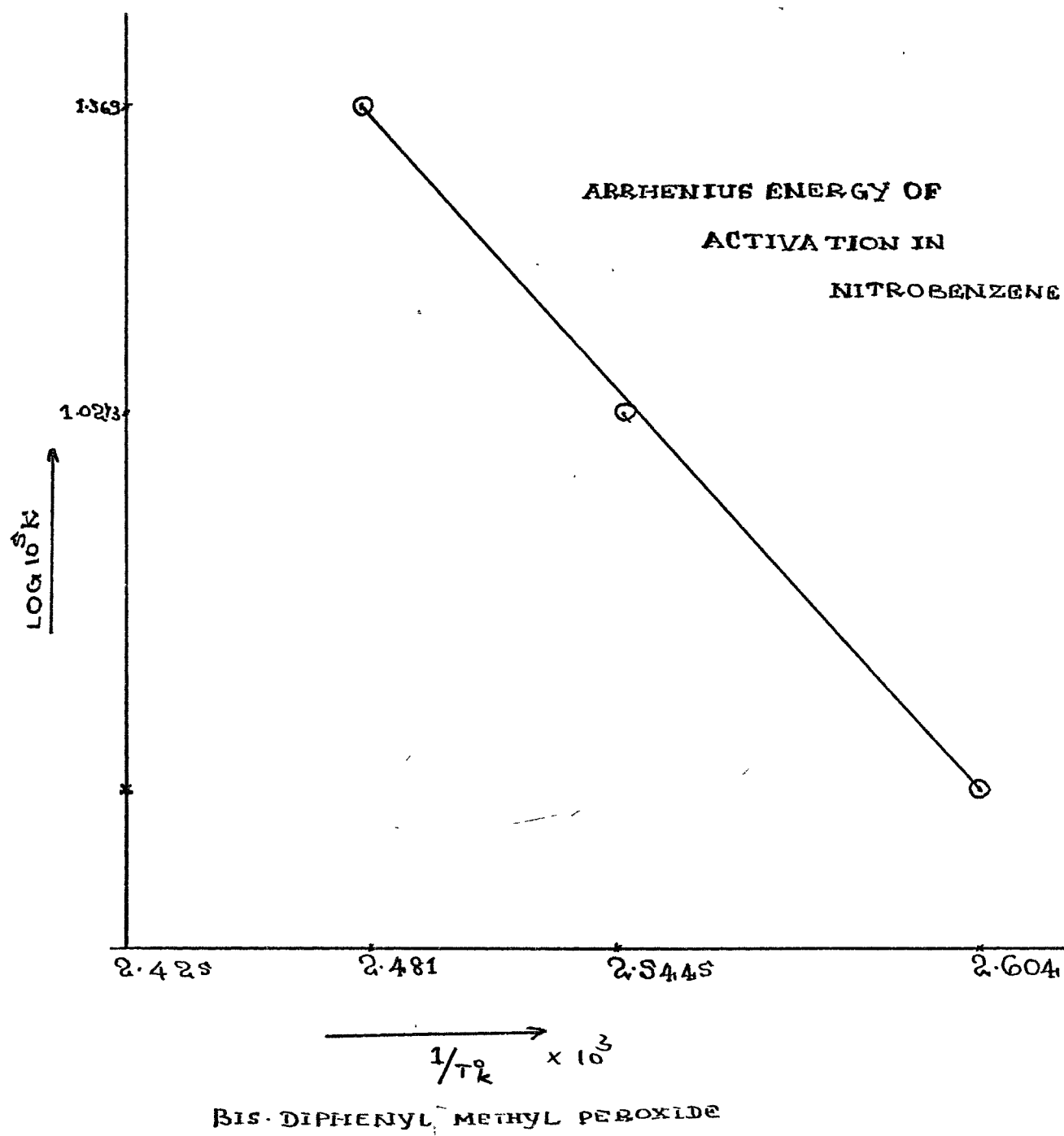


Table V

Rate Constants for the Thermal Decomposition of Diphenyl-
methyl Peroxide in Tetrachloroethylene

Temp. °C	a Conc. Mx10 ⁴	b Time Int. Hours	c Kx10 ⁵ sec ⁻¹	d Average Kx10 ⁵ sec ⁻¹	e E _A Kcal/mol	f Values Column	g Log A	h Δ S Cal/°K
111*	9.96	6	4.87	3.41				
	10	6	3.28					
	2.99	6	2.08					
120	4.98	5	8.80	8.60	26.6	.92	10.64	-11.8
	7.47	5	8.41					
130	4.60	1.5	18.20	18.74				
	9.20	1.5	19.28					

*The average for 11 determinations was 3.66×10^{-5} , with average deviation 0.83×10^{-5} ,
see Appendix.

a = Initial concentration of the peroxide
b = Time interval over which points were taken
c = First order rate constant
d = Average first order rate constant
e = Arrhenius energy of activation
f = correlation co-efficient
g = Log frequency factor
h = Entropy of activation

Table VI

Rate Constants for the Decomposition of Diphenylmethyl Peroxide in Toluene

Temp. °C	a Conc. M	b Time Int.	c $K \times 10^5$ sec ⁻¹	d Average $K \times 10^5$ sec ⁻¹	e E_A Kcal/mol	f Values Column	g Log A	h ΔS Cal/°K
111*	0.26	8	3.99	3.40				
	0.49	8	2.87					
	0.34	8	3.32					
120	0.72	5	9.20	9.20	28	0.98	11.6	-7.9
	0.72	5	9.20					
130	0.30	1.5	18.23	19.26				
	0.25	1.5	20.30					

* The average of 5 determinations was 3.47×10^{-5} with the average deviation 0.45×10^{-5} see Appendix.

a = Initial molar concentration of peroxide
b = Time interval over which points were taken
c = First order rate constants
d = Average first order rate constant
e = Arrhenius energy of activation
f = Correlation co-efficient
g = Log frequency factor
h = Entropy of activation

Table VII
Rate Constants for the Decomposition of Diphenylmethyl
Peroxide in Nitrobenzene

Temp. °C	a Conc. M	b Time int. Hours	c Kx10 ⁵ sec ⁻¹	d Average Kx10 ⁵ sec ⁻¹	e E _A Kcal/mol	f Values Column	g Log A	h ΔS Cal/°K
111	0.54	5	4.35	4.35	27	0.99	11.00	-10
120	0.55	4	10.40	10.65				
	0.46	4	10.90					
130	0.31	1.5	21.32	23.40				
	0.47	1.5	25.50					

a = Initial molar concentration of peroxide
 b = Time interval over which points were taken
 c = First order rate constants
 d = Average first order rate constant
 e = Arrhenius energy of activation
 f = Correlation co-efficient
 g = Log frequency factor
 h = Entropy of activation

Table VIII

Rate Constants for the Decomposition of Diphenylmethyl
Tertiary Butyl Peroxide in Toluene

Temp. °C	a Conc. M	b Time Int. Hours	c Kx10 ⁵ sec ⁻¹	d Average Kx10 ⁵ sec ⁻¹	e E _A Kcal/mol	f Values Column	g Log A	h ΔS Cal/°K
125	1.99	6	3.14	3.14				
135.5	1.85	5	11.77	10.90	38.6	.998	16.7	15
	1.99	5	10.03					
144	1.98	1.5	29.89	29.02				
	2.90	1.5	28.14					

a = Initial molar concentration of the peroxide
 b = Time interval over which points were taken
 c = First order rate constants
 d = Average first order rate constants
 e = Arrhenius energy of activation
 f = Correlation co-efficient
 g = Log frequency factor
 h = Entropy of activation

beginning of C_2Cl_4 cut off and the trouble in determining the infinity point.

(b) By n.m.r. The errors were ^{due to} the small size of the peak, the trouble in accurate integration and the instability of the A-60 over time required for the reaction.

The activation energies were determined by linear regression analysis using all measurements of rate constants. Arrhenius activation energy plots of $\log 10^5 k$ versus $1/T^\circ K$ are shown in Fig. 6, 7 and 8. Activation energies are found to be 26.6, 28.3, and 27 kcal/mole respectively in tetrachloroethylene, toluene and nitrobenzene. The log A factors are calculated to be 10.64, 11.6 and 11 respectively in the above solvents.

The entropies of activation were calculated as follows.

$$A = \frac{k^1 T}{h} e^{\Delta S / R}$$

where A = frequency factor

k^1 = Boltzman constant

h = Planck's constant

ΔS = Entropy of activation

R = gas constant

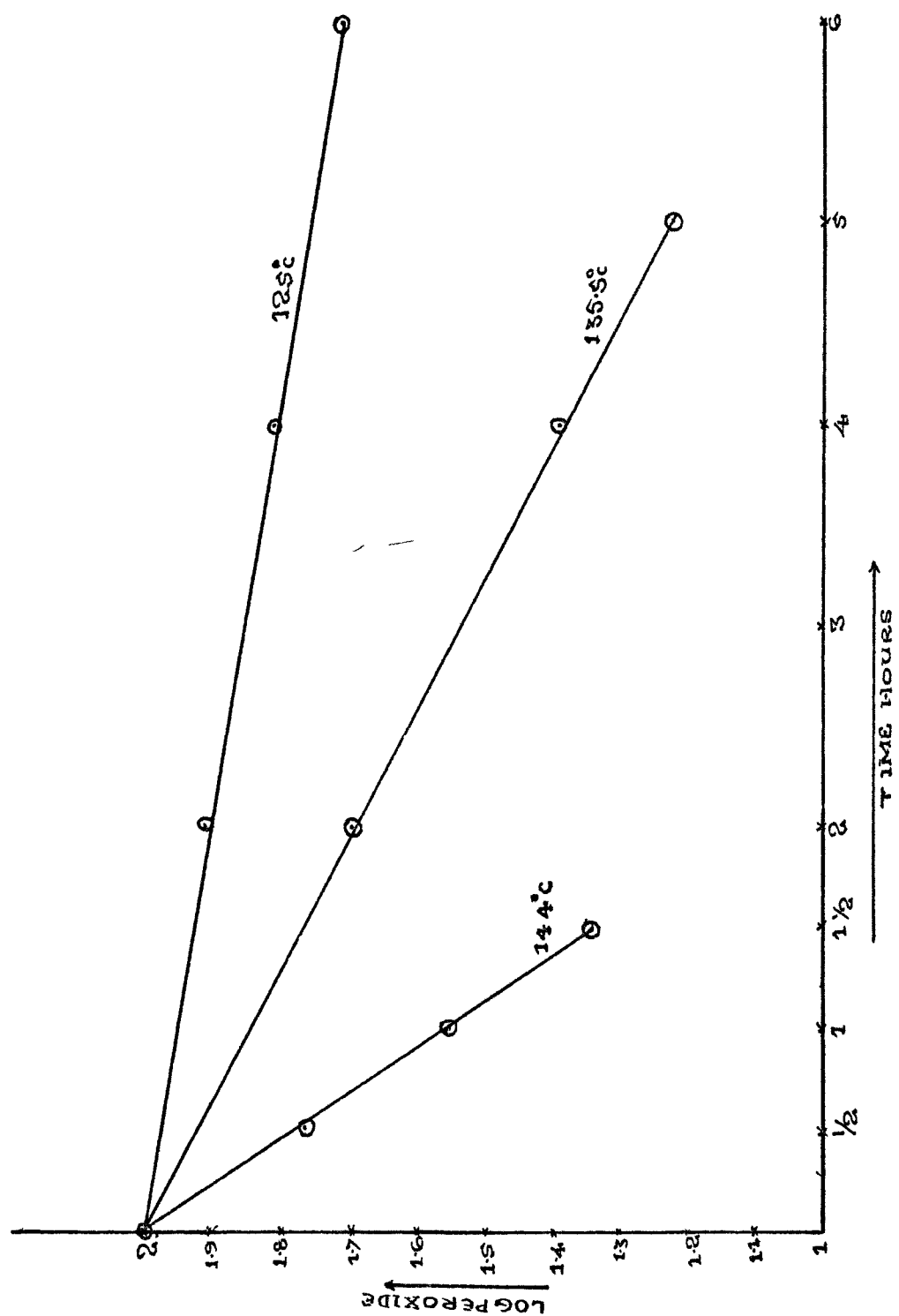
T = temperature

$$\ln A = \ln \frac{k^1 T}{h} + \frac{\Delta S}{R}$$

$$\log A = \log \frac{k^1 T}{h} + \frac{\Delta S}{R \times 2.303}$$

But $\log \frac{k^1}{h} = 10.75311$

Figure 9



RATE OF DECOMPOSITION OF DIPHENYLMETHYL
TERTIARY BUTYL PEROXIDE

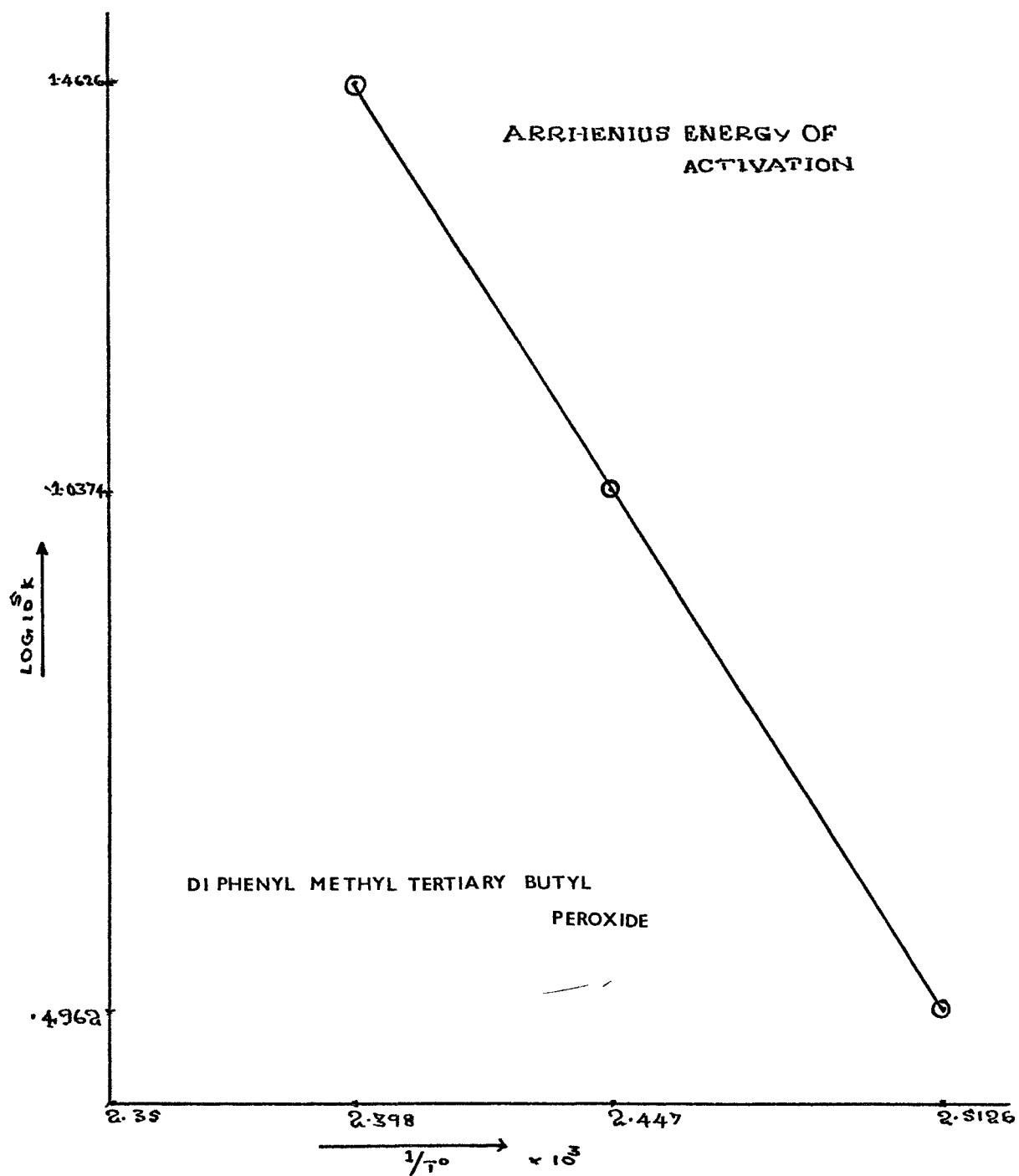


Figure 10

$$\log A = 10.75311 + \log T + \frac{\Delta S}{2.303R}$$

Thus the entropies of activation of the decomposition of bis-diphenylmethyl peroxide in tetrachloroethylene, toluene and nitrobenzene were found to be -11.8, -7.9 and -10 Cals/°K respectively.

4.1.2 Rates of decomposition of diphenylmethyl tertiary butyl peroxide

The dialkyl peroxide was decomposed in toluene at temperatures 125°C, 135.5°C and 144°C respectively. The rates were measured by n.m.r. following the decrease in the -C-H peak area of the peroxidic carbon at 6 PPM, at regular intervals of time. Plots of $\log [\text{Ph}_2\text{CHOO}(\text{CH}_3)_3]$ versus time were uniformly linear (Fig. 9). First order rate constants obtained from the slopes of these lines are shown in Table VIII. The rate constants are not dependent on the initial concentration of the peroxide showing the reaction was truly unimolecular.

The Arrhenius energy of activation was obtained by plotting $\log 10^5 k$ against $1/T^\circ\text{K}$ using linear regression analysis (Fig. 10) and was found to be 38.6 Kcals/mole. The log 'A' factor was calculated to be 16.7 and the entropy of activation to be +15 Cal/°K.

4.1.3 Rates of decomposition of trityl peroxide

Trityl peroxide was decomposed in tetrachloroethylene at 100, 110 and 120°C respectively. The rates were measured

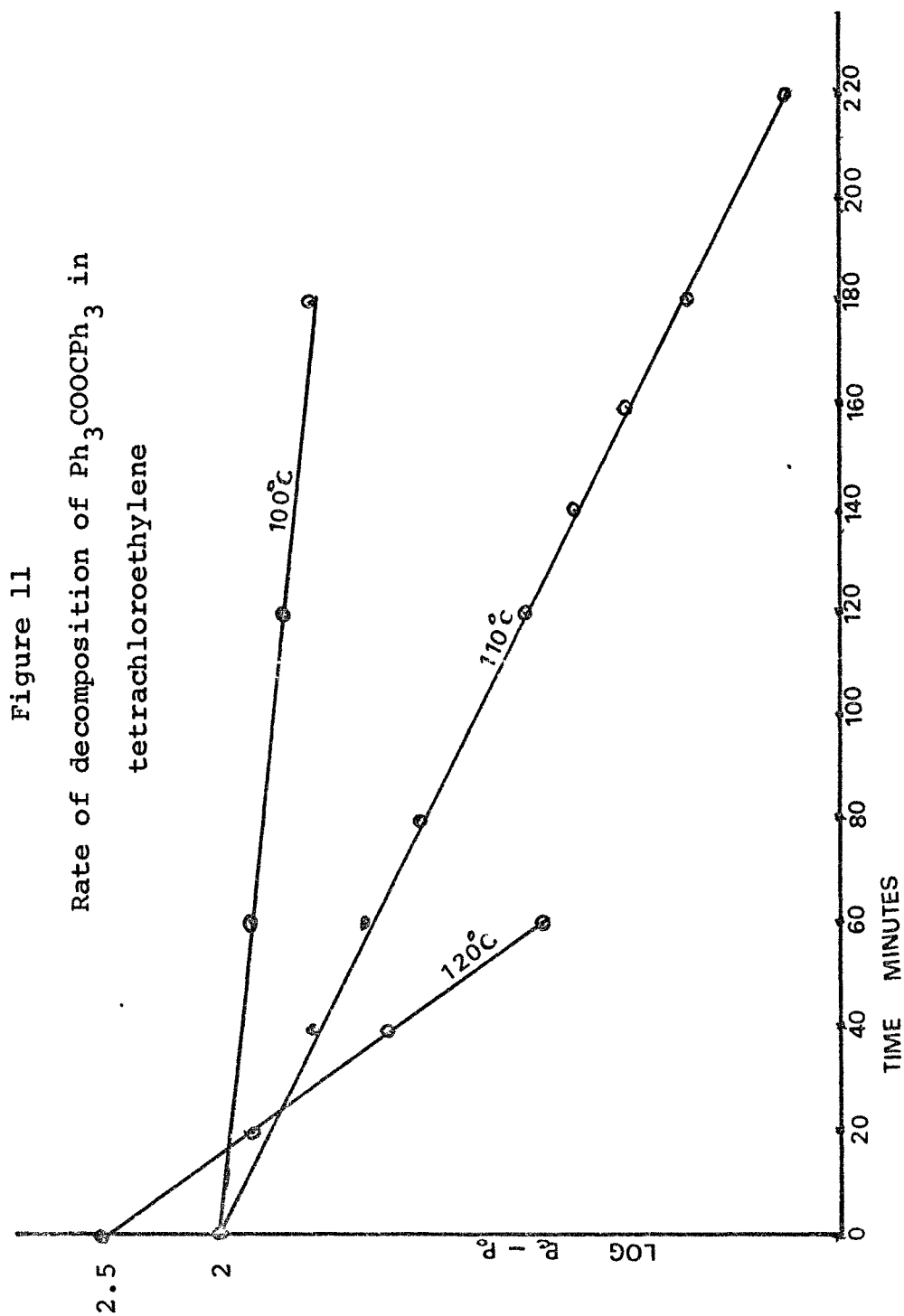
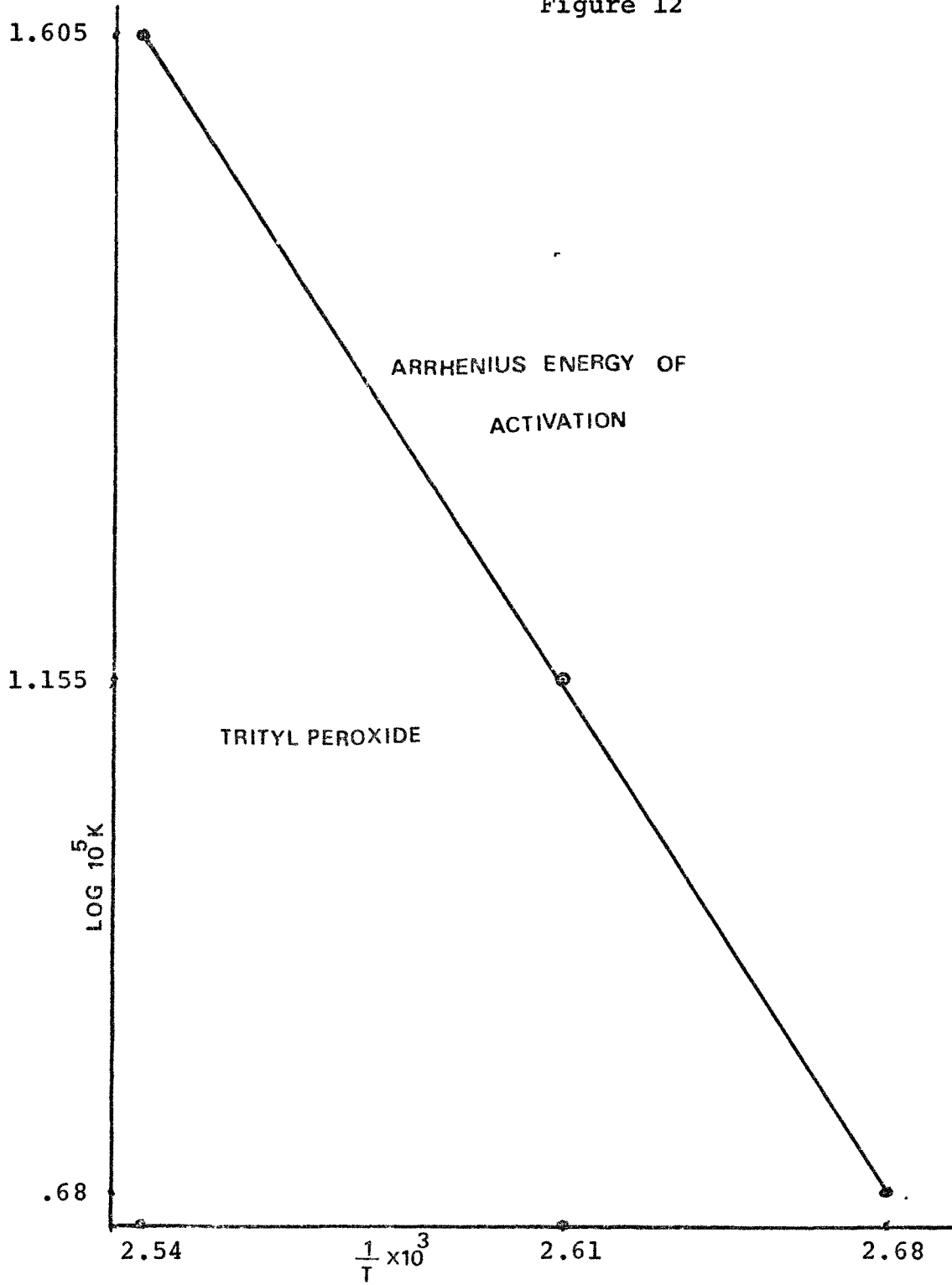


Figure 12



by following the increase in benzophenone peak at 287 by u.v. Plots of $\log [P_0 - P_t]$ versus time were found to be uniformly linear (Fig. 11). First order rate constants obtained from the slopes of these lines are shown in Table IX.

Table IX

Rate Constants for the Decomposition of
 $\text{Ph}_3\text{COOCPh}_3$ in Tetrachloroethylene

Temp. °C	* $\text{K} \times 10^5 \text{ sec}^{-1}$	Ea Kcals/mole	Log A	S
100	4.8	31	13.84	+2
110	14.3			
120	40.3			

*The initial concentration of the peroxide for kinetic studies in tetrachloroethylene was of the order of 10^{-3} M. But accurate measurement was not possible since the peroxide was not very soluble in that solvent.

The Arrhenius energy of activation was obtained by plotting $\text{Log } 10^5 K$ against $1/T^\circ\text{K}$ (Fig. 12) and was found to be 31 Kcals/mole. The log 'A' factor was 13.84 and the entropy of activation was +2 Cals/°K.

4.2 Products of Decomposition of Bis-Diphenylmethyl Peroxide

4.2.1 The liquid products were analysed by g.l.c. and the

gaseous products were analysed mass spectrographically. The gaseous product was found to be hydrogen, and was estimated quantitatively by pressure change calculations and applying the correction for cooling under liquid nitrogen. Preliminary investigations for the products in solution were done by using the contents in the n.m.r. tubes used for rate measurements. But more precise measurements were obtained by decomposing larger amount of samples in 200 ml break seal bulbs (heated for a time equal to at least ten half lives). The products obtained from the initial analysis from the kinetic runs and the products analysed from the bulbs, showed that the nature of the products remained the same qualitatively and quantitatively during the reaction so that the products after complete decomposition could be considered valid. However, the amount products obtained are corrected for the actual amounts based on the purity of the peroxide by n.m.r. (Tables X, XI, and XII).

Most of the work was done on the products of decomposition in toluene. The products were as shown in Table XI, benzophenone, benzhydrol, bibenzyl and hydrogen.

4.2.2 Decomposition of diphenylmethyl peroxide in halocarbon oil

A 0.171[M] peroxide sample 'D' in halocarbon oil was heated at 125°C for three days. The analysis of the gas showed a yield of 70% hydrogen which after correction for the actual amount of peroxide in sample 'D' was found to be

Table X

Products from the Decomposition of $(\text{Ph}_2\text{CHO})_2$ in Tetrachloroethylene

Temp. °C	^a peroxide Sample	Conc. Moles/ litre %	Benzophenone Moles/litre %	Benzhydrol Moles/litre %	Hydrogen [*] millimoles %	Total Ph ₂ C %
111	C	0.1879	0.24 63.8%	0.015 4%	1.20 65.5%	67.8%
120	C	0.170	0.22 64.7%	0.014 4%	1.03 61%	68.8%
130	D	0.1285	0.195 75.8%	0.016 6%	1.00 77%	82%
Products in Tetrachloroethylene Corrected for the Peroxide Purity						
Temp. °C	^a peroxide Sample	^b Conc. Corrected Moles/litre	Benzophenone Corrected Moles/litre %	Benzhydrol Corrected Moles/litre %	Hydrogen Cor- rected milli- moles % [*]	Total Ph ₂ C Corrected %
111	C	0.130	0.24 93%	0.015 6%	1.20 95%	99%
120	C	0.117	0.22 94%	0.014 6%	1.03 88%	100%
130	D	0.111	0.195 90%	0.016 7%	1.00 91.7%	97%

Excess H₂ to be accounted at 111°C = -0.66% 120°C = 2.7% 130°C = 2%. a = See experimental.
b = Correction based on the purity of peroxide by n.m.r., peroxide C was 68.75% pure and D was 84.5% pure.

*The yield of hydrogen was calculated by applying volume correction for cooling the reaction flask under liquid nitrogen temperature and by vapour pressure additivity method. (See experimental)

Table XI

Products from the Decomposition of $(\text{Ph}_2\text{CHO})_2$ in Toluene

Temp. °C	^a Peroxide Sample	Conc. [M]	Benzophenone [M] %	Benzhydrol [M] %	Bibenzyl [M] %	*Hydrogen millimoles %	Total Ph ₂ C %
111	C	0.167	0.211 63%	0.047 14%	0.01 6%	1.086 65%	77%
120	C	0.203	0.24 59%	0.066 16%	0.011 5.4%	1.398 69%	75%
130	D	0.132	0.19 72%	0.032 12%	0.008 6%	0.097 73%	84%
Products in Toluene Corrected for the Peroxide Purity							
Temp. °C	^a Peroxide Sample	^b Corrected Conc. [M]	Benzophenone [M] %	Benzhydrol [M] %	Bibenzyl [M] %	*Hydrogen millimoles %	Total Ph ₂ C %
111	C	0.115	0.211 92%	0.050 20%	0.010 9%	1.10 97%	112%
120	C	0.140	0.244 87%	0.70 24%	0.010 8%	1.40 100%	111%
130	D	0.111	0.190 85%	0.030 14%	0.008 7%	1.00 87%	99%

Excess H₂ to be accounted at 111° = 4% 120° = 9% 130° = 2%.

a = See experimental.

b = Correction based on the purity of peroxide by n.m.r.

Peroxide C was 68.75% pure and D was 84.5% pure.

*The yield of hydrogen was calculated by applying volume correction for cooling the reaction flask under liquid nitrogen temperature and by vapour pressure additivity. See experimental.

82.8%. This is comparable with the results obtained in other solvents (Tables X and XI).

Table XII
Product Analysis of Diphenylmethyl Peroxide
in Nitrobenzene Using Breakseal Bulbs

Temp. °C	Peroxide Sample	Concent- ration [M]	Corrected Concentra- tion [M]	Benzophen- one formed [M]	% of Benzo- phenone after Correction
120	C	0.445	0.306	0.575	94%
130	D	0.350	0.295	0.55	93%

4.2.3 Products from diphenylmethyl tertiary butyl peroxide

The decomposition was done in breakseal bulbs at a temperature of 125°C for at least 12 half lives. The gaseous products were analysed by mass spectra and estimated quantitatively by pressure change calculations. The products as shown in Table XIII are benzophenone, benzhydrol, bibenzyl, tertiary butanol, acetone and methane.

4.2.4 Products from the decomposition of triphenylmethyl peroxide

The products from the decomposition of this peroxide in C_2Cl_4 were not completely determined, but from i.r. and u.v. spectra it appeared to be mainly benzophenone. g.l.c. analysis gave a benzophenone yield of $70 \pm 10\%$, based on

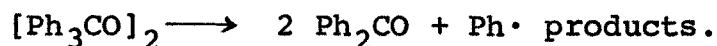


Table XIII

Products from the Decomposition of Diphenylmethyl
Tertiary Butyl Peroxide in Toluene

Temp. °C	Concen- tration Moles/ litre	Acetone Moles/ litre %	t-butanol Moles/ litre %	Benzophenone Moles/litre %	Benzhydrol Moles/litre %	Bibenzyl Moles/litre %	Methane Millimoles %
125	0.85	0.095 11%	0.76 89.6%	0.731 86%	0.12 14%	0.086 10%	
	0.377	.06 16%	0.315 83.5%	0.305 81%	0.06 16%	0.07 18.5%	0.42 11%
Product Balances - Concentration = 0.85 [M] - Ph ₂ CH							
					86% Benzophenone)	
					14% Benzhydrol)	= 100%
				(CH ₃) ₃ C-	89.6% t-butanol)	
					11% Acetone)	= 100.6%
			0.38 [M]	Ph ₂ CH	81% Benzophenone)	
					16% Benzhydrol)	= 97%
				(CH ₃) ₃ C	83.5% t-butanol)	
					16% Acetone)	= 99.5%
				Excess hydrogen atoms to be accounted)	= 8%

5. DISCUSSION

5.1 General Characteristics of Thermal Decomposition of Dialkyl Peroxides

Measurement of the rates of decomposition constitutes the largest single body of recent endeavour in the field of dialkyl peroxides. Decompositions are almost uniformly of the first order and are accompanied by little if any, radical induced decomposition. The activation energies are 34 to 37 Kcals/mole for the series ethyl peroxide through t-butyl peroxide.



Activation energies and 'A' factors of most of the dialkyl peroxides have been measured in the vapour phase.

Some of the results are shown in the table below.

Table XIV
Activation Energies and 'A' Factors for Thermal
Decomposition of Dialkyl Peroxides

Peroxide	Ea Kcals/mole	'A' sec ⁻¹	Ref.
Me ₂ O ₂ (gas phase)	36.9	4.1 x 10 ¹⁵	26
E ₂ O ₂ (gas phase)	37.3	3 x 10 ¹⁵	27
Pr ₂ O ₂ (gas phase)	36.5	2.5 x 10 ¹⁵	28
tBu ₂ O ₂ (gas phase)	36	4 x 10 ¹⁴	29
tBu ₂ O ₂ (gas phase)	39.1	3.2 x 10 ¹⁶	30
tBu ₂ O ₂ (gas phase)	37.4 [±] .5	2.5 x 10 ¹⁶	31
tBu ₂ O ₂ (liquid phase) (in cumene)	37.5	1.6 x 10 ¹⁶	32
tBu ₂ O ₂ (liquid phase) (in Butyl amine)	37	3.2 x 10 ¹⁶	32
(PhCMe ₂ O) ₂ (liquid phase) (in cumene)	34.5	4.3 x 10 ¹⁴	33

From the above results it is clear that the rates are virtually independent of structure and in the case of t-butyl peroxide it is shown to be independent of phase.

In all cases mentioned above the activation energies show only a slight variation. This is a clear indication that the oxygen-oxygen bond strength is not greatly affected by the variation of the alkyl groups.

Our result for the activation energy of diphenylmethyl tertiary butyl peroxide was 38.6 Kcals/mole (Table VIII). This agrees pretty well with the results shown in Table XIV, indicating that oxygen-oxygen bond rupture is the main mechanism in operation. But our results with bis diphenylmethyl peroxide were 26.6, 28, and 27 Kcals/mole in tetrachloroethylene, toluene and nitrobenzene respectively (Tables V, VI and VII). The difference in the activation energies in this case clearly shows other mechanisms besides the oxygen-oxygen bond rupture are important.

Intensive product studies have not been done for the dialkyl peroxides except for tert. butyl peroxide, although some work has been done - mainly by MacMillan on the photolytic decomposition of dialkyl and mixed dialkyl peroxides in the gas phase (34).

He found that in the first absorption region of the alkyl peroxides the primary photo dissociation proceeds with the rupture of the weak -O-O- bond.



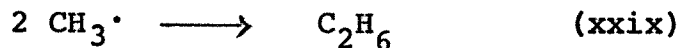
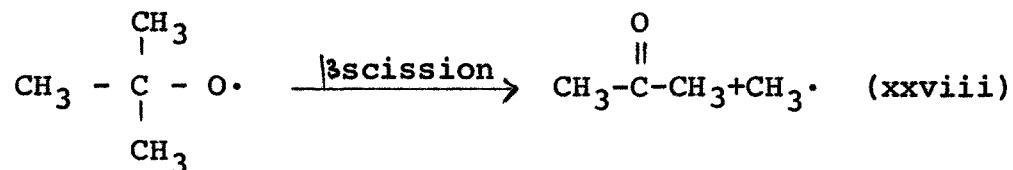
where $\text{RO}^{\bullet*}$ represents the excited radical.

The excess energy is carried off by the separating radicals providing ^{that} the pressure is low and product mixture are quite complex. At high pressure deactivation occurs by collision.

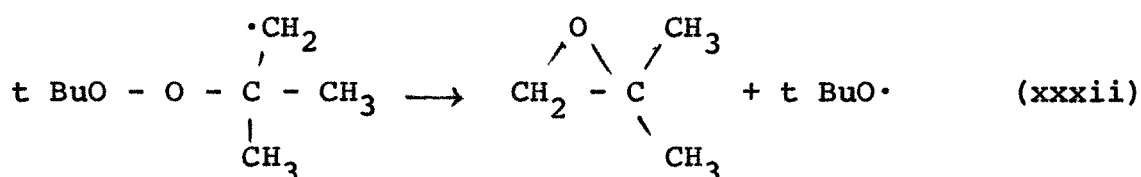
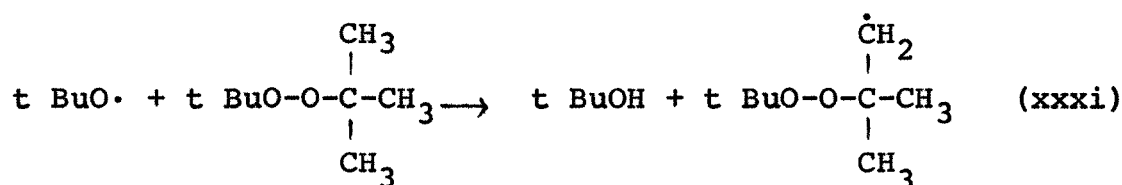
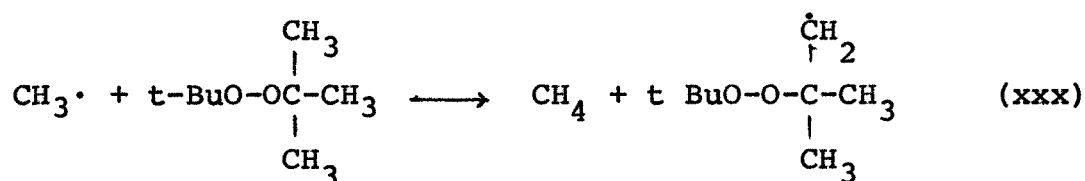
If the absorption occurred at 3130 \AA the excess energy carried off amounts to about 56 Kcals. This results in a large amount of fragmentation.

5.2 Induced Decomposition

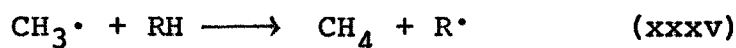
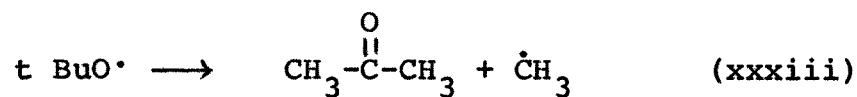
To interpret the results correctly it was important to know whether free radical induced decomposition was taking place in our reactions. Tertiary butyl peroxide is found to decompose mostly by a unimolecular nonchain path (a little induced decomposition exists) since the rate is almost the same in concentrated solution and in dilute gas phase, and also since the rate is not affected by the presence of inhibitors like nitric oxide (32). The mechanism of the decomposition of tert. butyl peroxide in vapour phase is as follows (35).

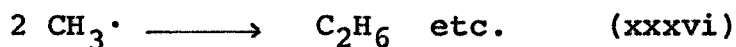


In pure liquid the products are isobutylene oxide, t-butanol, acetone, methane and ethane (35). Acetone and ethane results from (xxviii) and (xxix). The other products can be explained as follows (35).

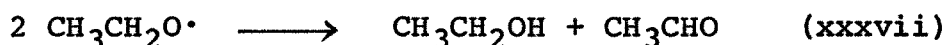


If the decomposition occurs in the presence of an active hydrogen donor, RH, the methyl and tert. butoxy radicals can react abstracting hydrogen from RH, thus increasing the yields of methane and t-butanol.

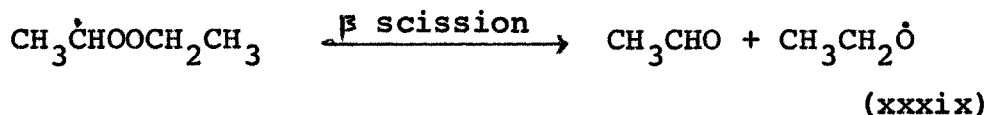
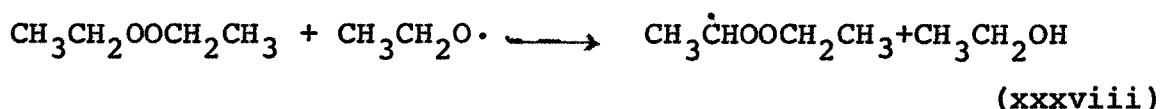




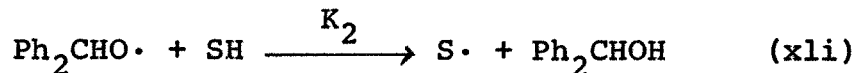
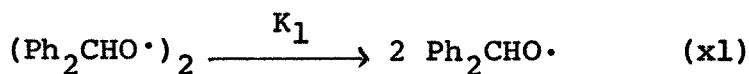
The products from ethyl peroxide have been reported (35) to be ethanol and acetaldehyde. These products could result from a disproportionation between ethoxy radicals.



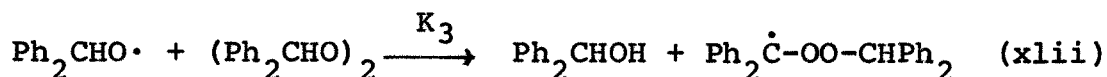
They could also result from a chain process in which an ethoxy radical abstracts an α hydrogen from a peroxide molecule which subsequently decomposes by β scission.

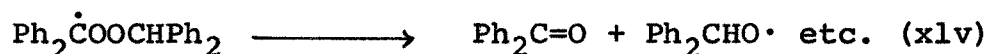
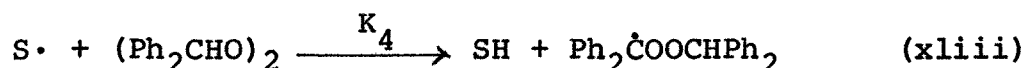


The structural influences of bis diphenyl methyl peroxide could easily lead to a chain process and thus leading to an induced decomposition.



(where SH is solvent)





The diphenylmethyl tertiary butyl peroxide can also follow a path of chain process as that of the t-butoxy radicals (eqn. xxxi and xxxii).

Pryor and co-workers (1c) have shown that the rate constants for chain transfer between polystyryl radicals and dialkyl peroxides are about the same for n-butyl, sec-butyl and tertiary butyl peroxides (Table XV).

Thus the primary and secondary peroxides appear to be no more easily attacked by free radicals than tertiary butyl peroxide is.*

Table XV

Chain Transfer Constants for Peroxides
in Polymerising Styrene (1c)

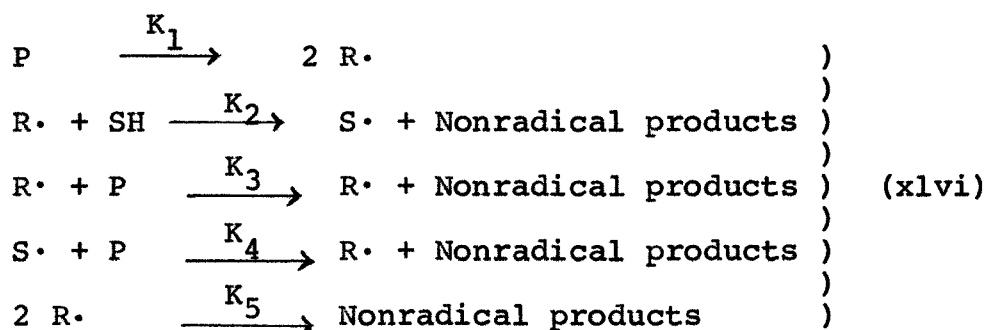
Peroxide	At 60°C	At 80°C
n butyl peroxide	7.6×10^{-4} mole/sec.	9.4×10^{-4} mole/sec.
sec. butyl peroxide	4.0×10^{-4} mole/sec.	21×10^{-4} mole/sec.
t-butyl peroxide	6.0×10^{-4} mole/sec.	22×10^{-4} mole/sec.

* Pryor suggested (1) that styryl radicals attacked peroxide by hydrogen abstraction rather than displacement at -O-O-. Since the rate of radical attack at analogous -S-S- (which occur by displacement at -S-S-) was strongly influenced by the nature of alkyl groups.

Induced decomposition can easily be detected by certain tests. The following are the tests.

(1) Kinetic Evidence:

Peroxide decompositions which goes through the path of homolysis and induced decomposition generally shows 1 + 3/2 order kinetics. It can be derived as follows:



(P is the peroxide, R· and S· are any radicals)

The kinetic order of the induced decomposition depends on the source of the radicals that effect the induced decomposition and on which type of termination occurs. If solvent radicals are not involved the K_4 step in the above equations vanishes. The disappearance of peroxide is then:

$$\frac{-dP}{dt} = K_1[P] + K_3[R\cdot][P] \quad (\text{xlvi})$$

Since radicals are very reactive it is reasonable to assume that their concentrations reach a steady state value very early in the reaction. The rate of formation of radicals

$$R_f = 2 K_1 [P]$$

and the rate of destruction is

$$R_d = 2 K_5 [R\cdot]^2$$

The factor '2' is included since two radicals are produced.

At steady state

$$R_f = R_d$$

$$2 K_1 [P] = 2 K_5 [R\cdot]^2$$

$$[R\cdot] = \left[\frac{K_1}{K_5} \right]^{1/2} [P]^{1/2}$$

Substituting the value of $R\cdot$ in (xlvii)

$$\frac{-dP}{dt} = K_1 [P] + \frac{K_3 K_1^{1/2}}{K_5^{1/2}} [P]^{1.5} \quad (\text{xlix})$$

$$= \frac{-dP}{dt} = K_1 [P] + K [P]^{3/2} \quad (1)$$

Such a dependence will not be shown in plots of $\log [P]$ versus time for individual runs, since the departure from linearity may be small. But it does show up if the initial concentration of the peroxide is varied and the first order rate constants for different initial concentrations of the peroxide are compared. K 's increase with increase in initial concentration of the peroxide.

Thus if K 's are independent of changes in the initial concentration of the peroxide it is a clearcut indication that the reaction is of true "first order" in nature.

The activation energies and 'A' factors will be lower if there is any induced decomposition, than the normal

activation energies and 'A' factors for the normal peroxide homolysis.

Looking at equation (xlix) the contribution due to induced decomposition is

$$\frac{K_1^{1/2}}{K_5^{1/2}} K_3 [P]^{3/2}$$

where K_1 is the rate constant for homolysis

K_5 is the rate constant for termination step

K_3 is the rate constant for the hydrogen abstraction
(induced decomposition)

$$E_a \text{ induced} = 1/2 E_{a \text{ homolysis}} + 1/2 E_{a \text{ termination}} + E_{a \text{ hydrogen abstraction}}$$

E_a homolysis is generally about 36 Kcals/mole (Table XIII). Since radical radical coupling is collision controlled E_a termination is zero. E_a hydrogen abstraction is approximately 7 to 10 Kcals/mole (39).

$$E_{a_i} = 1/2 (36 - 0) + 8 = 26 \text{ Kcal/mole}$$

Again looking at equation (xlix)

$$\log A \text{ induced} = 1/2 \log A_1 - 1/2 \log A_5 + \log A_3$$

$\log A_1$ = 'A' factor for homolysis approximately 16 (Table XIV)

$\log A_5$ = 'A' factor for termination approximately 11

$\log A_3$ = 'A' factor for hydrogen abstraction approximately

11 (39).

$$\log A_i = \frac{16}{2} - \frac{11}{2} + 11$$

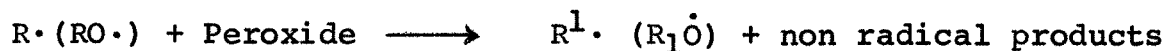
$\log A_i$ is approximately 13.5 which is lower than homolysis. eg. - The activation energy and 'A' factors for ethyl peroxide in the vapour phase was found to be

Activation Energy Kcals/mole	'A' factor sec^{-1}	Ref.
31.9	4.1×10^{14}	28
31.7	2.1×10^{13}	36
29.9	1.1×10^{12}	37

But C. Legget and Thymne obtained the normal activation energy for ethyl peroxide typical of the homolysis of peroxides, (Table XIV) by introducing nitric oxide as the free radical trap. Thus the low activation energies and 'A' factors obtained previously (as shown above) were explained by invoking the reaction path adopting an induced decomposition.

(2) Products of decomposition

Products of decomposition from the peroxide and the solvent can be indicative of induced decomposition or its absence. If the yields of products from the solvent radical coupling are relatively high it shows that much of the peroxide must decompose to free radicals. Radical induced decomposition destroys the peroxide with no net increase in radical concentration.



(3) Solvent effect

Induced decomposition is often very dependent on the nature of the solvents. Thermal decompositions of tertiary butyl hydroperoxide, for example, are very much faster in alkane solvents than in toluene or benzene. The difference has been shown to result from a much more efficient induced decomposition in the alkane (2c).

(4) Radical traps or inhibitors

Radical traps or inhibitors serve as good indicators to induced decomposition by trapping the radical from further attacking the peroxide. eg. - The low activation energies obtained for the thermal decomposition of ethyl peroxide (28, 36 and 37) was found to be due to induced decomposition by Legget, et al. (27) in their studies for the decomposition in presence of nitric oxide where nitric oxide served as the inhibitor. Also the decomposition of benzoyl peroxide in dioxane was found to show increased rates and orders higher than one. But in presence of inhibitors like iodine, styrene, trinitrobenzene, or any of several other inhibitors, the decomposition shows first order kinetics (35).

5.2.2 The application of these tests to our results

(1) Kinetics

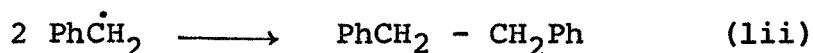
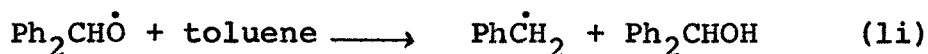
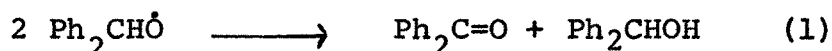
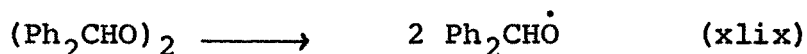
Tables V, VI and VII show our rate constants for differing initial concentrations of bis diphenylmethyl peroxide in three different solvents viz. - tetrachloroethylene, toluene and nitrobenzene. The rate constants show no consistent change with changes in the initial

concentration of the peroxide. But the initial concentration changes that we looked at differed only 2 to 3 fold in each solvent. However, the rates showed only very little solvent effect; i.e., were nearly the same in all three solvents (Tables V, VI and VII). Therefore the change in concentration of the peroxide from tetrachloroethylene to toluene and nitrobenzene was approximately 10^3 fold, in other words, the rates did not show any dramatic increase with increase in the concentration of the peroxide and hence the possibility of an induced decomposition seems unlikely. The same tables give the activation energies to be 26.6, 28 and 27 Kcal/mole respectively in tetrachloroethylene, toluene and nitrobenzene and 'A' factors to be 10.6 - 11.6. These low activation energies and log 'A' factors should then be due to some other deviations in the mechanism. Our rate studies with the mixed peroxide viz. - Diphenylmethyl tertiary butyl peroxide (Table VIII) shows no induced decomposition since rate changes are not observed with changes in the initial concentration of the peroxide and also since the activation energy (38.6 Kcals/mole) in toluene is quite normal for the homolytic scission. More information might have been obtained with further rate studies over a wider P_o change but within the time limit we did not attempt to explore this possibility further.

(2) Product studies

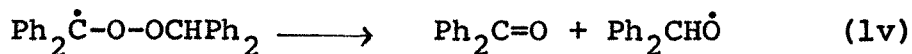
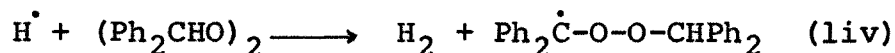
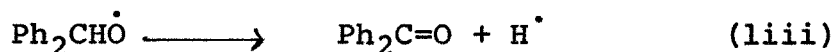
In the case of bis diphenylmethyl peroxide the main products obtained are benzophenone, hydrogen, benzhydrol and

an average of 7% bibenzyl (Table XI). The benzophenone and hydrogen yields are almost quantitative. The reaction can be represented in radical terms as follows.



The low yields of bibenzyl and Ph_2CHOH show that this radical mechanism is only a small part of the total reaction.

Induced decomposition path suggested earlier (equations xl to xlv, page(70)) does not explain the major products to be benzophenone and hydrogen. An induced chain path which would give these products is shown below.



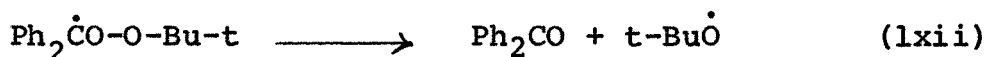
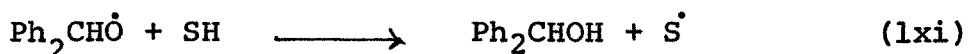
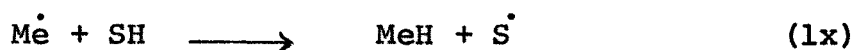
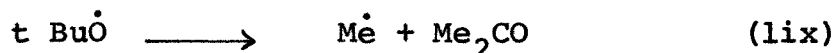
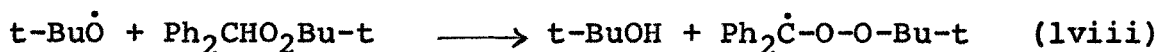
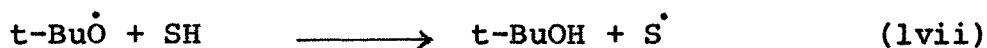
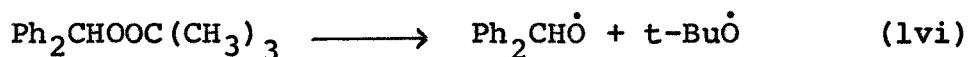
This path seems unlikely because (1) β scission to give hydrogen atoms is unknown at these temperatures.

(2) If hydrogen atoms were found they should react with the solvent, eg. with PhCH_3 to give $\text{Ph}\dot{\text{C}}\text{H}_2$ and hydrogen, and a much higher yield of bibenzyl would be expected. In C_2Cl_4 , H atoms would be expected to add to the double bond, and

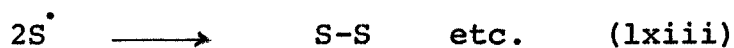
no hydrogen would be produced. Thus the low yields of bibenzyl and the absence of other products support the absence of an induced decomposition.

The products obtained from the mixed peroxide, on decomposing in toluene at 125°C are benzophenone* 81%, benzhydrol 16%, bibenzyl 18.5%, acetone 16%, tertiary butanol 83.5% and 11% methane, (the only gaseous product detected by mass spectrometry (Table XIII).)

The above mentioned products may be possibly formed by the rupture of the -O-O- bond forming the radicals and the subsequent attack of the radicals with the peroxide, the solvent or among themselves. (The possibilities leading through other mechanisms do not concern us at this point.) The equations can be well represented as given below.



*The molar percentages are given.



(Here SH is toluene)

The product studies in toluene with the mixed peroxide was done at two different concentrations. A 0.85 molar and 0.377 molar solutions were decomposed at 125°C. The product analysis did show a variation (Table XIII). The yields of bibenzyl are 10% at the high concentration and 18.5% at the low concentration. The lower yield of bibenzyl at the higher concentration suggests the presence of an induced decomposition. However, without conducting further studies we could not give a conclusive evidence for this.

(3) Solvent effect

The rates of decomposition of bis diphenylmethyl peroxide was found to be independent of the nature of the solvent (Tables V, VI and VII). However, we did not try the mixed peroxide with other solvents and therefore could not say anything concerned with solvent effect on that.

(4) Radical traps

Though radical traps would have been a good method to distinguish between radical and induced decompositions, due to experimental difficulties we did not try the effect of any inhibitor on the rate of decomposition.

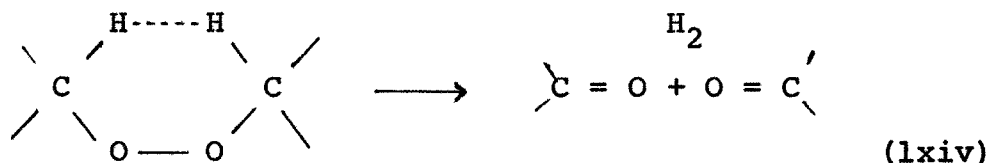
To conclude our results the radical induced decomposition for the bis diphenylmethyl peroxide is ruled out but casts some doubt of a radical induced decomposition for the mixed peroxide.

6. GENERATION OF H₂ FROM BIS-DIPHENYLMETHYL PEROXIDE

Bis-diphenylmethyl peroxide is a fairly stable symmetrical peroxide free from polar influences which favour a heterolytic scission. J. I. Cadogan et al (22) explained the formation of benzophenone by a radical mechanism on the mere basis that the reaction in isopropylbenzene yielded about 12% of di-*o*-cumyl.

Our results show (Tables X, XI, XII) that the benzophenone yield and hydrogen yield are nearly equal and very high, $85 \pm 10\%$. Free radical reactions to give this much hydrogen can be ruled out (see Discussion on induced decomposition).

The rates of decomposition (Tables V, VI and VII) and the products (Tables X, XI, XII) did not show any solvent effect and thus the chances of an ionic mechanism are ruled out. After discarding the possibilities of a radical and an ionic mechanism, the one open is the concerted mechanism.



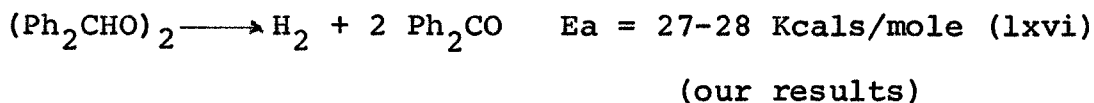
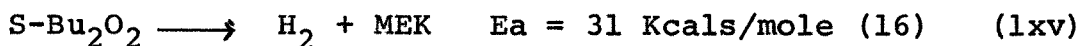
Hiatt et al (16) in their study of the thermal decomposition of deuterated and undeuterated sec-butyl peroxide found an activation energy of 31 Kcals/mole and an 'A' factor of 10^{12} for hydrogen evolution, which they

thought was not low enough for a concerted mechanism. They also found that the primary isotope effect was 1.68 which is too low to attribute for a concerted mechanism, and the secondary isotope effect of 1.47 which is too large to attribute to a simple homolysis. Thus they discarded all other possible mechanism for hydrogen evolution casting some doubt on the concerted mechanism.

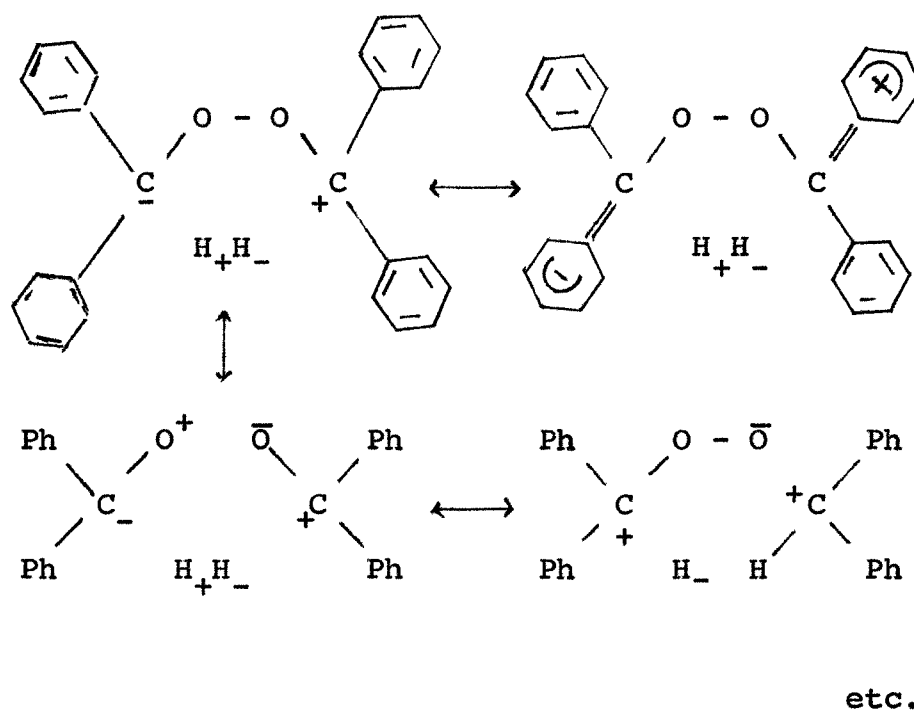
But calculations on sec-butyl peroxide (43) show 10^{12} is about right for 'A' factor for the concerted reaction.

Our result for the 'A' factor for the decomposition of bis-diphenylmethyl peroxide is 10^{11} to 10^{12} . Though this is for the total decomposition reaction, the fact that the yields of benzophenone and hydrogen are approximately 90% means that the true 'A' factor for the decomposition to these products must be very close to the measured value.

The great difference between sec.-butyl peroxide yielding hydrogen and methyl ethyl ketone and that of diphenylmethyl peroxide yielding benzophenone and hydrogen lies in the activation energy.



This must reflect weaker -C-H bonds in diphenylmethyl peroxide and a transition state in which these are greatly stretched. Also this low activation energy for diphenylmethyl peroxide seems reasonable since the resonance contribution stabilises the transition state far greater than the hyper conjugative forms suggested by Durham and Mosher (8).



But heavy contributions to the transition state from such resonance structures does not seem likely since the rate or the products did not change as the polarity of the solvent is increased from tetrachloroethylene to nitrobenzene.

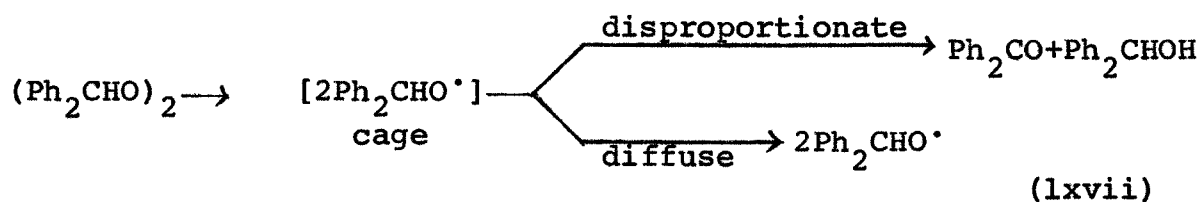
Deuterium isotope effects would have been useful on this point but we were not able to do any due to the lack of time. The data obtained by Hiatt and Szilagyi on the

decomposition of sec. butyl peroxide (16) may be inaccurate since sec. butyl peroxide yielded only 30% hydrogen and the data calculated by them was by separating the hydrogen evolution from homolysis (see Introduction). $\text{Ph}_2\text{CHOOCHPh}_2$ which gives approximately 90% hydrogen would be a better choice for measuring deuterium isotope effect.

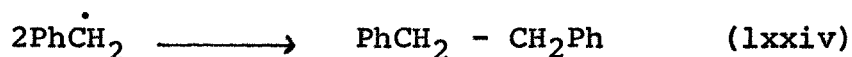
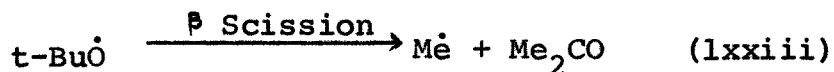
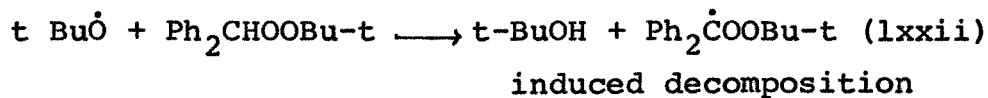
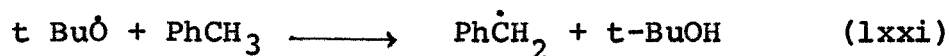
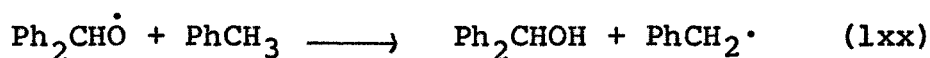
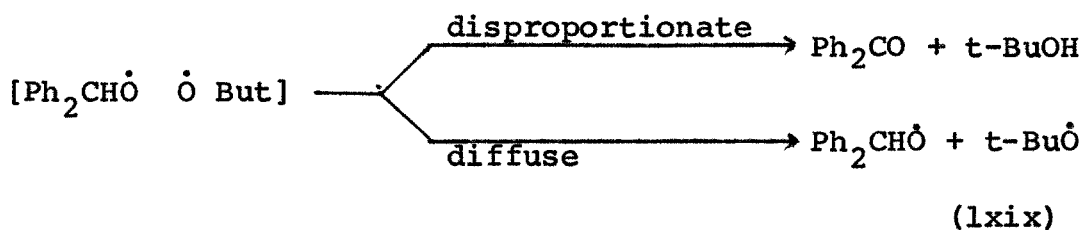
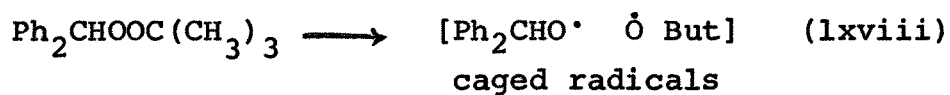
To conclude the evidence we obtained strongly favours a concerted mechanism.

6.2 Reactions of Alkoxy Radicals

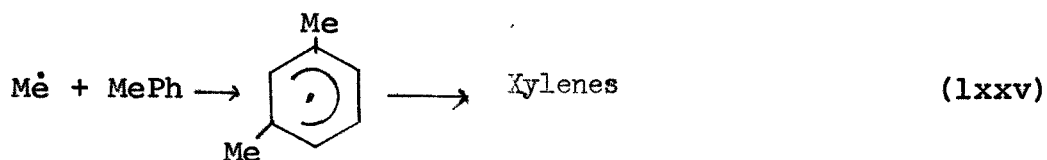
Examination of solvent cage interactions was an objective of this work. But the decomposition of bis-diphenyl methyl peroxide yielded only a small fraction -O-O- homolysis component and also the yields of benzhydrol could not be measured accurately (Experimental). However, the close correspondence of benzophenone and hydrogen, and the low yield of benzhydrol suggests very little of the benzophenone to come from the cage disproportionation.



The results from the mixed peroxide; i.e., diphenyl-methyl tertiary butyl peroxide are interesting but not conclusive. The products could be explained by the following reaction paths.



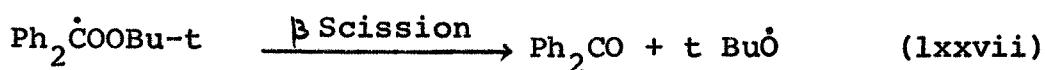
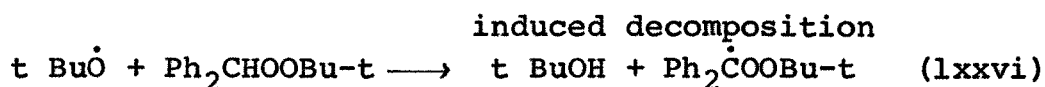
The low yields of bibenzyl and the high yield of t-butanol mean either that cage disproportionation of $\text{Ph}_2\text{CHO}^\bullet$ and $\text{t-Bu}\dot{\text{O}}$ is very important or that there is a lot of induced decomposition. The other alternative that radicals are lost via



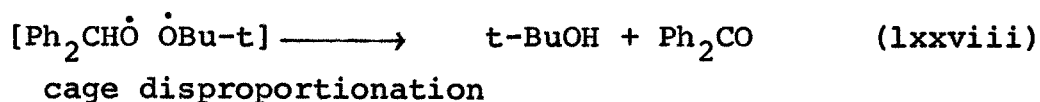
is ruled out by product balances (Table XIII). The yield of acetone 16% and the yield of methane 11% show close similarity within the experimental error.

The t-butanol/acetone ratio is found to be 5.2. This is higher than the expected value for t-BuO[•] radical in toluene at this temperature, so that there must be a better substrate for hydrogen abstraction in the system; eg., Hiatt et al (40) decomposed t-butyl peroxide in toluene at 171.5°C and obtained 52% acetone, 47% t-butanol and 80% bibenzyl. But Walling et al (41) obtained t-butanol/acetone ratio as 2.99 at 120°C in toluene at a pressure of 1 Kg/cm² (atmospheric) with increase of t-butanol with the increase of pressure.

In benzaldehyde, t-butyl peroxide decomposed (42) almost quantitatively producing t-butanol by hydrogen abstraction. Considering the similarity of benzaldehyde hydrogen (of the -CHO group) and the diphenyl methyl hydrogen of the peroxide or the alkoxy radical justifies the high yield of t-butanol in our work.



or



To conclude, either the cage disproportionation of the alkoxy radicals produced from $\text{Ph}_2\text{CHOOBu-t}$ far exceeds ^{their} diffusing apart or there is a lot of induced decomposition.

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APPENDICES

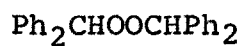
Ph₂CHOOCHPh₂
Kinetic runs in tetrachloroethylene at 111°C

Runs No.	Conc. [M] x 10 ³	Initial Absorption in u.v.	Final Ab- sorption in u.v.	u.v. Range	Rate Constants sec ⁻¹
1		6	74	0-2	4.13x10 ⁻⁵
2		8	74	0-2	3.69x10 ⁻⁵
3		8	79	0-2	3.22x10 ⁻⁵
4		15	84	0-2	4.79x10 ⁻⁵
5	1	8	76	0-2	4 x10 ⁻⁵
6	1	12	78	0-2	3.28x10 ⁻⁵
7	1	9	74	0-2	5 x10 ⁻⁵
8	.3	39	82	0-1	2.74x10 ⁻⁵
9	3	15.5	225	0-2	2.52x10 ⁻⁵
10	1	26	79	0-2	4.87x10 ⁻⁵
11	0.3	4	45	0-2	2.084x10 ⁻⁵

Average of 11 determinations = 3.7

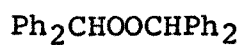
Average deviation = .8

Percent deviation = 23%



Kinetic runs in tetrachloroethylene at 120°C

Runs No.	Initial Conc. [M] $\times 10^4$	Initial u.v. Ab- sorption	Final u.v. Absorp- tion	u.v. Range	Rate Constants $\times 10^5$
1	5	6	50	0-2	8.8
2	3	4.5	44.5	0-2	5.63
3	7.5	9	59.5	0-2	8.41



Kinetic runs in tetrachloroethylene at 130°C

Runs No.	Initial Conc. [M] $\times 10^4$	Initial u.v. Ab- sorption	Final u.v. Absorp- tion	u.v. Range	Rate Constants $\times 10^5$
1	4.6	3	39	0-2	18.2
2	9.2	1	66	0-2	20.06

Kinetic runs in toluene by n.m.r. at 111°C

Runs No.	a Conc. M	b Time Int. Hrs.	c Peroxide Sample	Rate Constant $K \times 10^5$
1	0.263	10	C	4.09
2	0.263	8	C	3.99
3	0.490	8	A	2.88
4	0.29	12	C	3.10
5	0.34	8	D	3.32

Average of 5 determinations = 3.47

Average deviation = .45

Percent deviation = 13%

A typical set of data for the determination
of rate at 111°C is as follows:

Concentration = 0.34 Molar

Time Hrs.	Peroxide Peak Area	Methyl Peak Area	Relative Peroxide Peak Area	Relative Methyl Peak Area	Log Peroxide	Rate Constant $K \times 10^5$
0	28	263.75	100	941.96	2	
2	28.5	325	82.6		1.91	
4	21	312.5	63.29		1.80	
6	11	210	49.24		1.69	3.32
8	7.42	182.25	38.7		1.58	

a = Initial molar concentration of the peroxide

b = Time interval between the runs

c = Peroxide sample A, C and D are samples prepared at different times.



Kinetic runs in toluene at 120°C by n.m.r.

Runs No.	Conc. [M]	Time ^a Int. Hours	Peroxide Sample	Rate Constant $K \times 10^5$
1	.434	5	C	8.95
2	.722	5	D	9.20



Kinetic runs in toluene at 130°C by n.m.r.

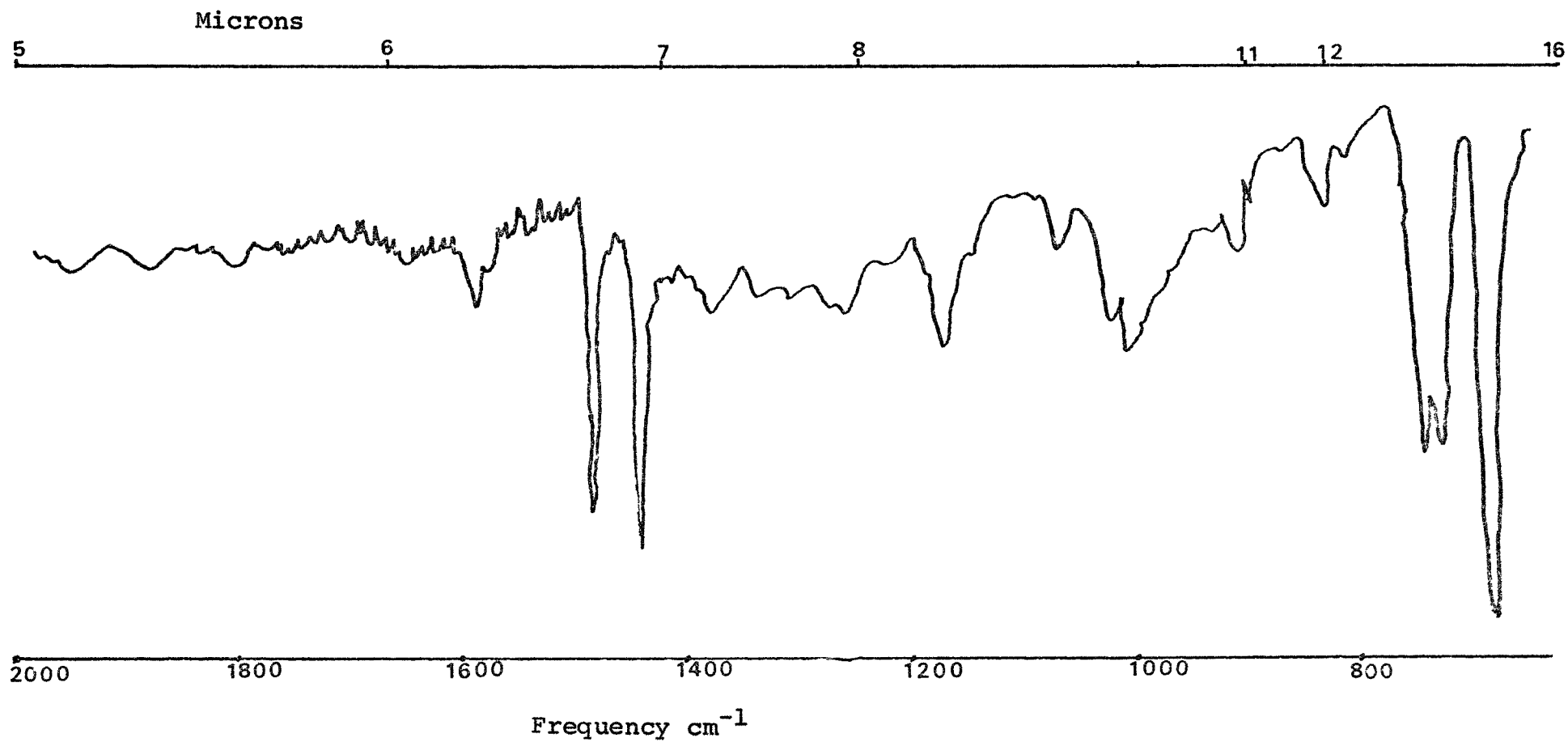
Runs No.	Conc. [M]	Time ^a Int. Hours	Peroxide Sample	Rate Constant $K \times 10^5$
1	.304	2	D	18.23
2	.29	1-1/2	D	20.3

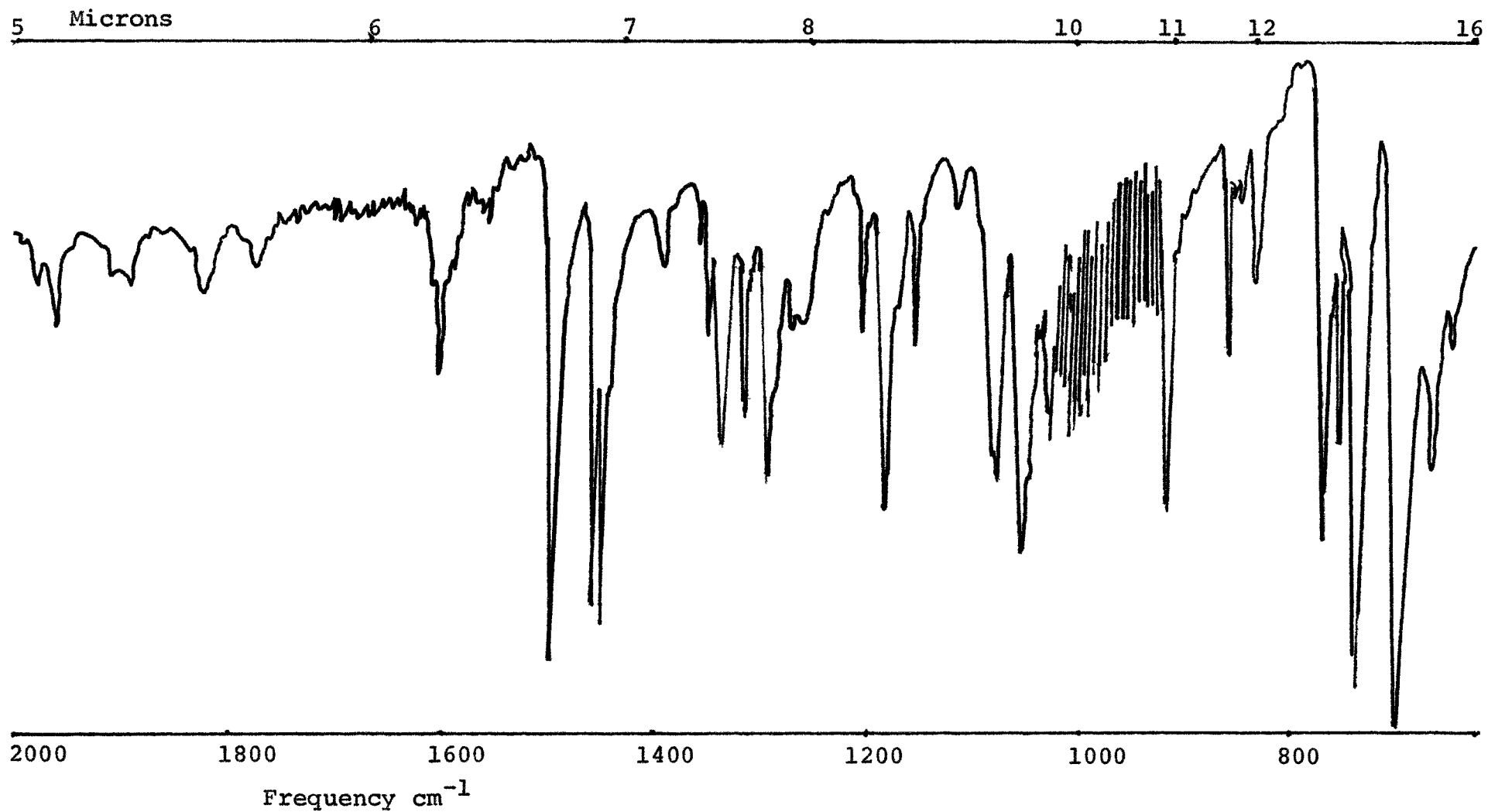
a = Time interval between the kinetic runs.

C and D are peroxide samples prepared at different times.

IR SPECTRUM

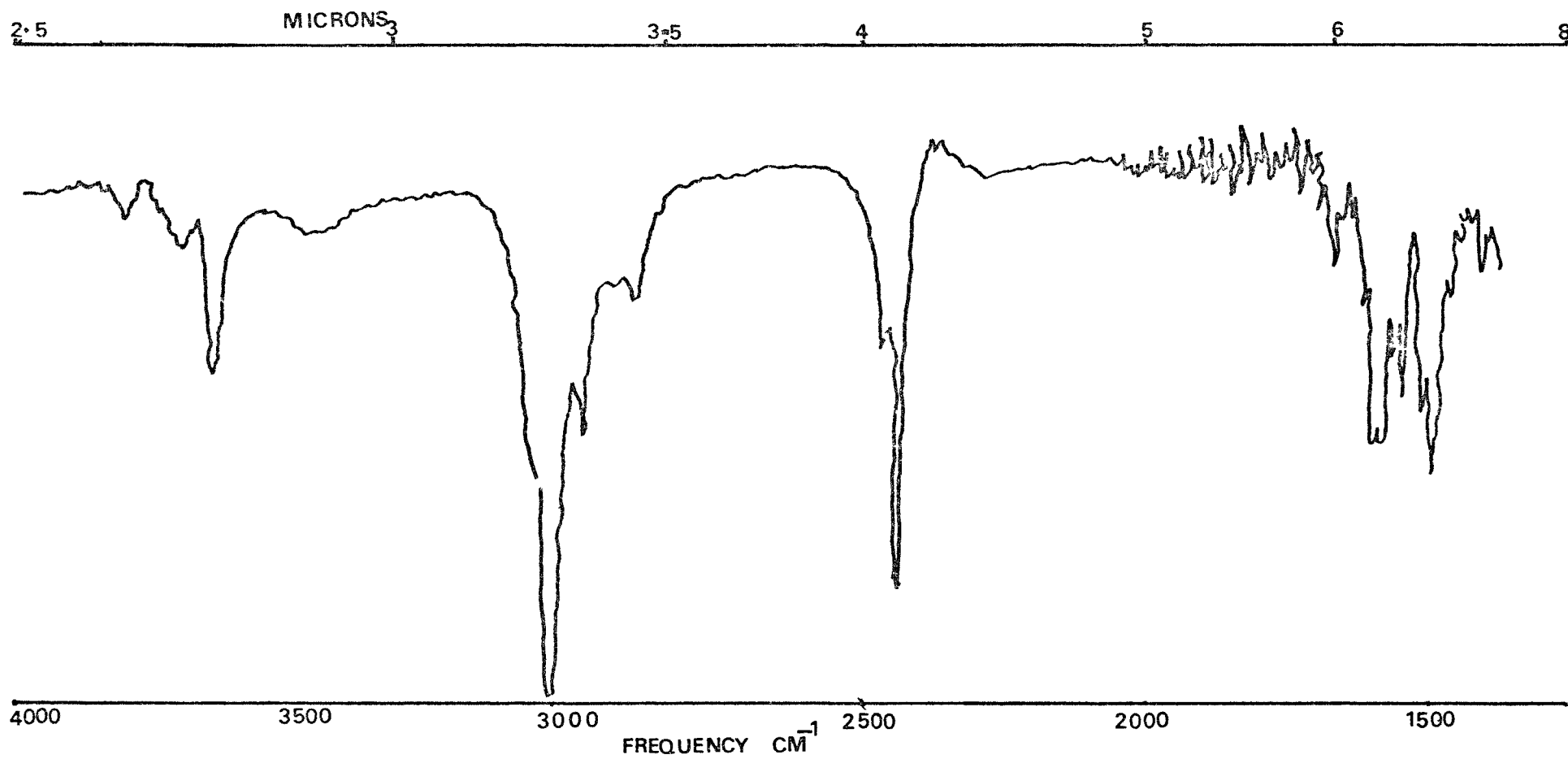
Ph_2CHOOH



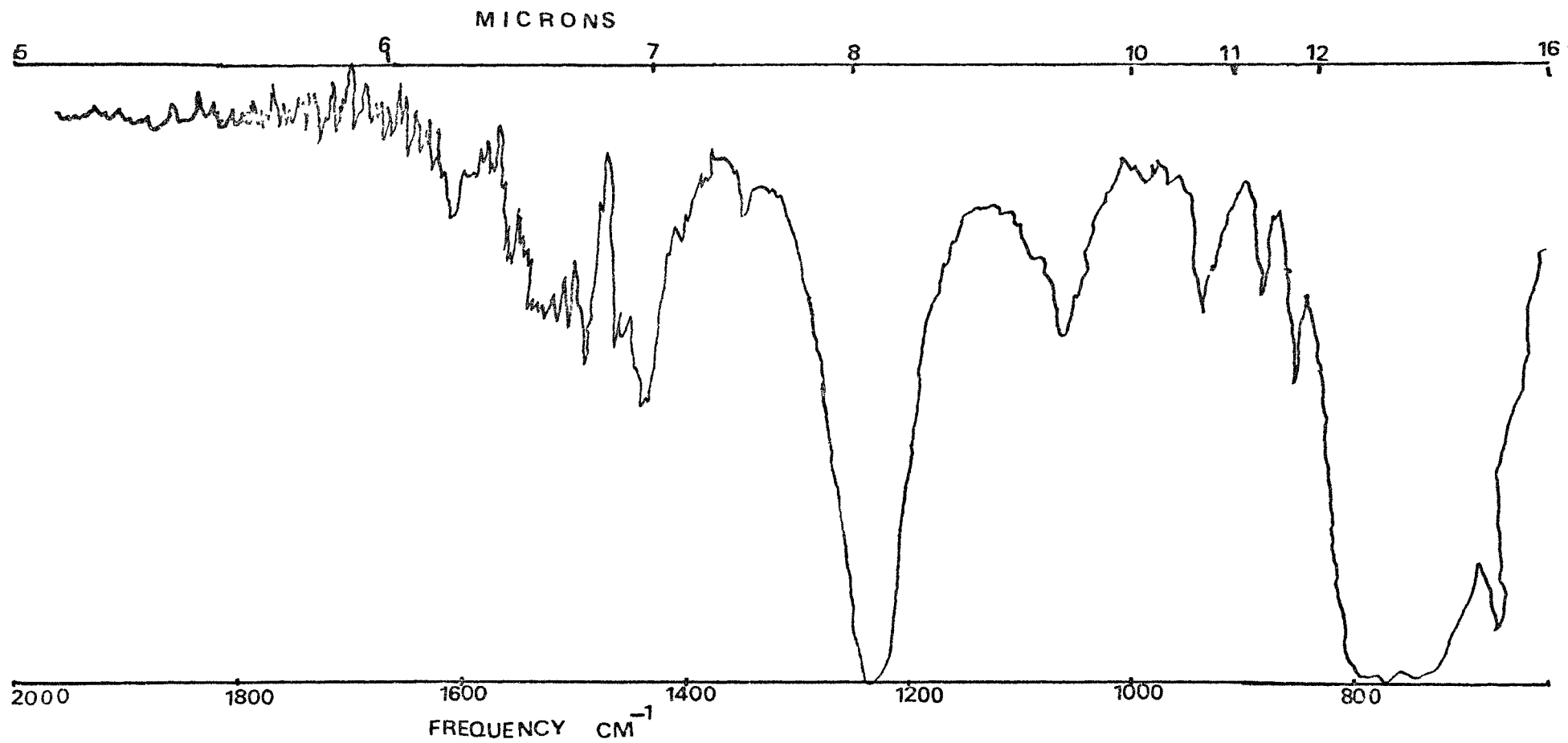


IR SPECTRUM $\text{Ph}_2\text{CHOOCHPh}_2$

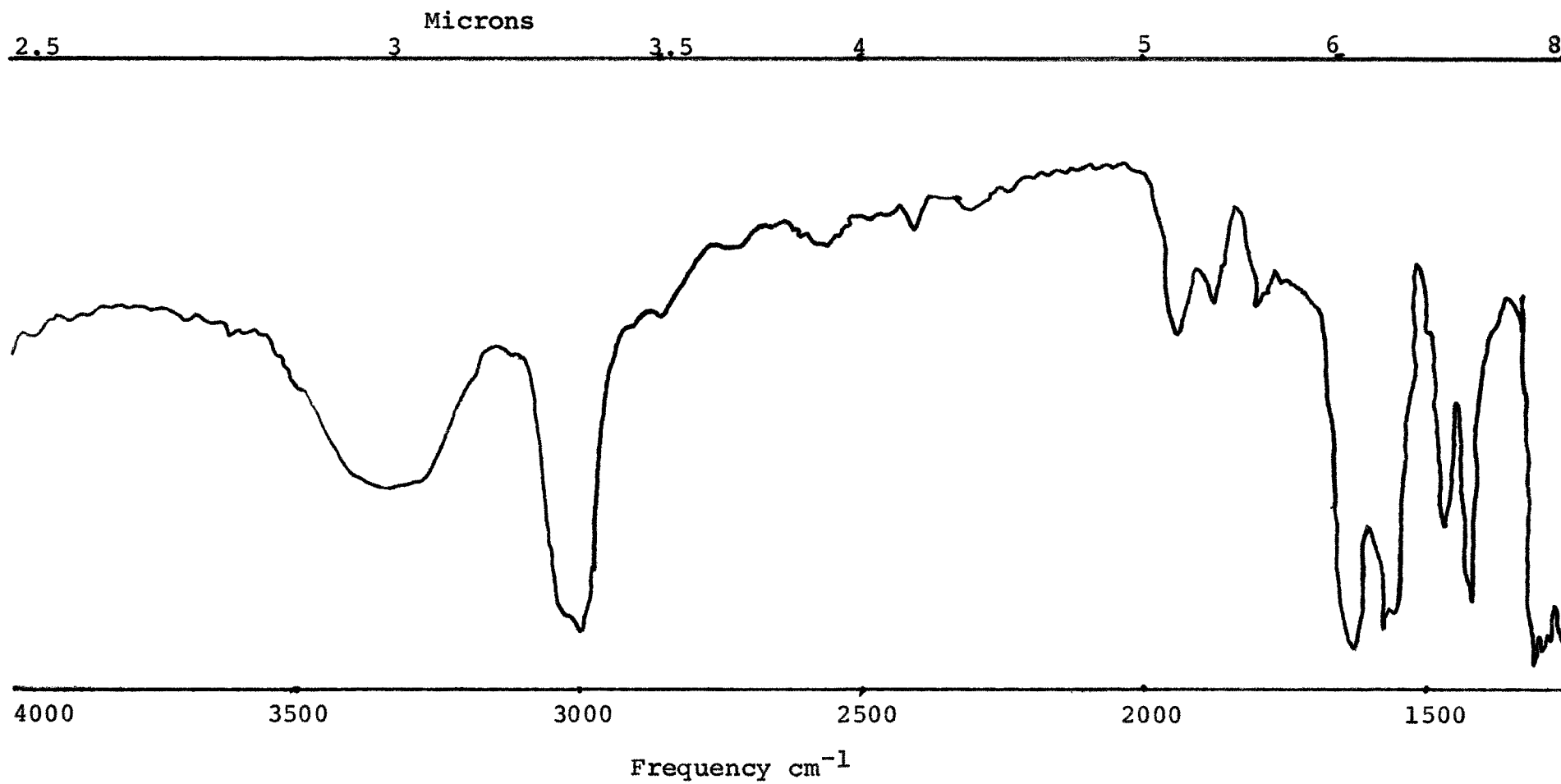
IR SPECTRUM IN CHLOROFORM
TRITYL PEROXIDE

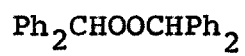


IR SPECTRUM
TRITYL PEROXIDE IN CHLOROFORM

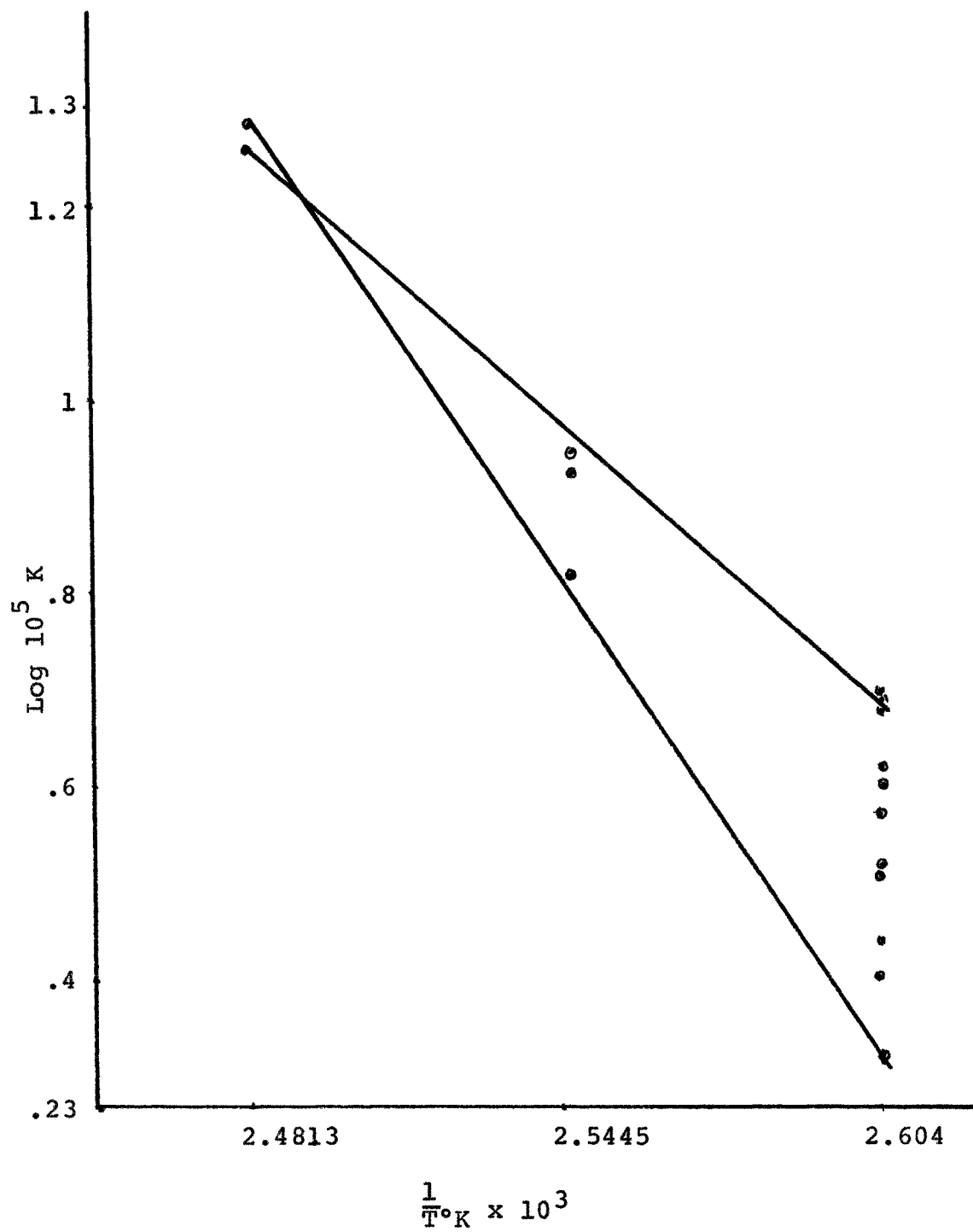


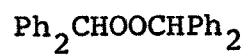
IR SPECTRUM - PRODUCTS OF DECOMPOSITION OF TRITYL PEROXIDE





Arrhenius Energy of Activation in C_2Cl_4





Arrhenius Energy of Activation in Toluene

