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A STUDY OF THE REACTIONS OF TRICHLOROMETHYL RADICALS WITH ALKANES

Abstract of PhD Thesis by Ian A. Matheson BSc

The reactions between trichloromethyl radicals and alkanes were examined by product analysis from gas phase ultraviolet photolyses at temperatures up to 271°C. The results were used to determine the mechanisms involved, and to estimate Arrhenius parameters for several of the radical transfer and termination reactions.

In section 1 CCl_2Br was used as the source of trichloromethyl radicals with cyclohexane as the alkane. It was shown that hydrogen abstraction from cyclohexane by CCl_3 radicals was not the only source of CHCl_2 ; although only trace quantities of HBr were present, the hydrogen atom is so easily abstracted that significant quantities of CHCl_2 arose from this route, precluding an estimation of the Arrhenius parameters for H abstraction from cyclohexane.

In section 2 an analogous system was studied using propane in place of cyclohexane. Results were similar to those observed in section 1. The effect of HBr on the system was studied by addition of traces of HBr to the photolyses. The rates of hydrogen abstraction by CCl_3 radicals at 182°C were $10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ (ex propane) and $1.4 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ (ex hydrogen bromide). The experimental data were compared with computer simulations for runs at various temperatures (no added HBr) and for runs at 182°C with several levels of added HBr . Good agreement was obtained when $A = 2.75 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ and $E = 4.25 \text{ kcal mol}^{-1}$ for hydrogen abstraction from HBr by CCl_3 .

In section 3 the CCl_4 /propane system was examined. k_d/k_c for CCl_3 and isopropyl radicals was estimated as 0.45. The rate of abstraction of hydrogen atoms from HCl by CCl_3 radicals was not significant. Rates of hydrogen abstraction from propane by CCl_3 and chlorine abstraction from CCl_4 by isopropyl radicals agree with results from analogous systems by other workers. However a secondary initiation step (yielding dichlorocarbene) rendered the calculation of Arrhenius parameters impossible.

Sections 4 and 5 describe the CCl_4 /cyclopentane system initiated by photolysis of CCl_4 and azocyclopentane respectively. The former study yielded problems analogous to those from section 3. The latter study exhibited none of the problems caused by HBr or CCl_2 in earlier sections and Arrhenius parameters were estimated for H abstraction from cyclopentane by CCl_3 and Cl abstraction from CCl_4 by cyclopentyl. These values were in good agreement with related studies by other workers. The combination rates were calculated for cyclopentyl radicals with themselves ($\log k = 8.13 \text{ l mol}^{-1} \text{ s}^{-1}$) and with CCl_3 ($\log k = 9.12 \text{ l mol}^{-1} \text{ s}^{-1}$). k_d/k_c for cyclopentyl radicals was measured as 1.40.

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A STUDY OF THE

REACTIONS OF TRICHLOROMETHYL RADICALS WITH ALKANES

RESEARCH TRAINING

The candidate entered the University of St. Andrews in October 1968 and graduated from the Faculty of Science with Second Class Honours (Division I) in Chemistry in July 1972.

The work described in this thesis was performed in the Chemistry Department, The University of St. Andrews between October 1972 and September 1975 under the supervision of Professor Lord Tedder and Dr. H.W. Sidebottom.

DECLARATION

I hereby declare that the following Thesis is a record of the results of experiments performed by me, and further that the Thesis is my own composition and has not previously been submitted for a higher degree.

IAN A. MATHESON

CERTIFICATE

I certify that IAN ALASTAIR MATHESON, B.Sc., has spent twelve terms at research work under my direction and that he has fulfilled the conditions of Ordinance No. 12 and Resolution of the University Court, 1967, No. 1 so that he is qualified to submit the following Thesis for the Degree of Doctor of Philosophy.

Professor Lord Tedder

ACKNOWLEDGEMENTS

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I would also like to thank the Chemistry Department of the University of St. Andrews for providing both the financial support and the research facilities for the pursuance of this work.

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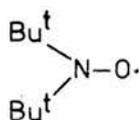
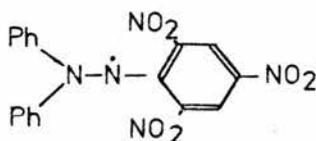
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GENERAL INTRODUCTION

A species possessing one or more unpaired electrons is called a radical. The simplest radicals are the odd electron monoatomic species such as halogen atoms and alkali metal atoms. e.g. F., Cl., Na., K. Odd electron transition metal ions such as Cu^{2+} and Fe^{3+} could also be considered to be radicals.

Unpaired electrons can also exist in polyatomic species where the electron can be located on an atom such as carbon, silicon or oxygen e.g. $\dot{\text{C}}\text{H}_3$, $\dot{\text{C}}\text{H}_2\text{Cl}$, $\dot{\text{S}}\text{iCl}_3$, $\text{C}_2\text{H}_5\dot{\text{O}}$.

The above are all examples of reactive radical species; however some radical species are considerably more stable, among the more well known resonance stabilised radicals being di-*t*-butylnitroxide and diphenylpicrylhydrazyl (DPPH).

di-*t*-butylnitroxide

diphenylpicrylhydrazyl

Some stable molecules are odd electron species e.g. NO, NO_2 and can therefore be classified as radicals. The ground state of the oxygen molecule has an electronic configuration in which two electrons are unpaired and have parallel spins (triplet state). The molecule exists therefore as a diradical.

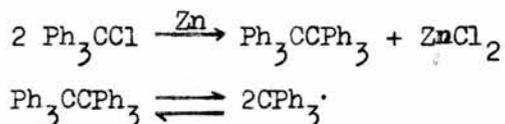
In the 1850's Wurtz reacted alkyl iodides with sodium metal to yield sodium iodide and the alkyl radicals.



However, Wurtz did not detect the free radicals as their dimerisation produced ethane and butane, the empirical formulae for which were reported as CH_3 and C_2H_5 . Shortly afterwards Couper and Kekule showed organic compounds graphically and the

valence of carbon was shown to be four in all cases studied.

There was some scepticism, therefore, when in 1900 Gomberg¹ produced the stable triphenylmethyl radical.

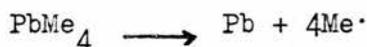


Reports of other free radicals were quick to follow², important discoveries being those of the radical mechanisms for styrene polymerisation in 1920³, and for the abnormal addition of HBr to alkenes in the 1930's^{4,5}. By the 1930's radical mechanisms had been used to explain many hitherto unexplained reaction systems and the study of radical reactions became an important sector of organic chemistry.

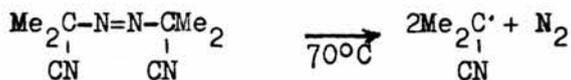
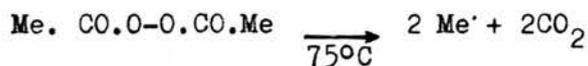
There are four main methods for the preparation of free radicals:-

- (a) Thermolysis Reactions
- (b) High Energy Radiation
- (c) Redox Reactions
- (d) Photolysis Reactions

Thermolysis involves rupturing a bond with thermal energy to produce radicals as fragments. Paneth and Hofeditz⁶ heated tetramethyl lead to obtain methyl radicals and metallic lead.

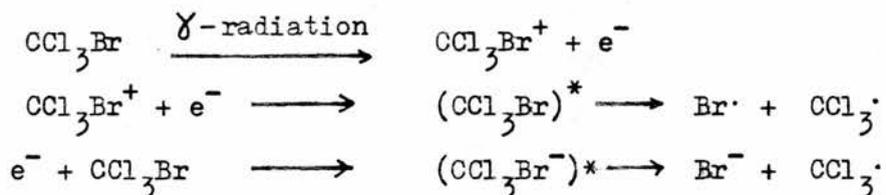


Although free radicals can be produced by the thermal decomposition of a large number of organic compounds⁷, kinetic data are most easily obtained from thermolysis systems wherein very high temperatures are not required e.g. thermolysis of peroxides and azo compounds such as diacetylperoxide⁸ or azobisisobutyronitrile^{9,10}.



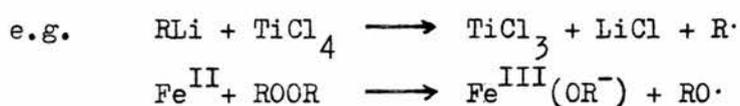
Such systems are preferred for industrial scale radical initiated processes such as polymerisation of vinyl chloride.

The most common high energy radiation used is γ -radiation, generally from a Co^{60} source. The mechanism of radical formation is:-



Initiations with X-rays or high energy electrons (ex. Van de Graaff generator) proceed with a mechanism similar to that described above.

Redox-type radical formation reactions proceed by electron transfer systems wherein the oxidation state of one species (usually a metal such as titanium or iron¹²) changes in the process.

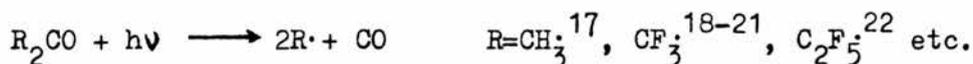


In photolysis reactions the radicals are formed as a result of bond fission using a light source (generally ultraviolet) to provide the necessary energy. This is the method used to produce the radicals in the systems described in this thesis.

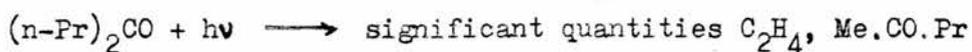
One of the simplest sources of radicals is the photolysis of a halogen molecule as employed by Dickinson¹³ ($\text{Cl}_2 + \text{C}_2\text{H}_4$) or Whittle¹⁴ ($\text{Br}_2 + \text{CF}_3\text{H}$).

Analogous to the thermolysis reaction of Paneth and Hofeditz⁶ described earlier, metal-carbon bonds can be broken photolytically to yield radicals using compounds such as $\text{Hg}(\text{CF}_3)_2$ ¹⁵ or $\text{Hg}(\text{CCl}_3)_2$ ¹⁶.

Ketones are commonly used as precursors for short chain alkyl or haloalkyl radicals:-



The CO can be measured to determine initiation rate. Higher ketones are not such good sources of alkyl radicals as R· and CO are not the only primary products.



As this additional reaction scheme is less significant with branched alkyl ketones, it has been suggested²³ that this alternative decomposition route is the result of formation of "hot" (i.e. vibrationally excited) species.

Another useful source of alkyl radicals is from the photolysis of azoalkanes:-



This route is described in more detail in Section 5 of this thesis, where azocyclopentane is used as a precursor for cyclopentyl radicals. Azoalkanes are not readily available and it has been reported²³ that in some systems the reactivity of the nitrogen double bond has posed problems. For these reasons the volume of work on azoalkane photolysis is somewhat limited.

The most common photolytic source of free radicals is from the fission of a carbon-halogen bond as in $\text{CF}_3\text{-Cl}$ ²⁴ or $\text{CH}_3\text{-I}$ ^{25,26}. The photolysis of $\text{CCl}_3\text{-Br}$ is discussed in Sections 1 and 2 of this thesis and the photolysis of $\text{CCl}_3\text{-Cl}$ in sections 3 and 4.

The most common methods for forming free radicals have been discussed in the foregoing paragraphs. The radicals produced are very reactive species and will rapidly participate in subsequent reactions. These reactions may yield yet another free radical species or may produce only stable molecular species. There are four main categories of reaction which will yield further radical species, viz.

- (a) Transfer Reactions
- (b) Addition Reactions
- (c) Rearrangements
- (d) Decompositions

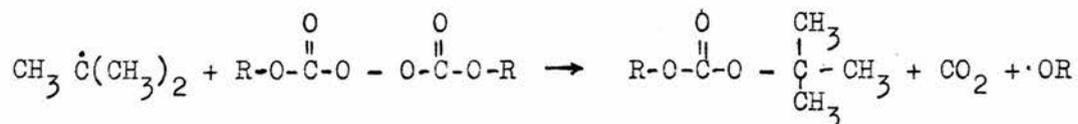
and there are two main categories of reaction which produce molecular species only

- (a) Radical Combinations
- (b) Radical Disproportionations

Radical transfer reactions can also be considered as displacement or abstraction reactions and take the general form-

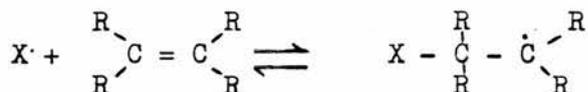


The most commonly abstracted species are hydrogen or halogen atoms but abstraction of a larger group can take place as in the following reaction²⁷ in which a carbonate radical is abstracted, followed by a decomposition reaction.



Hendry et al²⁸ have recently published a review of rate data calculated for the abstraction of a hydrogen atom in liquid phase by chlorine, alkyl, trichloromethyl, alkoxy and alkylperoxy radicals, and show that all these species will readily abstract a hydrogen atom.

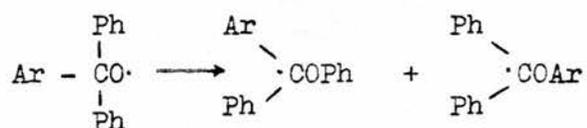
Because the unpaired electron on a free radical represents an electron deficient site, reactions in which a radical reacts with a double or triple bond are very common.



Kerr and Trotman-Dickenson²³ have shown that the reaction rates for addition of ethyl radicals to many alkenes, and of addition of many alkyl radicals to ethylene are very similar.

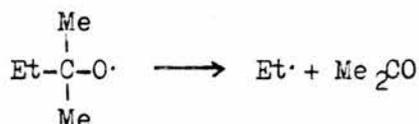
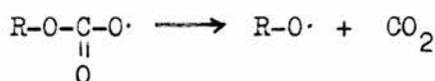
A similar reaction takes place when other multiple bonds are present. Radicals will add to acetylenes^{23,29}, aromatics²³ and carbonyls²³.

Rearrangements involving a 1,2-shift of a group or an atom are quite common in reactions of cationic intermediates. Although such rearrangements also occur in radical reactions they are much less common. In the system-



migrations of the aryl group have been reported for Ar=p-tolyl³⁰, β -naphthyl³⁰ and phenyl³¹. Similar rearrangements also take place where the migrating species is a halogen atom³², acyl group³³ etc. to yield a product of greater stability than the reactant.

The final group of radical reactions yielding radical products are decomposition reactions in which a radical generally decomposes to yield a more stable radical and a molecular species as in the decomposition of carbonate radicals²⁷ or tertiary alkoxy radicals²³.



Radical-radical reactions in which only molecular species are formed are very important as almost all absolute values for rate parameters of transfer reactions are measured relative to these

radical termination reactions. Absolute values have been obtained for radicals such as Cl and Br but the rate constants for combination of alkyl radicals have posed more problems. The combinations of methyl and halogenated methyl radicals have attracted the most attention and Table 1 shows the wide spread of results obtained by the many workers in the field.

TABLE 1

Radical Combination Rates for CX₃ Species

Radical	$\log_{10} k_c (l. mol^{-1} s^{-1})$	Reference
CH ₃	8.1	34
	9.0	35
	10.3	36
	10.4	37
CCl ₃	8.8	38
	9.6	39
	9.7	40
	9.9	41
	10.9	42
CF ₃	10.4(127°C)	43

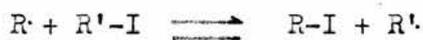
Hoh and coworkers⁴⁴ have proposed that the methyl radical is almost tetrahedral and Sieger and Calvert²¹ consequently proposed that combinations of methyl and higher alkyl radicals do not involve much structural rearrangement. It is for this reason that the rates of radical combinations are temperature independent i.e. they have zero activation energy. The exception is the trifluoromethyl radical

which is planar²¹. Hiatt and Benson⁴⁵ calculated a value of 0 ± 0.2 kcal mol⁻¹ for the activation energy for combination of ethyl radicals, and Walton⁴⁶ has pursued theoretical studies of zero activation energy radical combinations.

Dodd and Steacie⁴⁷ calculated that the combination rate of methyl radicals at 100 torr gas pressure was ten times the rate at 0.3 torr, and Brinton and Steacie⁴⁸ showed the pressure sensitivity of the ethyl radical combination rate was much less significant.

It was formerly thought²³ that the combination rate for ethyl and all higher alkyl radicals was more or less equal to 10^{11} l.mol⁻¹s⁻¹. However, more recent studies indicate that the radical recombination rates of many alkyl species are considerably lower than this value.

Hiatt and Benson⁴⁹ found that, for a pair of alkyl radicals of similar R-I bond energy, the reaction



could be used to provide a buffer system for radicals R and R'. By extension of this system the combination rates of several radicals have been estimated relative to that of methyl radicals. Table 2 shows the results of several workers for combination rates of alkyl radicals.

In this thesis several chain reactions are examined in which alkyl radicals are formed by abstraction of a hydrogen atom from the corresponding alkane by the trichloromethyl radical CCl₃. By variation of the alkane to yield alkyl radicals with different combination rates, and by variation of the trichloromethyl radical initiation source the mechanisms of each system have been deduced from product analysis from photolyses over a range of temperatures. Arrhenius parameters have been calculated for several of the reactions studied and relative rates of combination and disproportionation estimated for several radical-radical

TABLE 2Alkyl Radical Combination Rates

Radical	$\log_{10} k_c (l.mol^{-1} s^{-1})$	Reference
Ethyl	9.6	50
Isopropyl	8.6	50
Tert-butyl	5.6	51
Tert-butyl	9.6	34
Tert-butyl	7.5 — 10	52
Cyclohexyl	7	53

termination reactions. In the second section the results obtained for the photolysis of bromotrichloromethane in the presence of propane and, in some cases added hydrogen bromide, were used to simulate the system using a computer programme in which Arrhenius parameters were optimised to yield results similar to the experimental data.

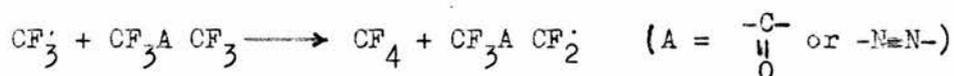
In the final section azocyclopentane was used as the radical initiation source and several additional experiments were carried out to study the photolysis of azocyclopentane alone.

SECTION 1

The Photolysis of Bromotrichloromethane With Cyclohexane

INTRODUCTION

Of the organic free radicals studied to date the most intensively investigated have been the methyl and halogenomethyl radicals. Of the latter category the trifluoromethyl radical has proved the most convenient to study as "clean" radical sources are most readily available. Trifluoromethyl radicals will not abstract a fluorine atom from trifluoromethyl groups on the radical initiating species^{15,54}.



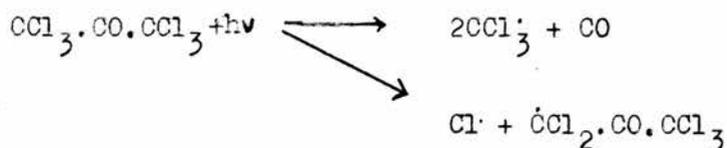
Some problems however may be encountered through addition of CF_3 radicals to the double bond of the carbonyl⁵⁵ or azo group^{56,57}.

Other sources of trifluoromethyl radicals have included photolysis of trifluoroacetaldehyde⁵⁸, trifluoroacetone²¹ and high temperature pyrolysis of hexafluoroethane⁵⁹.

Because of the different structure of the trichloromethyl and trifluoromethyl radicals^{10,21,44} and the large difference in polarity of the carbon-halogen bonds¹⁵, the chemistry of the CCl_3 radical varies significantly from that reported for the CF_3 radical.

One major hurdle has proved to be the difficulty in obtaining a "clean" source of trichloromethyl radicals without introducing other reactive chemical species which will disrupt kinetic calculations.

Gunning et al⁶⁰ obtained trichloromethyl radicals from the photolysis of hexachloroacetone. However, the existence of a secondary initiation step introduced chlorine atoms which are more reactive than the trichloromethyl radical itself.



Bis(trichloromethyl) mercury has been photolysed¹⁶ in both liquid phase and gas phase to yield trichloromethyl radicals but the involatility of the radical precursor and the presence of mercury in the reaction products render it rather unsuitable for many applications.

Photolysis of hexachloroethane will yield trichloromethyl radicals^{24,61} but the involatility of the C_2Cl_6 , the readiness with which the CCl_3 radicals will recombine and the probability of subsequent reactions between CCl_3 and C_2Cl_6 cause this also to be an unsatisfactory source of CCl_3 radicals. Pyrolysis of C_2Cl_6 ³⁰ requires temperatures of 350-400°C, too high for most kinetic investigations.

Trichloromethyl radicals have also been formed by gamma radiolysis of chloroform⁶² and carbon tetrachloride⁶³.

Carbon tetrachloride has been used by many workers as a source of trichloromethyl radicals by both radiolysis and photolysis but in each case reactive chlorine atoms are formed. Carbon tetrachloride initiated systems are described in more detail in Sections 3 and 4 of this thesis.

Analogous to carbon tetrachloride photolysis is the photolysis of bromotrichloromethane. In an early study Kharasch⁶⁴ described CCl_3Br as a preferred initiator to CCl_4 because:-

- (a) higher yields are obtained
- (b) CCl_3Br adds to allyl chloride and oct-2-ene; CCl_4 will not
- (c) CCl_3Br does not lead to polymerisation in styrene
- (d) CCl_3-Br bond weaker than CCl_3-Cl , hence easier initiation

The bromine atom is more easily abstracted⁶⁵ by other radicals, so longer chain lengths are obtained in chain reactions. In the present study this advantage was important. A further advantage

of CCl_3Br is that the bromine radical formed is less reactive than the CCl_3 radical and should "interfere" with kinetic studies to a lesser degree than chlorine radicals.

Poyer⁶⁶ et al have showed that trichloromethyl radicals can be formed from CCl_4 and CCl_3Br in biological systems by trapping the radicals with phenyl-tert-butyl nitron. Another trap which has proved useful for detecting CCl_3 radicals is $(\text{CF}_3)_3\text{CNO}$ ⁶⁷.

It was recently shown^{68,69} that the rate of photolytic cleavage of CCl_3Br is temperature dependent. Bromotrichloromethane was left in the dark for 18 hours at 195°C and no decomposition products were detected. At 205°C traces of bromine and hexachloroethane were detected. Photolysis carried out at 280°C yielded large quantities of tetrachloroethylene, indicating that the reaction



had probably taken place. All runs in this section were carried out at temperatures below 200°C, to prevent possible production of dichlorocarbene and also to prevent decomposition of cyclohexyl bromide, one of the products.

The earliest uses of CCl_3Br as a radical source were in studies of the trichloromethyl radical with double bonds. There are consequently many reports of reactions with olefins⁷⁰⁻⁷³ and halo-olefins⁷⁴⁻⁷⁵. CCl_3Br has also been used to telomerise vinyl acetate⁷⁶ and methyl methacrylate⁷⁷.

Although the trichloromethyl radical participates less in transfer reactions than the methyl or trifluoromethyl radicals^{78,79}, CCl_3Br has been used as a radical source in studies of transfer reactions with both aliphatic^{17,78,79} and aromatic⁸⁰⁻⁸² hydrocarbons.

The hydrocarbon which has been most studied in reactions with the trichloromethyl radical is cyclohexane. Table 1.1 shows that the heat combustion per methylene group is lowest for cyclohexane among the cycloalkanes. This indicates that the heat of

TABLE 1.1

Heat of Combustion (ΔH_c) per Methylene
Group For the Cycloalkanes, $(CH_2)_n$

n	ΔH_c (kcal mol ⁻¹)	Reference	n	ΔH_c (kcal mol ⁻¹)	Reference
3	-166.5	83	7	-158.2	83
4	-163.8	83	8	-158.5	83
5	-158.7	83	9	-158.7	83
6	-157.5	83	9	-158.5	84

formation of cyclohexane is lowest, hence the bonding is strongest and the strain in the ring structure is at a minimum. As all hydrogen atoms in cyclohexane are equivalent, there being no primary hydrogen atoms, and as the ring strain is minimal, there should be less complicating factors in the CCl_3 /cyclohexane system than in any other CCl_3 /alkane system.

Stone and Dyne⁸⁵ studied the γ -radiolysis of cyclohexane in dilute solutions of carbon tetrachloride and chloroform; Currie and coworkers⁵³ photolysed azocyclohexane in the presence of CCl_4 and cyclohexane. However, other workers in the CCl_3 /cyclohexane field

have obtained CCl_3 instead of $\text{c-C}_6\text{H}_{11}$ as the initiating radical source by γ -radiolysis⁸⁶⁻⁹⁰ or photolysis^{39,53} of carbon tetrachloride.

Earlier in this introduction several reasons were quoted for preferring CCl_3Br to CCl_4 as a source of trichloromethyl radicals, one of the most important being that the bromine atoms formed from CCl_3Br are considerably less reactive than the chlorine atoms from CCl_4 . To study the $\text{CCl}_3\text{X}/\text{cyclohexane}$ system further, Section 1 describes the photolysis of bromotrichloromethane in the presence of cyclohexane over the temperature range $37\text{-}197^\circ\text{C}$.

SECTION 1

The Photolysis of Bromotrichloromethane With Cyclohexane

EXPERIMENTAL

1.1 REACTANTS

(a) Cyclohexane:- was "Fisons" spectrograde reagent, and was tested and found to be chromatographically pure.

(b) Bromotrichloromethane:- was supplied by Schuchardt-München with a stated purity of 90% w/w. It was purified on a Pye 105 preparative chromatograph using a 30ft. glass column packed with 20% Silicone Oil on 60 - 100 mesh "Embacel". Separation was effected with a nitrogen pressure (carrier gas) of 13 lb.in^{-2} , hydrogen pressure of 15 lb.in^{-2} and an oxygen pressure of 53 lb.in^{-2} , at a column temperature of 108°C . Samples of 250 μl were injected and CCl_3Br was obtained with a purity greater than 99.5%. Once prepared, the CCl_3Br was stored in the dark in a deep freeze in a tube that could be attached to the vacuum line wherever needed.

1.2 APPARATUS

The apparatus used was a conventional mercury-free vacuum system made of "Pyrex" glass (Fig.1.1). Vacuum was obtained using an Edwards High Vacuum (model EDM 2) rotary pump with a "Speedivac" silicone oil diffusion pump (model 1SC 50B). Originally, all taps were ground glass type using silicone vacuum grease for lubrication but these were later replaced by greaseless taps to counteract any effects caused by dissolution of the reactants in the grease. The line had three storage bulbs (A, B and C) of volume 216 ml, 1224 ml and 2568 ml. respectively. The volume of the manifold + vacuum gauge was 888 ml. All volumes were calculated by using Boyles Law ($P_1V_1=P_2V_2$) with the reaction vessel volume of 298.8 ml being taken as a basis for calculation. When filled with distilled water the reaction vessel contained 298.25 g water at 22°C (volume of $1\text{gH}_2\text{O}$ at $22^{\circ}\text{C} = 1.002 \text{ ml}^{91}$).

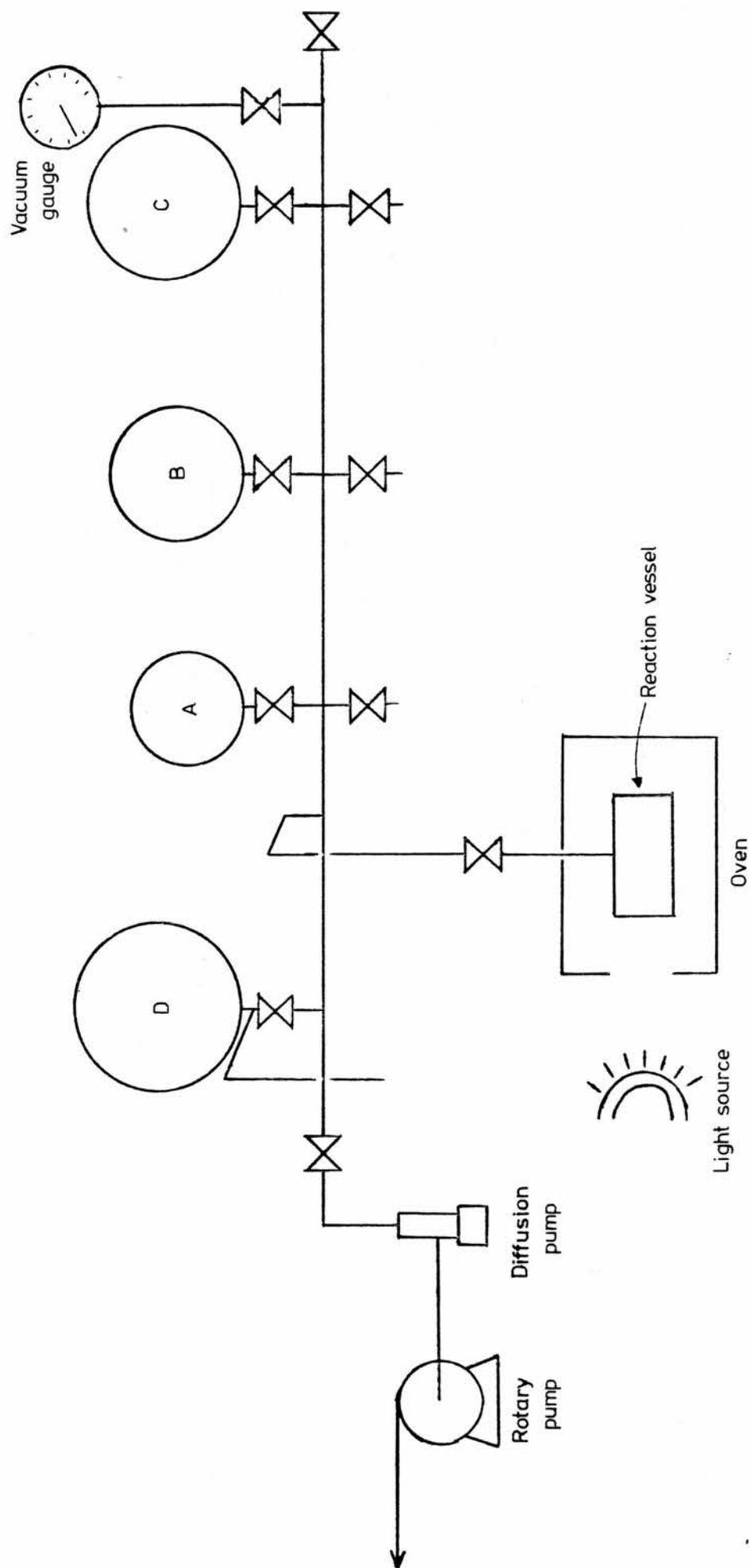


FIGURE 1.1 Diagram of Pyrex Glass Vacuum System.

The reaction vessel was made of "Pyrex" glass, was spherical in shape and was connected to the vacuum line by a capillary tube to minimise the volume of reactants outwith the oven. Pressures were measured using a Speedivac barometrically compensated capsule dial guage (model CG3) with a range of 0-100 torr. The reaction vessel was heated by a furnace, the temperature of which was varied using a 0-250V "Variac" transformer. The temperature, as measured by a mercury in glass thermometer, was constant throughout the furnace volume and constant to within $\pm 3^{\circ}\text{C}$. for any one experiment. Illumination was by a Hanovia UVS 220 medium pressure arc lamp. The light passed through a cylindrical entrance on one side of the furnace to strike the centre of the reaction vessel.

1.3 EXPERIMENTAL PROCEDURE

Cyclohexane was stored in a tube on the vacuum line. The bromotrichloromethane was stored in the deep freeze in a tube which could also be attached to the vacuum line when required. Before use each compound in turn was "degassed". This procedure entailed removing all dissolved air from the compound by allowing the compound, frozen with liquid nitrogen, to warm to room temperature, thus boiling out dissolved gas. The compound was then frozen down again and the tap to the tube opened to the main line and the pumps. The tap was closed again and the process repeated several times for each compound.

Finally, the "degassed" cyclohexane was allowed to expand into the vacuum line manifold and into one of the bulbs (bulb A) until the required pressure was reached (60 torr). The bulb tap was then closed and the remaining cyclohexane in the line redistilled back by cooling the storage tube with liquid nitrogen. The measured amount of cyclohexane was then distilled from bulb A to the evacuated reaction

vessel by cooling the reaction vessel with liquid nitrogen and allowing the gas to be distilled from bulb A. The reaction vessel was then closed and a similar procedure adopted for the bromotrichloromethane, whereby 20 torr was charged to bulb A and thence to the reaction vessel. The preheated furnace was then raised into position and the temperature allowed to stabilise. An opaque shutter was used to cover the aperture in the side of the oven until the reaction was due to commence. The lamp was switched on and allowed to warm up for about 15 minutes and, with the lamp at full power and the oven temperature stable, the shutter was lifted and reaction started. On completion of the reaction the products were distilled to a small tube on the main line. The tube was then capped and stored in liquid nitrogen. Samples for chromatographic analysis were withdrawn directly from the tube. When greaseless taps were introduced on the line the small tube was capped with a rubber septum cap through which a syringe could be inserted for sample removal. The products were then stored in acetone/solid carbon dioxide to prevent air from liquefying in the tube.

1.4 ANALYSIS

A Griffin and George D6 gas chromatograph was used to analyse the products in all kinetic runs. A Honeywell-Brown potentiometric chart recorder (1mv) with an attenuation range of "X1" to "X100" was used to record the peaks. The detector in the gas chromatograph was a gas density balance for which the relationship $q = KAM/(M-m)$ holds (q = sample weight, K = constant, A = area of peak, M = molecular weight of sample, m = molecular weight of carrier gas, in this case nitrogen). Thus the concentration of any material, given by q/M is readily obtainable, being equal to $KA/M-m$.

The stationary phase used was 15 wt% silicone oil supported on 60 - 100 mesh "Embacel" packed in a 6 ft. x $\frac{3}{8}$ in. column.

A column temperature of 100°C and nitrogen carrier gas flow rate of 35 ml min⁻¹ (12.5 lb.in⁻²) were employed and good separation was obtained (Fig.1.2). Samples were injected using 6 µl stainless steel capillary needles.

Peak areas were measured using either a Honeywell Linear Amplifier and Precision Integrator or a Du Pont 310 Curve Resolver. The former was found to yield more consistent results with the tall narrow peaks of volatile compounds but the latter yielded more consistent areas for the broad peaks of the heavier compounds.

Four or five analyses were made of each reaction mixture and an average concentration for each compound, relative to one of the reagents was obtained.

1.5 IDENTIFICATION OF PRODUCTS

The typical chromatogram of the reaction products showed six peaks, as shown in Fig 1.2. Two non-kinetic (high conversion) runs were carried out (at 70°C and 172°C) and in each case all products were visible. Bromotrichloromethane, chloroform, cyclohexane and hexachloroethane were identified by comparison of retention times with those for authentic samples. G/C coupled mass spectrometry was employed to identify the other peaks. Bromocyclohexane was identified in this manner; however the magnitude of the first peak was insufficient to obtain a reasonable mass spectrogram. It was deduced from the mechanism that this peak was either hydrogen bromide or cyclohexene.

1.6 RESULTS

It was observed during the first few runs that there was a build-up of a dark coloured deposit on the side of the reaction vessel facing

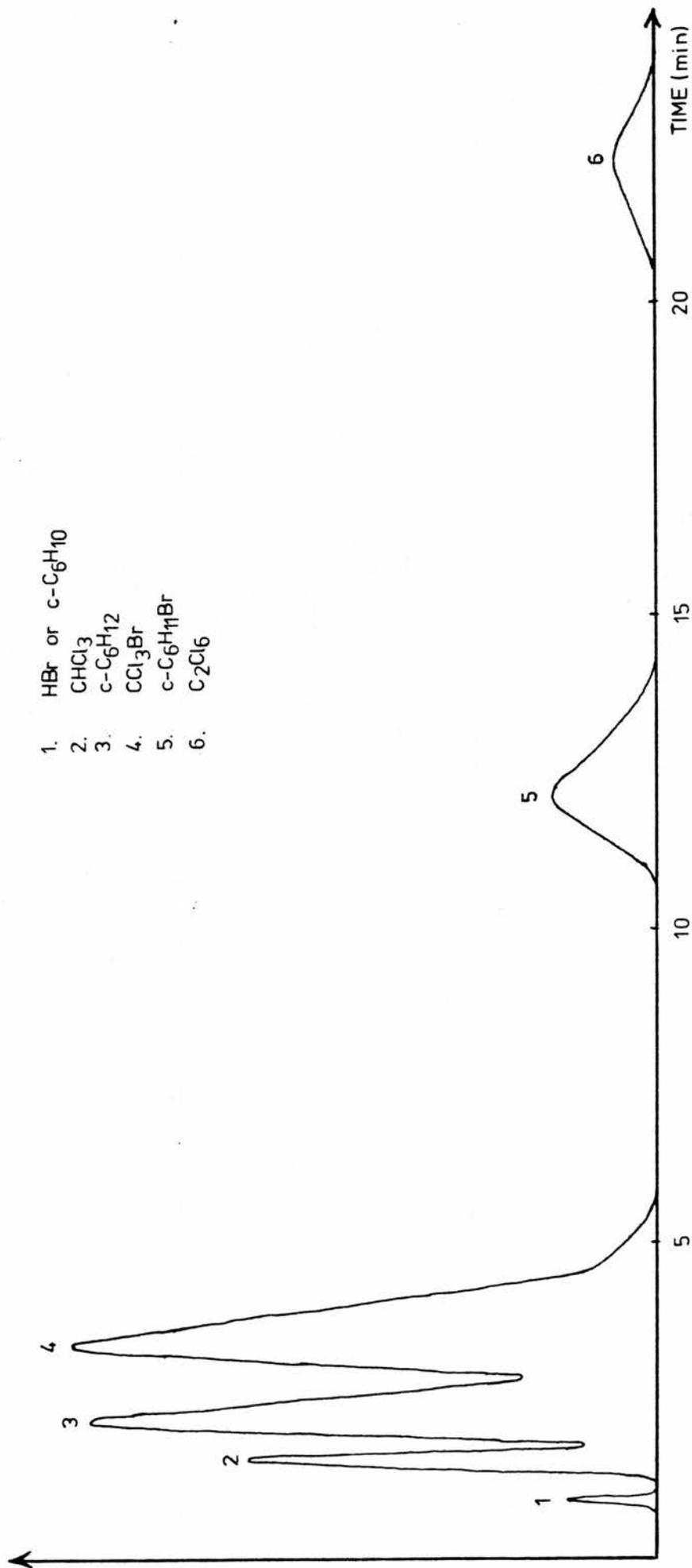


FIGURE 1.2 G1c Trace of Products from $\text{CCl}_3\text{Br} + c\text{-C}_6\text{H}_{12}$ Photolysis.

the light. Lest this act as a filter and reduce the intensity of the light within the reaction vessel, the reaction vessel was thoroughly cleaned after each run with nitric acid, followed by cleansing with Decon 90 detergent for several hours in an ultrasonic bath heated to about 80°C. Finally, it was rinsed several times with distilled water and dried. The rates of formation of products from the first kinetic series are shown in Table 1.2.

After these runs it was observed that the grease from the taps on the line had become sticky and in some places had started to run. A sample of bromotrichloromethane was mixed with a spot of vacuum grease and was seen to dissolve the grease. In case the kinetic runs had been affected by dissolution of reactants or products in the grease, the taps were replaced by greaseless taps and another series of runs were carried out. The results of this second kinetic series are shown in Table 1.3.

TABLE 1.2

Photolysis of Trichlorobromomethane in the Presence of
Cyclohexane (before installation of greaseless taps)

Temp(°C)	1000/T(°K)	Time(s)	R_{CHCl_3} (mol.l ⁻¹ s ⁻¹)	$R_{\text{c-C}_6\text{H}_{11}\text{Br}}$ (mol.l ⁻¹ s ⁻¹)	$R_{\text{C}_2\text{Cl}_6}$ (mol.l ⁻¹ s ⁻¹)	$\log(R_{\text{CHCl}_3} / (R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}} [\text{RH}])$
37	3.226	3000	2.670x10 ⁻⁹	1.045x10 ⁻⁸	8.860x10 ⁻¹⁰	- 1.403
42	3.175	3000	5.822x10 ⁻⁹	5.930x10 ⁻⁹	1.094x10 ⁻⁹	- 1.110
60	3.005	1800	5.166x10 ⁻⁹	6.678x10 ⁻⁹	1.265x10 ⁻⁹	- 1.193
64	2.967	2400	6.903x10 ⁻⁹	1.112x10 ⁻⁸	1.407x10 ⁻⁹	- 1.091
76	2.865	2100	7.886x10 ⁻⁹	8.567x10 ⁻⁹	1.059x10 ⁻⁹	- 0.971
93	2.732	3600	1.067x10 ⁻⁸	8.454x10 ⁻⁹	1.237x10 ⁻⁹	- 0.873
117	2.564	900	1.525x10 ⁻⁸	1.415x10 ⁻⁸	1.151x10 ⁻⁹	- 0.073
121	2.538	1200	1.842x10 ⁻⁸	2.382x10 ⁻⁸	1.517x10 ⁻⁹	- 0.681
150	2.364	720	3.805x10 ⁻⁸	6.111x10 ⁻⁸	3.594x10 ⁻⁹	- 0.553
179	2.212	1200	6.429x10 ⁻⁸	3.978x10 ⁻⁸	4.004x10 ⁻⁹	- 0.349

$$[\text{c-C}_6\text{H}_{12}]_{t=0} = 2.267 \times 10^{-3} \text{ mol. l}^{-1}$$

$$[\text{CCl}_3\text{Br}]_{t=0} = 7.557 \times 10^{-4} \text{ mol. l}^{-1}$$

A plot of $\log_{10} (R_{\text{CHCl}_3} / (R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}} [\text{c-C}_6\text{H}_{12}])$ vs $10^3/T$ (°K) yields a straight line of gradient = -0.923 ± 0.197

intercept on y-axis = 1.660 ± 0.071

TABLE 1.3

Photolysis of Trichlorobromomethane in the Presence of
Cyclohexane (after installation of greaseless taps)

Temp(°C)	1000/T(°K)	Time(s)	R _{CHCl₃} (mol.l ⁻¹ s ⁻¹)	R _{c-C₆H₁₁Br} (mol.l ⁻¹ s ⁻¹)	R _{C₂Cl₆} (mol.l ⁻¹ s ⁻¹)	log(R _{CHCl₃} / (R _{C₂Cl₆}) ^{1/2} [RH])
40	3.195	1800	3.661x10 ⁻⁹	1.074x10 ⁻⁸	5.262x10 ⁻⁹	- 1.573
121	2.538	1800	2.094x10 ⁻⁸	3.024x10 ⁻⁸	8.850x10 ⁻⁹	- 0.929
138	2.433	1800	2.232x10 ⁻⁸	2.618x10 ⁻⁸	4.269x10 ⁻⁹	- 0.743
197	2.128	1800	7.754x10 ⁻⁸	9.475x10 ⁻⁸	1.178x10 ⁻⁸	- 0.422

$$[c - C_6H_{12}]_i = 1.889 \times 10^{-3} \text{ mol. l}^{-1}$$

$$[CCl_3Br]_i = 9.447 \times 10^{-4} \text{ mol. l}^{-1}$$

A plot of $\log_{10} (R_{CHCl_3} / (R_{C_2Cl_6})^{1/2} [c - C_6H_{12}])$ vs $10^3/T(^{\circ}K)$ yields a straight line: gradient = -1.077 ± 0.139

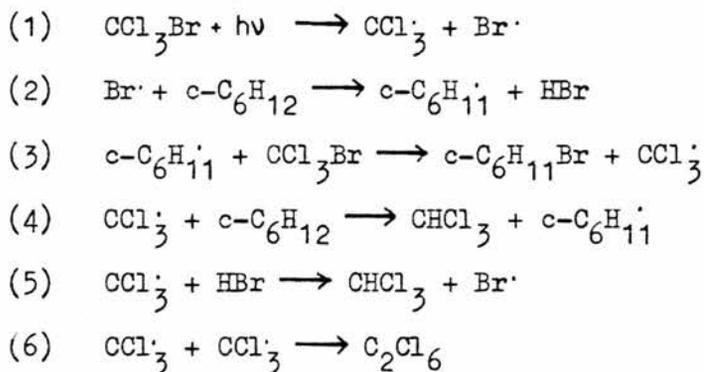
$$\text{y-axis intercept} = 1.854 \pm 0.053$$

SECTION 1

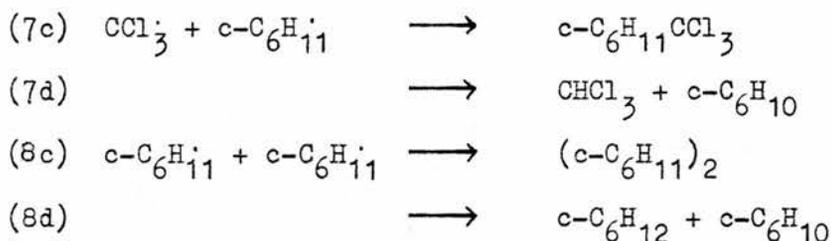
The Photolysis of Bromotrichloromethane With Cyclohexane

DISCUSSION

The results in Table 1.2 were consistent with the reaction mechanism proposed by previous workers.



Other possible steps are:



In their study of the carbon-tetrachloride/cyclohexane system in the temperature range 110°-175°C White and Kuntz³⁹ observed a peak which they tentatively identified as the cross termination product trichloromethylcyclohexane (produced by reaction 7c). They noted that this product became detectable at $\text{CCl}_4 < 7 \times 10^{-6}$ mol/cc. They did not observe any bicyclohexyl, the termination product from reaction 8c. In subsequent work on the carbon tetrachloride/cyclohexane photolysis Currie, Sidebottom and Tedder⁵³ reported that the only termination product observed over the temperature range 35-285°C was hexachloroethane, but use of azocyclohexane as initiator in the system showed presence of trichloromethylcyclohexane over their range 111-202°C. Bicyclohexyl was also observed at the upper end of this range.

In the temperature range of this study (37-179°C) hexachloroethane was the only detectable termination product. Currie, Sidebottom and Tedder concluded that disproportionation step (7d) was unimportant. The disproportionation-to-combination ratio for cyclohexyl radicals has been reported as 0.99⁵³ and 1.1 ± 0.1⁹². This precludes the possibility

of the termination steps (7) and (8) taking place to produce only disproportionation products.

Although White and Kuntz observed the cross termination product at $\text{CCl}_4 < 7 \times 10^{-6}$ mol/cc, the threshold for detectability in the bromotrichloromethane system will be lower than this. The strength of the $\text{CCl}_3\text{-Cl}$ bond was reported as 68⁹³, 72⁹⁴ and 76⁹⁵ kcal/mol. whereas that of the $\text{CCl}_3\text{-Br}$ bond was considerably lower, having been reported as only 49⁹³ kcal/mol. Thus reaction (3), the halogen abstraction by cyclohexyl radicals, will be more facile with CCl_3Br than CCl_4 . White and Kuntz argued that bicyclohexyl was not observed because reaction (3) was faster than reaction (4) and consequently the steady state concentration of cyclohexyl radicals was lower than that of trichloromethyl radicals, causing hexachloroethane to be the main, and in some cases only termination product. Currie, Sidebottom and Tedder however believed reaction (4) to be the faster and attributed the termination in C_2Cl_6 to the very low combination and cross-combination rates of the cyclohexyl radical. As the halogen abstraction step (3) is faster with CCl_3Br than with CCl_4 , the steady state concentration of cyclohexyl radicals will be lower than in the carbon tetrachloride system. As a consequence the lack of termination products in this study, even at $\text{CCl}_3\text{Br} = 7.6 \times 10^{-7}$ mol/cc. can be satisfactorily explained by modification of the argument of White and Kuntz for the carbon tetrachloride system. Any termination step involving Br can be ruled out as the relatively high concentration of cyclohexane is sufficient to remove all bromine atoms by reaction (2). As the experiments were all carried out with less than 5% conversion the cyclohexane concentration can be assumed constant throughout.

With hexachloroethane as the only termination product it can be calculated that

$$2R_{C_2Cl_6} + R_{CHCl_3} = R_{RBr} + R_{HBr}$$

and $R_{HBr} = R_{C_2Cl_6}$ where R_x = Rate of formation of x

These can be combined to give the material balance

$$R_{CHCl_3} + R_{C_2Cl_6} = R_{RBr}$$

The experimental values in Tables 1.2 and 1.3 are consistent with this equation within the bounds of experimental error. This confirms the reaction system proposed earlier.

In earlier work with bromotrichloromethane, McGrath and Tedder⁷⁹ studied hydrogen abstractions from propane, n-butane and isobutane and measured the relative rates of bromination of primary, secondary and tertiary sites. They noted reactions (3) and (4) or reactions (2), (3) and (5) as being the two possible chain-propagating systems. The first system did not involve HBr whereas in the second system the chloroform in the reaction products originated from hydrogen abstraction from HBr by CCl_3 . If the second system was the main chain propagation step, addition of HBr would only alter the magnitude of R_{CHCl_3} and $R_{C_2Cl_6}$ but not the ratio $R_{CHCl_3}/R_{C_2Cl_6}^2$. In fact this ratio was significantly altered by addition of HBr and they deduced that the second chain system did not occur to an important extent. This theory was supported by Tedder and Watson⁷⁸ in their measurement of absolute Arrhenius parameters for hydrogen abstraction from n-butane.

This being the case, then the chloroform in the reaction products originated primarily from reaction (4) and the following equations hold -

$$R_{\text{CHCl}_3} = k_4 [\text{CCl}_3] [\text{c-C}_6\text{H}_{12}]$$

and $R_{\text{C}_2\text{Cl}_6} = k_6 [\text{CCl}_3]^2$

Hence $\frac{R_{\text{CHCl}_3}}{(R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}}} = \frac{k_4 [\text{c-C}_6\text{H}_{12}]}{k_6^{\frac{1}{2}}}$

and so a graph plotting $\log \frac{R_{\text{CHCl}_3}}{(R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}} [\text{c-C}_6\text{H}_{12}]}$ versus the reciprocal of temperature should yield an intercept on the y-axis of $\log A_4 - \frac{1}{2} \log A_6$ and a gradient of $(E_4 - \frac{1}{2} E_6)/2.303 R$.

The activation energy E_6 for trichloromethyl radical combination is assumed to equal zero.⁹⁶ Melville, Robb and Tutton⁹⁷ believed E_6 to be very low and Sieger and Calvert²¹ proposed that an activation energy would only be likely in the extreme case of CF_3 combination where a structural adjustment is necessary for recombination. It is now generally accepted that most radical recombinations have zero activation energy.⁴⁵ Various values have been reported for the rate of recombination of trichloromethyl radicals^{38,39,40,41,42,98} A value of $\log A_6 = 9.7$ has been used in the calculations. The graphs are shown in Figs 1.3 and 1.4 for the systems using grease taps and greaseless taps respectively.

Both graphs are straight lines and calculations give

$$\begin{aligned} \text{Fig 1.3} \quad E_4 &= 4.22 \pm 0.90 \text{ kcal mol}^{-1} \\ \log A_4 &= 6.51 \pm 0.07 \quad \text{l mol}^{-1} \text{s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Fig 1.4} \quad E_4 &= 4.93 \pm 0.64 \text{ kcal mol}^{-1} \\ \log A_4 &= 6.70 \pm 0.05 \quad \text{l mol}^{-1} \text{s}^{-1} \end{aligned}$$

The similarity of these results indicated that although bromo-trichloromethane was slightly soluble in the vacuum grease, this had had little effect on the kinetic data.

Previous estimations of these rate parameters by White and Kuntz³⁹ and by Currie, Sidebottom and Tedder⁵³ yielded values for

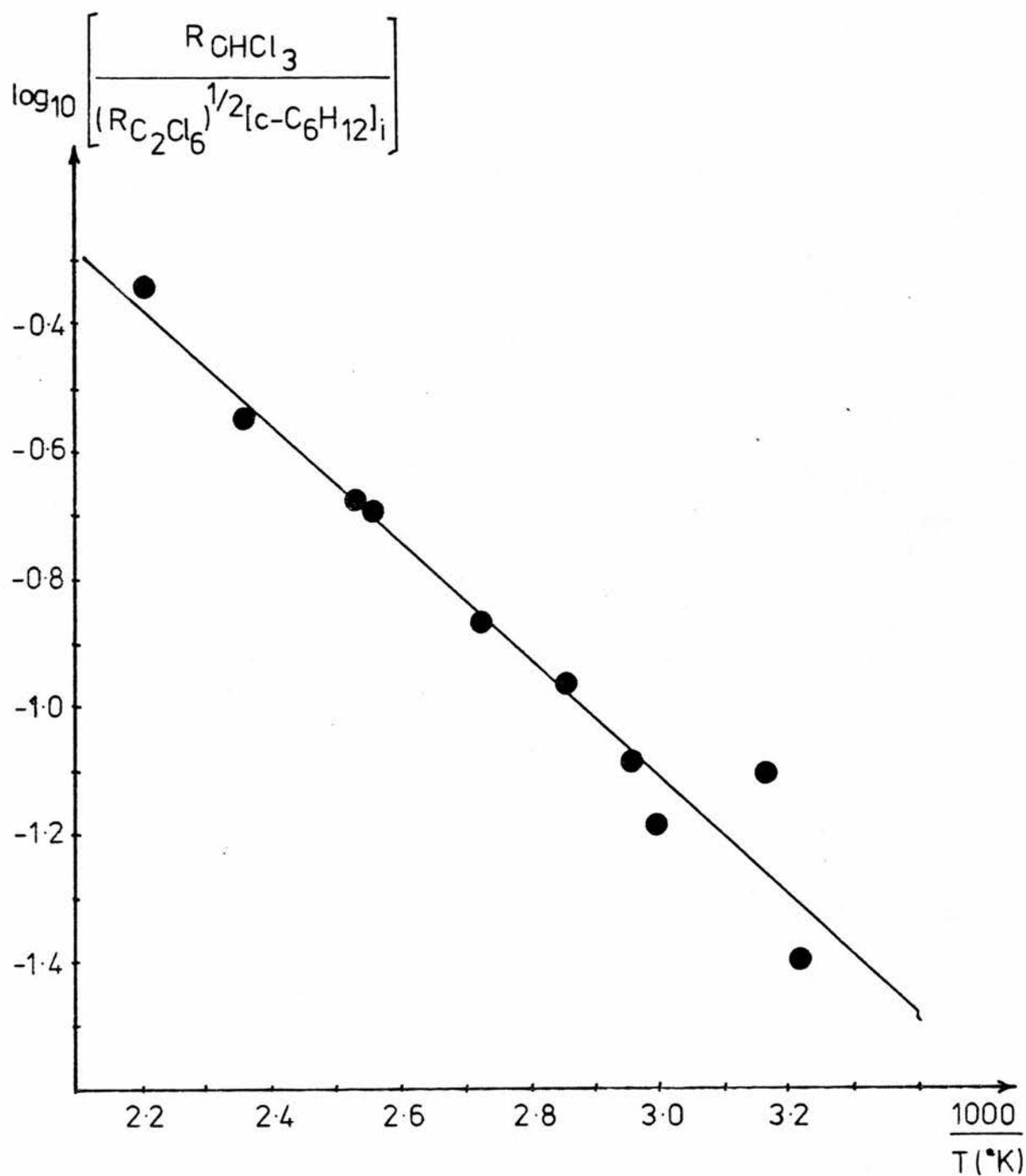


FIGURE 13 Graph of $\log_{10} \left[\frac{R_{\text{CHCl}_3}}{(\text{RC}_2\text{Cl}_6)^{1/2} [\text{c-C}_6\text{H}_{12}]_i} \right]$ versus the reciprocal of temperature for the cyclohexane - bromotrichloromethane system.

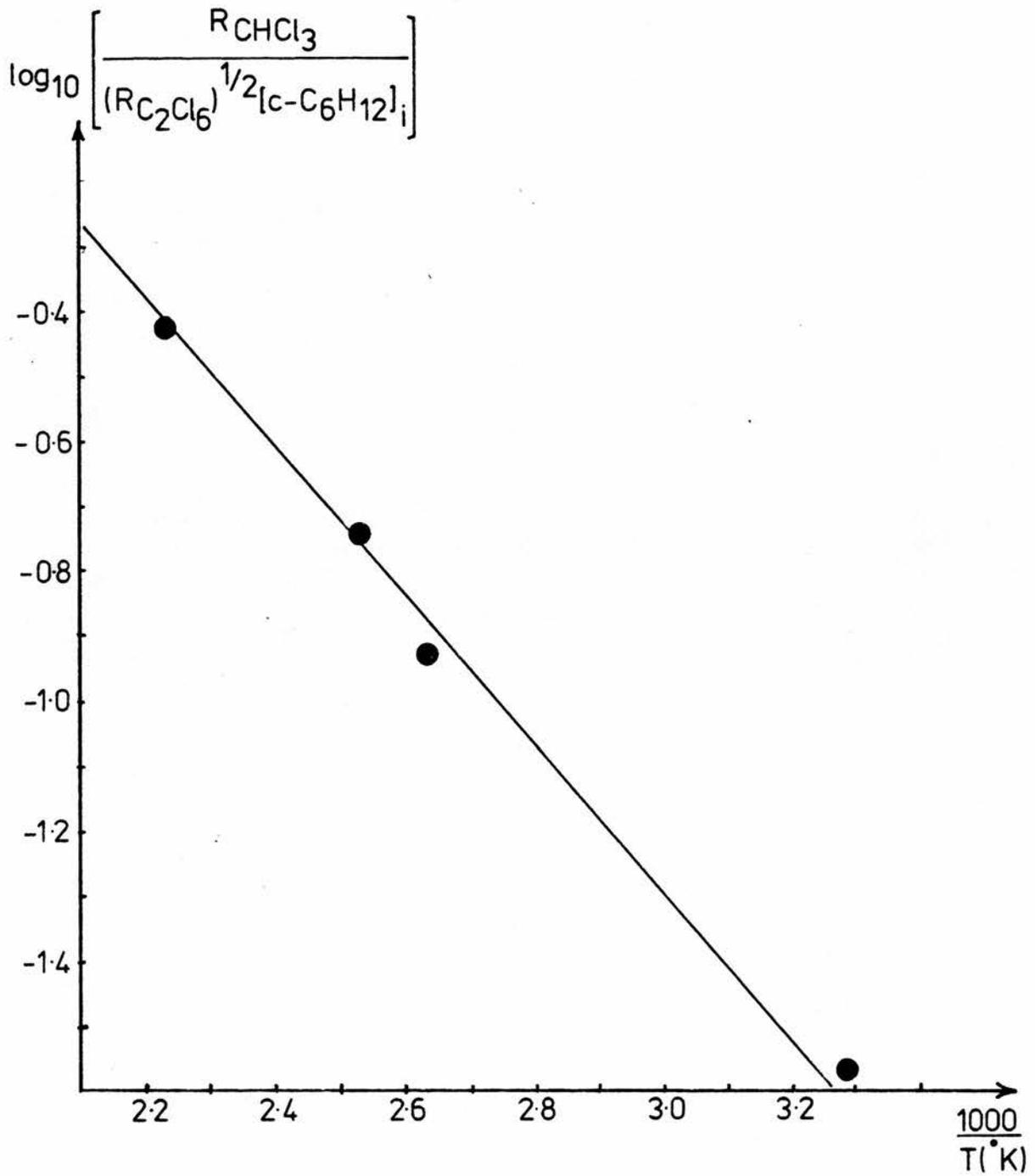


FIGURE 1.4 Graph of $\log_{10} \left[\frac{RCHCl_3}{(RC_2Cl_6)^{1/2} [c-C_6H_{12}]_i} \right]$ versus the reciprocal

of temperature for the cyclohexane-bromotrichloromethane system (after installation of greaseless taps).

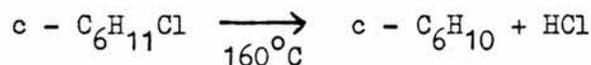
this hydrogen abstraction of $k_4 = 10^{8.79} \exp\left(-\frac{10700 \text{ cal}}{RT}\right)$ and $k_4 = 10^{8.86} \exp\left(-\frac{10000 \text{ cal}}{RT}\right)$ respectively. There is a considerable difference between these Arrhenius parameters calculated from the carbon tetrachloride system and the values obtained in this work. Indeed, the values from the present study show considerable deviation from results obtained for hydrogen abstraction from any secondary carbon sites on other alkanes by trichloromethyl radicals.⁹⁹

Calculations at $T=100^\circ\text{C}$ using the parameters of Currie and coworkers⁵³ yielded $\log k_4 = 3.01 \text{ mol}^{-1} \text{ s}^{-1}$ and the parameters from this investigation yielded $\log k_4 = 3.8 - 4.01 \text{ mol}^{-1} \text{ s}^{-1}$. Simultaneous solution of these two sets of results showed that at 344°C both series of rate parameters yielded $\log k_4 = 5.0 \text{ mol}^{-1} \text{ s}^{-1}$.

It was stated earlier that the above calculations of Arrhenius parameters were based on the assumption that all the chloroform produced in the reaction was formed through reaction (4). If, however, the abstraction rate of a hydrogen from hydrogen bromide by CCl_3 was sufficiently high, then an alternative source of chloroform would be obtained. McGrath,⁷⁹ in his assessment of chain-propagating systems, assumed the rates of abstraction from HBr and cyclohexane to be of similar order of magnitude and deduced that the greater concentration of cyclohexane would cause the HBr chain to be of no major significance. In section 1.5 (Identification of Products) of this study it was stated that a small peak was observed on the gas chromatogram which was believed to be either hydrogen bromide or cyclohexene, each of which had the same retention time under the analytical conditions employed. Hydrogen bromide would be detected more easily in a gas density balance than in a flame ionisation detector, as used in the gas-liquid chromatograph coupled mass

spectrometer. This could have been the cause of the peak being observed throughout the kinetic runs but not being detected to a sufficient extent for a confirmatory mass spectrograph to be obtained.

Currie and coworkers found that chlorocyclohexane, produced in their system started to decompose thermally at temperatures in excess of 160°C.



It would be expected that bromocyclohexane would begin to decompose at a slightly lower temperature but this would certainly not produce a detectable amount of cyclohexene at temperatures < 100°C and so in the absence of cyclohexene from reactions (7d) and (8d) the first peak was deduced to be hydrogen bromide. Huyser⁸¹ studied the bromination of various substituted toluenes by bromotrichloromethane and detected HBr among the products, formed from hydrogen abstraction by bromine atoms.

If the activation energy for hydrogen abstraction from HBr is much lower than that for abstraction from cyclohexane, then in the lower temperature range of this study a small concentration of HBr would have a large effect on the rate of production of chloroform. The chain length of the cycle involving reactions (3), (4) and (6) would be very short. Moreover, each molecule of hydrogen bromide participating in reaction (5) to yield a molecule of chloroform would be regenerated by reaction (2), the only trap present for bromine atoms apart from (-5), with the ultimate production of one molecule of bromocyclohexane by reaction (3). Thus, while the material balance discussed earlier was maintained, the rate of chloroform production would be considerably greater than by a propagating chain involving reactions (3) and (4) alone. As the temperature was increased the rates of reactions (4) and (5) would tend towards equality, the chain length of the first

propagation system would increase and the large concentration of cyclohexane compared with hydrogen bromide would render the hydrogen bromide a less significant source of chloroform. The shape of the Arrhenius plot in Figs 1.3 and 1.4 should therefore be a curve, the gradient at lowest temperatures representing the activation energy for abstraction from HBr and the gradient at highest temperatures representing the activation energy for abstraction from $c\text{-C}_6\text{H}_{12}$; experimental difficulties such as thermal decomposition of products, however, prevent the study of a temperature range sufficiently wide to illustrate this. The rate of hydrogen abstraction from hydrogen chloride has been calculated⁴¹ as $K = 10^{8.68} \exp\left(-\frac{11200 \text{ cal}}{RT}\right)$. This is slower than the reported rates of abstraction from cyclohexane and explains why valid Arrhenius plots were obtained with carbon tetrachloride despite the analogous presence of the hydrogen halide.

Complications arising in previous $\text{CCl}_3\text{Br} + \text{alkane}$ studies due to the temperature dependence^{68,69} of reaction (1) did not arise in the present calculations as the expression $R_{\text{CHCl}_3} / (R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}}$ is independent of the initiation rate. Tedder and Watson⁷⁸ calculated Arrhenius parameters using the expression $R_{\text{CHCl}_3} / R_{\text{C}_2\text{Cl}_6}$ which is initiation-dependent. The results were adjusted for the temperature dependence^{69,100} and brought into line with results of other workers.

The results from the present work, therefore, do not yield Arrhenius parameters comparable with those obtained by other workers from related systems; all the deviations, however, have been accounted for and in so doing a comprehensive picture of the reaction system and associated kinetics has been built up.

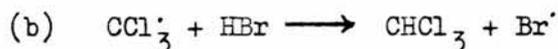
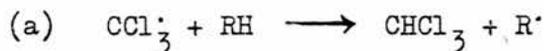
SECTION 2

The Photolysis of Bromotrichloromethane With Propane

(and Hydrogen Bromide)

INTRODUCTION

In the first section the calculation of Arrhenius parameters for the abstraction of a hydrogen atom from cyclohexane proved impossible, because the chloroform in the reaction products originated from two sources.



No such problems have been encountered in previous studies of hydrogen atom abstraction from cyclohexane by trichloromethyl radicals^{39,53,87}, as earlier data had been obtained using carbon tetrachloride as the source of trichloromethyl radicals. In the introduction to the first section the advantages of using CCl_3Br instead of CCl_4 were listed, based on the experiences of earlier workers. Section 1, however, indicates that the ease of abstraction of a hydrogen atom from HBr is so great that the small quantities of HBr present can significantly affect kinetic calculations in the non-chain region.

Many previous workers have measured the rate of abstraction of a hydrogen atom from HCl by various radical species. The corresponding hydrogen abstraction from HBr has not been so intensively investigated. Table 2.1 shows the Arrhenius parameters for hydrogen abstraction from HCl and HBr by CH_3 , CF_3 and CCl_3 radicals.

The results for abstraction by methyl radicals show little difference in the abstraction rate from HBr and HCl. However the activation energy for abstraction by trichloromethyl radicals is very much greater than that calculated for methyl or trifluoromethyl radicals. This high activation energy would explain the importance of reaction (b) in the CCl_3Br system and not in the CCl_4 system if it is found that the corresponding activation energy for abstraction from HBr was significantly lower.

TABLE 2.1

Hydrogen Abstraction From HCl and HBr

R	HX	$\log A(1 \text{ mol}^{-1} \text{ s}^{-1})$	$E(\text{kcal mol}^{-1})$	Reference
CH_3	HBr	8.95	2.9	101
CH_3	HCl	8.4	2.3	25
CH_3	HCl	-	2.5	26
CCl_3	HCl	8.65	11.3	41
CF_3	HCl	7.94	5.16	22*

*recalculated⁴¹ from the original literature value using a combination rate for CF_3 radicals¹⁰² of $\log k = 9.7 \text{ l mol}^{-1} \text{ s}^{-1}$.

The earliest studies of the rates of abstraction of hydrogen atoms by bromine atoms were by Van Artsdalen and coworkers who studied hydrogen abstraction from isobutane¹⁰³, neopentane^{104,105} and toluene^{106,107}. The accuracy of these results was later disputed by Benson and Buss¹⁰⁸ who claimed that the Arrhenius parameters were too high as a result of the concentration of bromine atoms never attaining steady state. Kerr and Trotman-Dickenson²³ correlated data for hydrogen abstraction from methane and from other primary, secondary and tertiary sites by various radicals including bromine, chlorine and methyl. Some of these results are shown in table 2.2. These Arrhenius parameters indicate that the pre-exponential term is similar for abstraction by both bromine and chlorine atoms and is lower for methyl radicals. The

activation energy for hydrogen abstraction is very low for chlorine radicals compared with methyl or bromine radicals, abstraction by bromine having the highest values of activation energy E.

TABLE 2.2

Hydrogen Abstraction By CH₃; Cl; Br.

Abstracting Species	Arrhenius Parameter	CH ₃ -H	RCH ₂ -H	R ₂ CH-H	R ₃ C-H
CH ₃	log A (1 mol ⁻¹ s ⁻¹)	8.2	8.3	8.0	7.9
	E (kcal mol ⁻¹)	12.8	10.4	8.3	7.5
Cl	log A (1 mol ⁻¹ s ⁻¹)	9.8	10.2	10.3	10.2
	E (kcal mol ⁻¹)	3.9	1.0	0.3	0
Br	log A (1 mol ⁻¹ s ⁻¹)	10.8	10.9	10.2	10.3
	E (kcal mol ⁻¹)	18.3	13.4	10.2	7.5

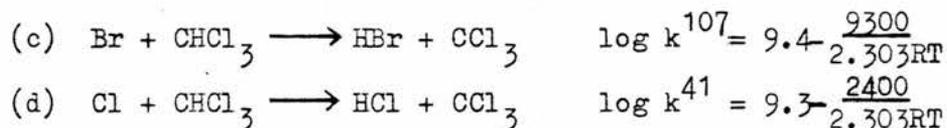
From these Arrhenius parameters shown in Table 2.2 the reaction rates can be calculated in the temperature range studied. Table 2.3 shows the relative reaction rates at 50°C and 182°C. It can be seen that the rate of hydrogen atom abstraction by a chlorine atom is

TABLE 2.3

Rates of Hydrogen Abstraction By CH₃; Cl; Br.

Abstracting Species	Rate(Temperature)	CH ₃ -H	RCH ₂ -H	R ₂ CH-H	R ₃ C-H
CH ₃	log k (50°C)	0.81	0.98	2.16	2.62
	log k(182°C)	1.80	3.10	3.85	4.15
Cl	log k (50°C)	7.05	9.50	10.09	10.20
	log k(182°C)	7.85	9.70	10.15	10.20
Br	log k (50°C)	-2.09	1.46	3.02	5.02
	log k(182°C)	1.65	4.20	5.10	6.55

several orders of magnitude greater than the corresponding abstraction by a bromine atom. The rate of formation of HCl in the RH/CCl₄ system will therefore be considerably greater than the rate of formation of HBr in the RH/CCl₃Br system. This comparative ease of hydrogen abstraction by the chlorine atom also applies to the reactions (c) and (d) whence it can be calculated that reaction (d) will have a rate constant about four orders of magnitude



greater than reaction (c). In comparing the CCl₃Br and the CCl₄ systems we therefore calculate that the rate of formation of the hydrogen halide is considerably greater with CCl₄, but that the ease of hydrogen abstraction from the hydrogen halide is considerably greater with CCl₃Br. The rates of back reactions (c) and (d) also indicate that the net rate of hydrogen abstraction from the hydrogen halide, determined as (rate forward reaction - rate back reaction) will be greater in the case of HBr arising in the CCl₃Br system.

It is therefore not easy to predict whether the presence of a hydrogen halide will lead to significant complications in the calculation of Arrhenius parameters for the CCl₃X - RH systems. It is interesting to note that Huyser⁸² did not even consider reaction (b) in his study of the CCl₃Br - toluene system.

In section 2 an analogous system to that of section 1 is studied, the cyclohexane having been replaced by propane. If the arguments proposed in the discussion to section 1 were valid, it would be expected that the measured Arrhenius parameters would be lower than the actual values. Experiments were also carried out with added hydrogen bromide to investigate further the effects of HBr on the system.

Finally, a computer program was used to simulate the reaction with and without added HBr. Although an exact match with experimentally obtained data was not obtained, the similarity between computer simulated and experimental Arrhenius plots was sufficient to provide confirmation that the mechanism proposed was a fairly accurate representation of the system and that the Arrhenius parameters employed were reasonably accurate.

SECTION 2

The Photolysis of Bromotrichloromethane With Propane

(and Hydrogen Bromide)

EXPERIMENTAL

2.1 REACTANTS

- (a) Bromotrichloromethane:- supplied by Schuchardt-München. The stated purity was 90% w/w. The purification and storage of CCl_3Br were described in Section 1.
- (b) Propane:- Matheson Gas Products "Research Grade" with a stated purity of 99.99%. This was used without further purification.
- (c) Hydrogen Bromide - British Oxygen Company high purity gas. The stated purity was 99.8%. This was used without further purification.

2.2 APPARATUS

The spherical "Pyrex" reaction vessel was similar to that described for the cyclohexane-bromotrichloromethane system. The volume was measured by completely filling the vessel with distilled water and was calculated to be 294 ml. Reaction temperature was controlled by means of a furnace as described in Section 1.

The vacuum line was modified for this series of experiments. An additional bulb (bulb D in Figure 1) was added to the manifold of the vacuum line for storage of propane. A side-arm was fitted to this bulb so that excess gas could be distilled back to the bulb after the required pressure of propane had been charged to bulb A prior to a run. It was not necessary to measure the volume of bulb D. The remainder of the apparatus was the same as described in Section 1 and illustrated in Figure 1.1. All taps were greaseless except for the main valve between the manifold and the liquid nitrogen trap guarding the evacuation system.

2.3 PROCEDURE

The procedure was similar to that described in Section 1. To add the propane to the reaction flask, bulb A and the manifold were pressured up to 50 torr with propane from bulb D. Bulb A was isolated and the excess propane frozen back into bulb D. Bulb D was then isolated and the contents of bulb A distilled into the reaction vessel. The CCl_3Br was added by a similar procedure but with a pressure of 25 torr instead of 50 torr.

The pressures of hydrogen bromide added in the experiments described by Table 2.6 were too low to handle by the above method. The volume ratio of (bulb A + manifold): bulb A is $(888 + 216) : 216 \cong 5:1$. Bulb A was therefore pressured up with five times the required pressure of HBr; this pressure could be more accurately measured with the vacuum guage. The bulb was isolated and the manifold evacuated. The contents of bulb A were then released into the manifold and the bulb isolated again. The pressure within the bulb should then have been one fifth of the pressure originally measured. The manifold was again evacuated and the contents of bulb A distilled to the reaction vessel. When extremely small quantities of HBr were required this method of five-fold dilution was repeated again before distillation of the HBr into the reaction vessel.

It was observed that after each run there was a dark deposit (probably carbon) on the window of the reaction vessel facing the light source. This will have acted as a light filter and reduced the intensity of light entering the reaction vessel. The extent of this deposit was variable; at worst the affected glass of the reaction vessel was almost completely opaque. After each run the reaction vessel was cleaned by completely

filling the globe with a solution of Decon 90 detergent and immersing the whole vessel in a Decon 90 solution in an ultrasonic bath for 6 hours at 80°C. The vessel was then thoroughly rinsed by extensive washing with demineralised water. The water was then removed by washing the vessel out several times with redistilled acetone. The vessel was then replaced on the vacuum line, heated to >100°C and opened to the pumps to remove the last traces of acetone.

2.4 ANALYSIS OF PRODUCTS

The apparatus and column for the gas liquid chromatographic analyses were as described in Section 1. The conditions employed for the cyclohexane system did not, however, give adequate separation of the more volatile components of this system - propane, isopropylbromide and chloroform. Consequently it was found necessary to analyse the volatile components at a lower temperature and carrier gas flow rate. The relative concentrations of C_3H_8 , $i-C_3H_7Br$, $CHCl_3$ and CCl_3Br were calculated using a column temperature of 35°C and with a nitrogen flow rate of 40 $mlmin^{-1}$. The relative concentrations of CCl_3Br and C_2Cl_6 were then measured by product separation at 100°C with a nitrogen flow rate of 70 $mlmin^{-1}$.

In the reactions where HBr had been added the products were passed through "Carbosorb" (soda lime, to remove any HBr remaining) into the product collection tube. HBr was not therefore detected among the products. In other runs the products were distilled directly to the collection tube. The tube was then sealed with a rubber septum cap and stored in cardice/acetone. The syringe needle was cooled in liquid nitrogen then injected through the septum cap to withdraw the sample. 6 μ l samples were used in all analyses.

2.5 IDENTIFICATION OF PRODUCTS

The chromatograms of the reaction products showed six peaks, as shown in Figure 2.1. Five of these peaks were sufficiently large for gas liquid chromatography coupled mass spectroscopy to be used for identification purposes. Results from the mass spectrograph are shown in Table 2.4. The sixth peak, occurring between isopropylbromide and chloroform was tentatively identified as that of n-propyl bromide by comparison of retention times with a standard. As the magnitude of this peak was ~5% of the area of the isopropyl bromide peak, the total rate of formation of propyl bromide in this section was assumed to be equal to the rate of formation measured from the isopropyl bromide peak alone.

2.6 RESULTS

Mixtures of bromotrichloromethane and propane were photolysed over the temperature range 29-271°C. The rates of formation of the products were calculated and are shown in Table 2.5.

The effect of addition of small quantities of HBr to the reactants was studied and the rates of formation of the products from this system are shown in Table 2.7. To determine whether light intensity would affect product ratios a run was carried out in the absence of the HBr but under similar C_3H_8 and CCl_3Br concentrations and at similar temperature to the experiments reported in Table 2.7 with a filter fitted between the light source and the reactor. The light intensity was thus reduced to 27% of normal. The results of this experiment are shown in Table 2.8.

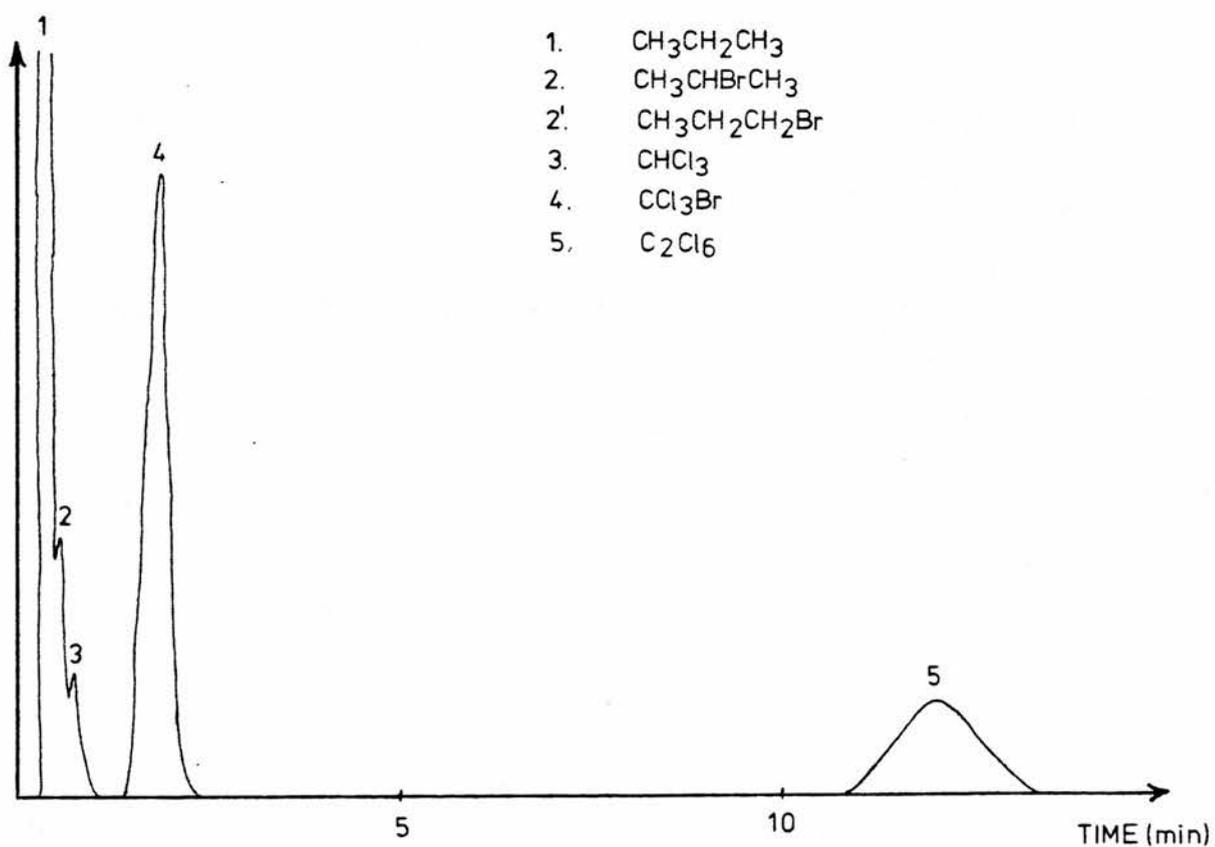
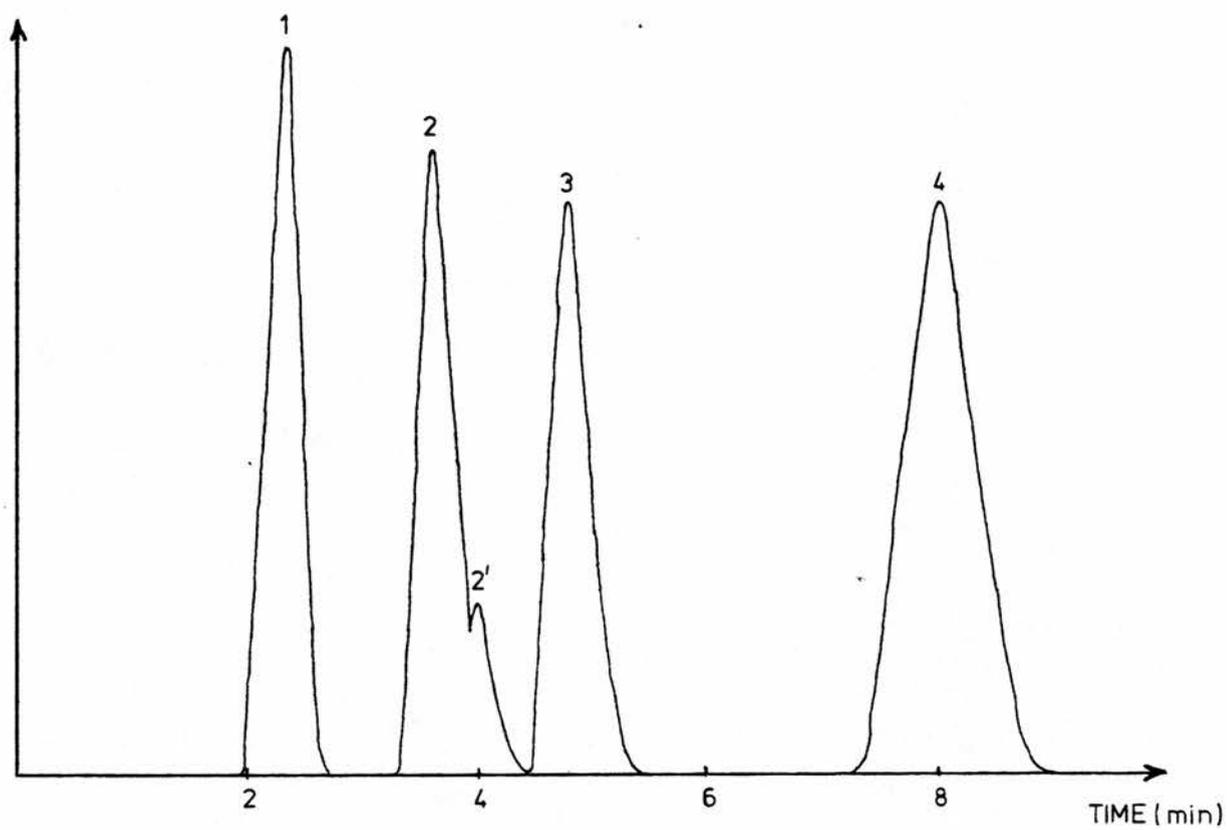


FIGURE 2.1

Glc Analyses at 35°C (above) and 100°C (below) of the Photolysis of Bromotrichloromethane in the Presence of Propane.

TABLE 2.4

Product Identification by GLC-Coupled Mass Spectroscopy

Peak A	29	Intensity	100+	m/e	28	Intensity	81	m/e	44	Intensity	67	m/e	43	Intensity	65	m/e	27	Intensity	46	m/e	39	Intensity	38	m/e	41	Intensity	28	m/e	42	Intensity	12
C ₃ H ₈ Standard	29	100	100	28	28	40	62	44	44	40	34	43	43	27	34	39	27	32	32	39	39	17	42	41	41	15	42	42	6		
Peak B	43	100++	100++	41	41	100	100+	27	27	62	100	39	39	122	62	124	122	32	32	124	42	30	42	42	21	28	28	19			
i-C ₃ H ₇ Br Standard	43	100	100	41	41	25	30	27	27	23	25	122	122	124	23	39	124	20	20	39	39	11	44	44	3	42	42	3			
Peak C	83	100++	100++	85	85	88	100+	47	47	42	88	87	87	48	42	49	48	41	41	49	49	38	82	82	32	35	35	32			
CHCl ₃ Standard	83	100	100	85	85	21	66	47	47	10	21	87	87	48	10	49	48	10	10	49	49	7	35	35	5	82	82	3			
Peak D	117	100	100	119	119	38	95	163	163	31	38	82	82	121	31	161	121	31	31	161	161	29	47	47	26	165	165	21			
CCl ₃ Br Standard	117	100	100	119	119	52	97	163	163	34	52	82	82	161	34	121	161	32	32	121	121	31	47	47	31	165	165	23			
Peak E	117	100+	100+	119	119	100	100+	201	201	69	100	203	203	199	69	166	199	60	60	166	166	38	121	121	21	164	164	21			
C ₂ Cl ₆ Standard	117	100	100	119	119	81	97	201	201	51	81	203	203	199	51	166	199	49	49	166	166	42	164	164	32	121	121	31			
C ₃ H ₆ Standard	41	100	100	42	42	64	64	39	39	26	64	27	27	40	26	38	40	24	24	38	38	14	37	37	9	26	26	6			
(i-C ₃ H ₇) ₂ Standard	43	100	100	42	42	28	90	41	41	22	28	27	27	71	22	39	71	15	15	39	39	13	29	29	9	15	15	7			
CCl ₄ Standard	117	100	100	119	119	32	97	121	121	19	32	82	82	47	19	84	47	13	13	84	84	13	35	35	6	49	49	4			
CCl ₂ Br ₂ Standard	163	100	100	161	161	45	62	165	165	23	45	79	79	81	23	82	81	22	22	82	82	21	207	207	16	47	47	15			

TABLE 2.5
Rates of Product Formation in the Bromotrichloromethane-Propane System in $\text{mmol l}^{-1} \text{s}^{-1}$
 $([\text{CCl}_3\text{Br}]_i = 1.417 \text{ mmol l}^{-1}, [\text{C}_2\text{H}_6]_i = 2.834 \text{ mmol l}^{-1})$

Temp. (°C)	Time (s)	RCHCl ₃ (assuming CCl ₃ Br _i)	RRBr (assuming CCl ₃ Br _i)	RC ₂ Cl ₆ (assuming CCl ₃ Br _i)	[CCl ₃ Br] _f mmol l ⁻¹	RCHCl ₃ (assuming CCl ₃ Br _f)	RRBr (assuming CCl ₃ Br _f)	RC ₂ Cl ₆ (assuming CCl ₃ Br _f)	[C ₂ H ₆] _f mmol l ⁻¹
29	6000	3.826x10 ⁻⁹	4.652x10 ⁻⁹	2.409x10 ⁻⁹	1.367	3.691x10 ⁻⁹	4.488x10 ⁻⁹	2.324x10 ⁻⁹	2.807
57	1800	6.282x10 ⁻⁹	8.937x10 ⁻⁹	6.830x10 ⁻⁹	1.393	6.176x10 ⁻⁹	8.786x10 ⁻⁹	6.715x10 ⁻⁹	2.818
73	1800	7.424x10 ⁻⁹	8.817x10 ⁻⁹	9.525x10 ⁻⁹	1.384	7.251x10 ⁻⁹	8.612x10 ⁻⁹	9.303x10 ⁻⁹	2.818
82	1800	8.785x10 ⁻⁹	1.244x10 ⁻⁸	7.912x10 ⁻⁹	1.374	8.519x10 ⁻⁹	1.206x10 ⁻⁸	7.672x10 ⁻⁹	2.812
101	1800	1.047x10 ⁻⁸	1.643x10 ⁻⁸	1.342x10 ⁻⁸	1.366	1.009x10 ⁻⁸	1.584x10 ⁻⁸	1.294x10 ⁻⁸	2.805
105	1800	1.543x10 ⁻⁸	1.913x10 ⁻⁸	1.204x10 ⁻⁸	1.349	1.469x10 ⁻⁸	1.821x10 ⁻⁸	1.146x10 ⁻⁸	2.801
115	1800	1.611x10 ⁻⁸	2.040x10 ⁻⁸	1.383x10 ⁻⁸	1.342	1.526x10 ⁻⁸	1.932x10 ⁻⁸	1.310x10 ⁻⁸	2.799
138	1800	2.307x10 ⁻⁸	2.826x10 ⁻⁸	1.275x10 ⁻⁸	1.335	2.173x10 ⁻⁸	2.662x10 ⁻⁸	1.201x10 ⁻⁸	2.786
150	1800	2.661x10 ⁻⁸	3.196x10 ⁻⁸	1.047x10 ⁻⁸	1.336	2.509x10 ⁻⁸	3.013x10 ⁻⁸	9.871x10 ⁻⁹	2.780
166	1800	6.227x10 ⁻⁸	5.358x10 ⁻⁸	1.614x10 ⁻⁸	1.265	5.588x10 ⁻⁸	4.783x10 ⁻⁸	1.441x10 ⁻⁸	2.748
184	1800	6.069x10 ⁻⁸	6.211x10 ⁻⁸	1.818x10 ⁻⁸	1.261	5.401x10 ⁻⁸	5.527x10 ⁻⁸	1.618x10 ⁻⁸	2.735
200	1800	9.142x10 ⁻⁸	8.557x10 ⁻⁸	1.842x10 ⁻⁸	1.219	7.865x10 ⁻⁸	7.362x10 ⁻⁸	1.585x10 ⁻⁸	2.701
216	1920	9.535x10 ⁻⁸	9.329x10 ⁻⁸	1.166x10 ⁻⁸	1.221	8.216x10 ⁻⁸	8.039x10 ⁻⁸	1.005x10 ⁻⁸	2.680
234	600	1.455x10 ⁻⁷	1.382x10 ⁻⁷	1.719x10 ⁻⁸	1.326	1.362x10 ⁻⁷	1.293x10 ⁻⁷	1.609x10 ⁻⁸	2.756
238	2160	2.192x10 ⁻⁷	1.912x10 ⁻⁷	1.229x10 ⁻⁸	1.033	1.598x10 ⁻⁷	1.394x10 ⁻⁷	8.959x10 ⁻⁹	2.533
245	900	3.092x10 ⁻⁷	2.809x10 ⁻⁷	2.991x10 ⁻⁸	1.148	2.505x10 ⁻⁷	2.276x10 ⁻⁷	2.423x10 ⁻⁸	2.629
252	1200	2.359x10 ⁻⁶	1.751x10 ⁻⁶	3.861x10 ⁻⁸	0.463	7.707x10 ⁻⁷	5.721x10 ⁻⁷	1.261x10 ⁻⁸	2.147
271	840	5.214x10 ⁻⁶	3.521x10 ⁻⁶	5.246x10 ⁻⁸	0.341	1.254x10 ⁻⁶	8.473x10 ⁻⁷	1.262x10 ⁻⁸	2.122

TABLE 2.6

Calculation of $\log_{10} (R_{\text{CHCl}_3} / (R_{\text{C}_2\text{Cl}_6})^{1/2} [\text{C}_3\text{H}_8]_{\text{av}})$

Temp °C	$\frac{1000}{T^{\circ}\text{K}}$	$[\text{C}_3\text{H}_8]_{\text{av}}$ mmol l ⁻¹	$\log_{10} \frac{R_{\text{CHCl}_3}}{R_{\text{C}_2\text{Cl}_6}^{1/2} [\text{C}_3\text{H}_8]_{\text{av}}}$
29	3.311	2.821	-1.566
57	3.030	2.826	-1.574
73	2.890	2.826	-1.575
82	2.817	2.823	-1.463
101	2.674	2.820	-1.502
105	2.646	2.818	-1.312
115	2.577	2.817	-1.325
138	2.433	2.810	-1.151
150	2.364	2.807	-0.967
166	2.278	2.791	-0.778
184	2.186	2.785	-0.817
200	1.114	2.768	-0.646
216	2.045	2.757	-0.527
234	1.972	2.795	-0.414
238	1.957	2.684	-0.201
245	1.931	2.732	-0.280
252	1.905	2.491	+0.440
271	1.838	2.478	+0.654

$$[\text{C}_3\text{H}_8]_{\text{av}} = \frac{1}{2} ([\text{C}_3\text{H}_8]_{\text{i}} + [\text{C}_3\text{H}_8]_{\text{f}})$$

TABLE 2.7

Addition of Hydrogen Bromide to the Photolysis of Propane + Bromotrichloromethane

HBr (mmol l ⁻¹)	Reaction Temp. (°C)	Reaction Time (s)	CCl ₃ Br _f (mmol l ⁻¹ s ⁻¹)	R _{CHCl₃} (mol l ⁻¹ s ⁻¹)	R _{RBr} (mol l ⁻¹ s ⁻¹)	R _{C₂Cl₆} (mol l ⁻¹ s ⁻¹)	$\frac{R_{CHCl_3}}{(R_{C_2Cl_6})^{\frac{1}{2}}}$
0	182	1200	1.304	5.835x10 ⁻⁸	5.488x10 ⁻⁸	1.771x10 ⁻⁸	4.385x10 ⁻⁴
0	184	1800	1.261	5.401x10 ⁻⁸	5.527x10 ⁻⁸	1.618x10 ⁻⁸	4.246x10 ⁻⁴
4.53x10 ⁻³	188	1200	1.276	9.123x10 ⁻⁸	9.634x10 ⁻⁸	1.301x10 ⁻⁸	7.998x10 ⁻⁴
5.38x10 ⁻²	185	2400	0.780	2.490x10 ⁻⁷	1.996x10 ⁻⁷	8.320x10 ⁻⁹	2.730x10 ⁻³
5.67x10 ⁻²	182	1200	1.074	2.727x10 ⁻⁷	2.344x10 ⁻⁷	6.659x10 ⁻⁹	3.342x10 ⁻³
1.13x10 ⁻¹	183	1200	0.917	4.061x10 ⁻⁷	3.070x10 ⁻⁷	5.120x10 ⁻⁹	5.675x10 ⁻³
1.42x10 ⁻¹	181	1200	0.951	3.829x10 ⁻⁷	3.243x10 ⁻⁷	2.457x10 ⁻⁹	7.725x10 ⁻³
1.70x10 ⁻¹	184	1200	0.838	4.770x10 ⁻⁷	3.687x10 ⁻⁷	3.080x10 ⁻⁹	8.595x10 ⁻³
2.27x10 ⁻¹	182	1200	0.808	5.057x10 ⁻⁷	4.518x10 ⁻⁷	1.219x10 ⁻⁹	1.448x10 ⁻²

$$\left[\text{CCl}_3\text{Br} \right]_i = 1.417 \text{ mmol l}^{-1}$$

$$\left[\text{C}_3\text{H}_8 \right]_i = 2.834 \text{ mmol l}^{-1}$$

TABLE 2.8

Variation of Light Intensity in Photolysis of Propane -
Bromotrichloromethane Mixtures

Light Intensity (%)	Temp. (°C)	Reaction Time (s)	$[CCL_3Br]_f$ (mmol l ⁻¹)	R_{CHCl_3} (mol l ⁻¹ s ⁻¹)	R_{HBr} (mol l ⁻¹ s ⁻¹)	$R_{C_2Cl_6}$ (mol l ⁻¹ s ⁻¹)	C_3H_8 (mmol l ⁻¹)	C_3H_8 (mmol l ⁻¹)	$\log \frac{R_{CHCl_3}}{(R_{C_2Cl_6})^{\frac{1}{2}}(C_3H_8)^{\frac{1}{2}}}$	$\frac{R_{CHCl_3}}{R_{C_2Cl_6}^{\frac{1}{2}}(C_2Cl_6)^{\frac{1}{2}}}$
100	182	1200	1.304	5.835×10^{-8}	5.488×10^{-8}	1.771×10^{-8}	2.768	2.801	-0.805	4.385×10^{-4}
27	178	3600	1.289	2.979×10^{-8}	2.675×10^{-8}	2.915×10^{-9}	2.738	2.786	-0.703	5.518×10^{-4}

$$[CCL_3Br] \text{ initial} = 1.417 \times 10^{-3} \text{ mol l}^{-1}$$

$$[C_3H_8] \text{ initial} = 2.834 \times 10^{-3} \text{ mol l}^{-1}$$

TABLE 2.9

Addition of Hydrogen Bromide to the Photolysis
Of Propane + Bromotrichloromethane At High Propane Concentration

HBr (mmol l ⁻¹)	Temp (°C)	1000/T (°K)	time (s)	[CCl ₃ Br] _f (mmol l ⁻¹)	R _{CHCl₃} (mol l ⁻¹ s ⁻¹)	R _{PrBr} (mol l ⁻¹ s ⁻¹)
Nil	188	2.168	1200	1.046	3.091x10 ⁻⁷	2.935x10 ⁻⁷
Nil	188	2.168	1200	1.256	1.346x10 ⁻⁷	1.208x10 ⁻⁷
5.67x10 ²	190	2.159	1080	0.826	5.285x10 ⁻⁷	4.757x10 ⁻⁷
1.13x10 ⁻¹	192	2.150	1080	0.722	6.433x10 ⁻⁷	5.574x10 ⁻⁷
2.84x10 ⁻¹	190	2.159	600	0.927	8.164x10 ⁻⁷	7.036x10 ⁻⁷

$$[\text{CCl}_3\text{Br}]_i = 1.417 \text{ mmol/l}$$

$$[\text{C}_3\text{H}_8]_i = 22.672 \text{ mmol/l}$$

Reaction with equal quantities of HBr and CCl_3Br ($1.417 \times 10^{-3} \text{ mol l}^{-1}$) in the absence of propane did not result in a detectable level of C_2Cl_6 termination product being produced. At 28°C the rate of formation of CHCl_3 was $1.87 \times 10^{-8} \text{ mol l}^{-1} \text{ s}^{-1}$ but in the absence of detectable C_2Cl_6 no kinetic parameters could be obtained.

In an attempt to reduce the ratio of HBr to C_3H_8 to lower levels than those described in Table 2.7, the initial concentration of propane was increased from $2.834 \times 10^{-3} \text{ mol l}^{-1}$ to $2.267 \times 10^{-2} \text{ mol l}^{-1}$. The quantities of HBr employed were similar to those used in the experiments reported in Table 2.7. The C_2Cl_6 was again undetectable. The rates for formation of chloroform and isopropyl bromide are shown in Table 2.9.

SECTION 2

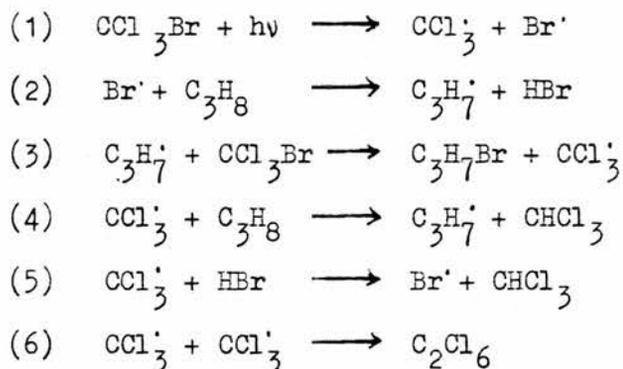
The Photolysis of Bromotrichloromethane With Propane

(and Hydrogen Bromide)

DISCUSSION

2.7.1. Propane + Bromotrichloromethane (No added HBr)

The results listed in Table 2.5 indicate that the mechanism of the photolysis of bromotrichloromethane in the presence of propane is very similar to that obtained in Section 1 where cyclohexane was used in place of propane. We have



It was stated earlier in this section that there was some evidence to suggest that both n-propyl bromide and isopropyl bromide were detected in the reaction product mixture. The former compound was only present in small proportions and it is assumed in this discussion that the rate of reaction (3) is equal to the rate of production of isopropyl bromide. Tedder and Watson⁷⁸ measured the relative rates of abstraction of primary and secondary hydrogen atoms from n-butane by trichloromethyl radicals. They found that

$$\frac{k_s}{k_p} = (0.67 \pm 0.10) \exp(3.64 \pm 0.15 \text{ kcal/RT})$$

Hence, it can be calculated that at 400°A, $\frac{k_s}{k_p} \cong 60$. This value is consistent with the results observed in the propane-bromotrichloromethane system, propane having a ratio of primary hydrogen atoms to secondary atoms of 3 compared with a ratio of 1.5 for n-butane.

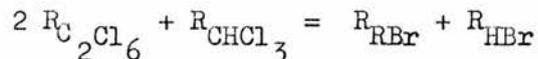
In the mechanism described by reactions (1) - (6) the only termination reaction is the dimerisation of trichloromethyl radicals, the product being hexachloroethane. Although chlorodifluoromethyl radicals and difluoromethyl radicals can disproportionate with themselves⁶⁰ to form difluorocarbene and the corresponding halomethane no such reaction occurs with trichloromethyl radicals and hexachloroethane was the only termination product. Reaction (3) will take place very readily due to the ease of abstraction of a bromine atom from CCl_3Br ($D(\text{CCl}_3\text{-Br})=49 \text{ kcal/mol}^{93}$). Consequently, the large quantity of CCl_3Br present will constitute an effective trap for propyl and the steady state concentration will be too low for a significant termination step involving propyl radicals. There was no trace in the products of 2,3-dimethylbutane or 1,1,1-trichloro-2-methylpropane (the termination products of isopropyl radicals with themselves or with trichloromethyl radicals).

The experiments were carried out over an extensive temperature range 29-271°C. For kinetic calculations it is necessary to assume steady state conditions, and for such conditions the concentration of reactants should not change significantly over the course of the experiment. In this series of runs it was discovered that the chain length (i.e. the number of propagation steps occurring per termination step in a particular reaction cycle) was very high at the top end of the temperature scale. If the degree of conversion was restricted to <5%, say, no termination product would have been detectable. The runs carried out at temperatures in excess of 250°C were therefore run to conversions considerably greater than 5%. Furthermore, it has been shown⁶⁰ that at such high temperatures tetrachloroethylene can be formed from the photolysis of bromotrichloromethane on its own. These runs

were not, therefore, included in kinetic calculations. The degree of conversion with respect to either CCl_3Br or C_3H_8 can be measured by comparison of the final concentrations shown in Table 2.5 with the initial concentrations of 1.417 and 2.834 mmol l^{-1} respectively. All runs at temperatures less than 250°C had conversions of about 7% or less based on propane.

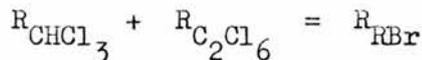
The experiments described in Section 1 ($\text{CCl}_3\text{Br} + \text{c} - \text{C}_6\text{H}_{12}$) were limited at the upper end of the temperature scale by the rate of thermal decomposition of cyclohexyl bromide, one of the major products. This decomposition assumed significant proportions at temperatures in excess of 160°C . Maccoll and Thomas¹¹⁰ have investigated the thermal stability of isopropyl bromide and calculated that at temperatures of 200, 250 and 300°C . the percentage decomposition was 0,0 and 11.2% respectively. The rate constant for decomposition was given by $k = 4.17 \times 10^{13} \exp \frac{-47,800}{RT} \text{ (s}^{-1}\text{)}$. As only those experiments carried out below 250°C were included for kinetic calculations in the present work, the thermal decomposition of isopropyl bromide should not affect the results.

From reactions (1) - (6) it can be seen that



and $R_{\text{HBr}} = R_{\text{C}_2\text{Cl}_6}$ where $R_x = \text{Rate of formation of } x$.

These can be combined to give the material balance



Substitution of the values calculated in Table 2.5 into this equation shows that the equality nearly holds, there being a slight excess on the left hand side. The discrepancy is slightly greater at higher temperatures. Although the factors described

earlier in this discussion (the decomposition of RBr and the assumption that $R_{PrBr} = R_{Pr} i_{Br}$) would result in an inequality of this nature it is very unlikely that such minor effects would be relevant. It seems more likely that such results could have arisen though inaccurate product analysis. The isopropyl bromide and chloroform peaks in the glc trace were situated between the larger C_3H_8 and CCl_3Br peaks, and separation of the peaks was not absolute. The deviation from equality was, however, only slight and confirms that reactions (1) to (5) provide a reasonably accurate description of the mechanism in operation.

In Section 1 it was explained that previous work by Tedder, M^cGrath and Watson^{78,79} had suggested that reaction (5) did not occur to a significant extent and that reaction (4) was the main source of chloroform. If the chloroform produced in reaction (5) is considered negligible, we have:-

$$R_{CHCl_3} = k_4 [CCl_3] [C_3H_8]$$

and

$$R_{C_2Cl_6} = k_6 [CCl_3]^2$$

Hence

$$\frac{R_{CHCl_3}}{(R_{C_2Cl_6})^{1/2}} = \frac{k_4 (C_3H_8)}{k_6^{1/2}} \quad \text{-----} \quad (A)$$

A graph of $\log R_{CHCl_3} / (R_{C_2Cl_6})^{1/2} [C_3H_8]$ versus the reciprocal of temperature should yield an intercept on the y-axis of $\log A_4 - \frac{1}{2} \log A_6$ and a gradient of $-(E_4 - \frac{1}{2}E_6) / 2.303R$. In the high conversion runs described earlier ($> 250^\circ C$) there is a significant change in $[C_3H_8]$ over the course of the experiment. Steady state conditions cannot therefore be assumed. To reduce the error the initial and final propane concentrations have been calculated and an average value $[C_3H_8]_{av}$ is calculated in Table 2.6. To further reduce the errors present through over-conversion the final concentration of CCl_3Br has been calculated as:-

$$[\text{CCl}_3\text{Br}]_f = [\text{CCl}_3\text{Br}]_i - [\text{CHCl}_3]_f - 2 [\text{C}_2\text{Cl}_6]_f$$

When the reaction products were analysed the concentrations of each were measured relative to the final concentrations of CCl_3Br . We have therefore:-

$$[\text{CCl}_3\text{Br}]_f = [\text{CCl}_3\text{Br}]_i - \frac{[\text{CHCl}_3]_f}{[\text{CCl}_3\text{Br}]_f} [\text{CCl}_3\text{Br}]_f - 2 \frac{[\text{C}_2\text{Cl}_6]_f}{[\text{CCl}_3\text{Br}]_f} [\text{CCl}_3\text{Br}]_f$$

$$\therefore [\text{CCl}_3\text{Br}]_f = \frac{[\text{CCl}_3\text{Br}]_i}{1 + \frac{[\text{CHCl}_3]_f}{[\text{CCl}_3\text{Br}]_f} + 2 \frac{[\text{C}_2\text{Cl}_6]_f}{[\text{CCl}_3\text{Br}]_f}}$$

As each term on the right hand side of this equation is known, a value can be obtained for $[\text{CCl}_3\text{Br}]_f$. This value is shown in Table 2.5. From this final concentration, absolute production rates can be calculated for all products from the expression:-

$$(R_x)_{\text{abs.}} = \frac{[x]_f}{[\text{CCl}_3\text{Br}]_f} \times [\text{CCl}_3\text{Br}]_f \times \frac{1}{\text{Reaction time}}$$

These rates of production are also calculated in Table 2.5 and are used in subsequent kinetic calculations. Using these rates and an average value for $[\text{C}_3\text{H}_8]$ for each run, values have been calculated for

$$\log_{10} \frac{R_{\text{CHCl}_3}}{(R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}} [\text{C}_3\text{H}_8]} \quad \text{and} \quad \frac{1000}{T^{\circ}\text{K}}$$

and are shown in Table 2.6. A graph plotting the logarithmic term against the temperature term yields a curve as shown in Figure 2.2 This differs from the straight line that would be predicted by equation A. Linearity is observed in the range $1000/T \cong 1.9-2.7$, corresponding to a temperature range of 100-250°C. At temperatures above 250°C the points lie above the line; it has been explained

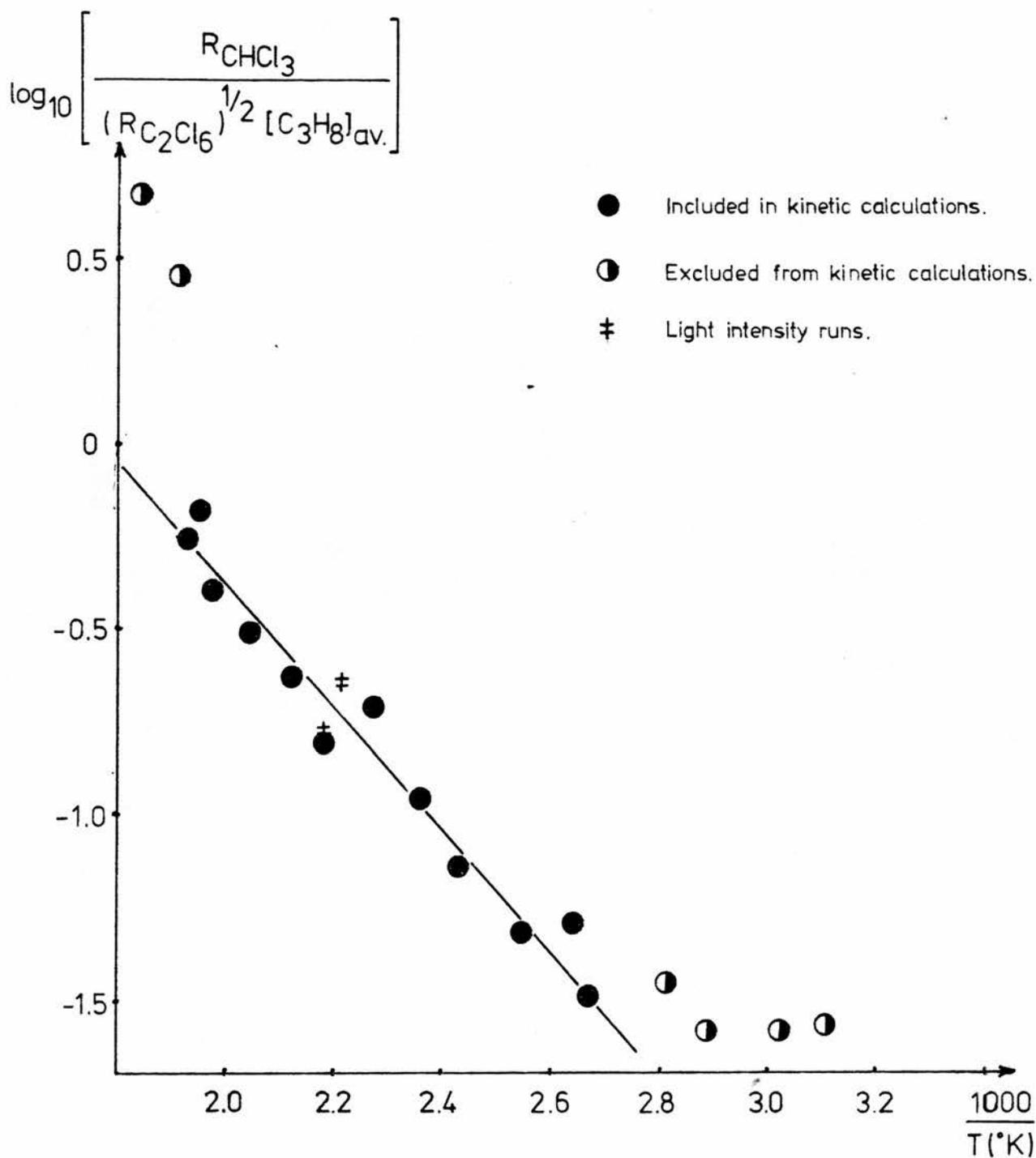


FIGURE 2.2

Graph of $\log_{10} \left[\frac{R_{\text{CHCl}_3}}{(\text{RC}_2\text{Cl}_6)^{1/2} [\text{C}_3\text{H}_8]} \right]$ versus the reciprocal

of temperature for the propane - bromotrichloromethane system.

earlier that the relationship plotted on the graph is not valid at high reactant conversions. There is also a deviation from linearity at lower temperatures ($< 100^{\circ}\text{C}$). This deviation is small down to about 50°C . The single run carried out below this temperature (at 29°C) yielded a point which lies well above the line drawn through the points obtained at temperatures between 100 and 250°C .

The reason for this low temperature effect is probably the assumption in derivation of equation A that all the chloroform present originated from reaction (4) and that chloroform from reaction (5) could be neglected. The concentration of HBr will always be extremely low relative to the concentration of propane. However, at low temperatures the abstraction of hydrogen from propane will be very slow due to the moderate activation energy. If the activation energy for abstraction of hydrogen from hydrogen bromide is significantly lower than that of hydrogen abstraction from propane then at sufficiently low temperatures the chloroform produced from reaction (5) will become significant. The "chain length" (as measured by the number of chloroform molecules formed by chain propagation per hexachloroethane molecule formed by chain termination) will therefore be higher than the value that would be obtained in the absence of reaction (5). The consequence of such a situation would be that the value of $\log_{10}(\frac{R_{\text{CHCl}_3}}{R_{\text{C}_2\text{Cl}_6}})^{\frac{1}{2}} [\text{C}_3\text{H}_8]_{\text{av}}$ would be higher than expected. This would explain a deviation of the nature observed in Figure 2.2. The effect of addition of HBr to this system is described in the second part of this discussion and the third part describes the results obtained when the system was modelled by a computer programme. In this final section it is shown that the HBr

concentration increases with time and that the longer a reaction progresses the higher becomes the value of $\log_{10} (R_{\text{CHCl}_3} / (R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}} [\text{C}_3\text{H}_8]_{\text{av}})$. The run carried out at 29°C was continued for a considerably longer reaction time than the other runs in order to obtain a sufficiently high concentration of products for reasonably accurate quantitative measurements. The result of this extension of reaction time would be to increase the deviation from the line obtained from the runs between 100 and 250°C, as was observed in Figure 2.2.

As explained in the key to Figure 2.2., the points which were outwith the range 100 to 250°C are represented on the graph by empty circles and were not included in the least squares calculation of the gradient and intercept of the line. The points within this temperature range are denoted by solid circles. The least squares calculation based on these points yields:-

$$\text{Gradient} = -1.56 \pm 0.20$$

$$\text{y-axis Intercept} = 2.70 \pm 0.09$$

As stated earlier in this discussion, the gradient provides a means of calculation of activation energy E_4 .

$$\text{Gradient} = - \frac{E_4 - \frac{1}{2}E_6}{2.303 R}$$

In the previous section ($\text{CCl}_3\text{Br} + \text{c-C}_6\text{H}_{12}$) it was explained that the activation energy for radical-radical combinations can be taken to be zero, i.e. $E_6=0$

$$\text{Therefore } E_4 = 4.574 \times (1.56 \pm 0.20) = (7.13 \pm 0.91) \text{ kcal mol}^{-1}$$

We have also the relationship:-

$$\text{y-axis Intercept} = \log A_4 - \frac{1}{2} \log A_6$$

Using the value of $A_6 = 9.7$ which was used in the cyclohexane system we have:-

$$\log A_4 = (2.70 \pm 0.09) + 4.85 = 7.55 \pm 0.09 \text{ l mol}^{-1} \text{ s}^{-1}$$

In their studies of hydrogen abstraction from alkanes by trichloromethyl radicals Wampler and Kuntz⁹⁹ obtained activation energies between 8.2 kcal mol⁻¹ (tertiary H abstraction from 2,3-dimethylbutane) and 10.8 kcal mol⁻¹ (hydrogen abstraction from n-hexane) and pre-exponential logarithmic terms between 7.88 l mol⁻¹ s⁻¹ (2,3-dimethylbutane) and 9.11 l mol⁻¹ s⁻¹ (cyclooctane). If one assumes from these values an activation energy of 10.5 kcal/mol and an A-factor of $2.5 \times 10^{-8} \text{ l mol}^{-1} \text{ s}^{-1}$ (i.e. $\log A = 8.4$) we obtain a rate $\log k_4 = 2.3$ at 100°C. The results calculated from the line in Figure 2.2 yield a rate at 100°C of $\log k_4 = 3.4$.

It is believed that this apparent increased reaction rate is the result of reaction (5) participating to a significant extent. As stated earlier in this discussion, a low activation energy from this hydrogen abstraction from HBr would result in the small concentration of HBr providing an easy source of chloroform and thus yielding an exaggerated value for k_4 in the above calculations. This low activation energy is confirmed in the second part of this discussion.

It was feared that the carbon deposit observed on the face of the reaction vessel (as described earlier in this section) may have introduced a significant error into the calculations. The carbon would act as a filter and the light intensity within the reaction flask would progressively diminish. By carrying out photolyses with no external light filter and with a filter calibrated to allow 27% of the light beam pass an indication of the effect of light intensity was obtained. A temperature midway through the

straight line section of Figure 2.2 was selected (180°C). In an attempt to run both photolyses to similar conversions the reaction time of the photolysis with filter inserted was three times that of the photolysis without the filter.

It can be seen from the last two columns of Table 2.8 that the differences between the two photolyses did not result in any effect of a sufficient magnitude to alter the calculated Arrhenius parameters. The values of $\log_{10} (R_{\text{CHCl}_3} / R_{\text{C}_2\text{Cl}_6}^{1/2} [\text{C}_3\text{H}_8])$ were plotted on Figure 2.2 and it can be seen that both points lie very close to the least squares line calculated from the data in Table 2.6. However, computer simulation of this system, as described in Section 2.7.3., shows that the value of $R_{\text{CHCl}_3} / (R_{\text{C}_2\text{Cl}_6})^{1/2}$ will rise as conversion increases. Thus, the formation of a carbon "filter" on the face of the reaction vessel will reduce conversion and decrease the value of $\log_{10} (R_{\text{CHCl}_3} / (R_{\text{C}_2\text{Cl}_6})^{1/2} [\text{C}_3\text{H}_8]_{\text{av}})$. Consequently, as the carbon formed more extensively at elevated temperatures, the gradient of the curve in Figure 2.2 will be lower than the true value. The effect of light intensity was not checked across the whole temperature range employed.

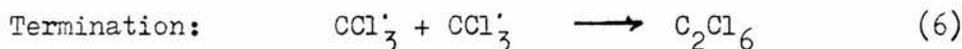
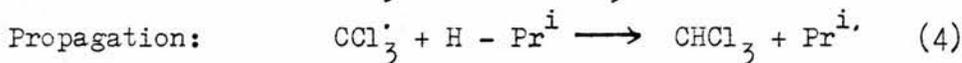
2.7.2 Propane + Bromotrichloromethane + Hydrogen Bromide

The temperature selected for this series of experiments was 182°C as this temperature represented approximately the midpoint of the linear section of Figure 2.2.

In the first series of experiments with added HBr the concentrations of CCl_3Br and C_3H_8 employed were 1.417 and 2.834 mmol l^{-1} respectively. The concentration of HBr was raised progressively from zero to 0.227 mmol l^{-1} . The results of this series of experiments are shown in Table 2.7. It can be seen that even at these low

concentrations of HBr (up to 8% of the propane concentration) there is a marked increase in the chain length of the reaction (i.e. the number of propagation steps undergone per termination). This confirms the observations predicted from the cyclohexane + bromotrichloromethane and the propane + bromotrichloromethane systems that the hydrogen atom in HBr is abstracted by CCl_3 very much more readily than is a secondary hydrogen atom in saturated hydrocarbons. When the concentration of HBr added to the reaction was greater than $0.227 \text{ mmol l}^{-1}$, no C_2Cl_6 termination product could be detected at all.

Within the trichloromethyl radical system we have



From reactions (4), (5) and (6) we have

$$\begin{aligned} \frac{R_{\text{CHCl}_3}}{(R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}}} &= \frac{k_4[\text{RH}][\text{CCl}_3\cdot] + k_5[\text{HBr}][\text{CCl}_3\cdot]}{k_6^{\frac{1}{2}}[\text{CCl}_3\cdot]} \\ &= \frac{k_4[\text{RH}] + k_5[\text{HBr}]}{k_6^{\frac{1}{2}}} \quad \text{(A)} \end{aligned}$$

Over the series of experiments the initial concentration of RH (propane) was not changed and it is assumed that the concentration remained essentially unchanged over the course of the reaction. In practice the maximum conversion took place at the run with highest HBr initial concentration (i.e. $2.27 \times 10^{-1} \text{ mmol l}^{-1}$)

$$\text{We have } \frac{[\text{RBr}]_f}{[\text{CCl}_3\text{Br}]_f} \text{ measured} = 0.542$$

$$[\text{CCl}_3\text{Br}]_f = 0.808 \text{ mmol l}^{-1} \text{ (from Table 2.6)}$$

$$[\text{RBr}]_f = 0.438 \text{ mmol l}^{-1}$$

$$\text{As } [\text{RH}]_f = [\text{RH}]_i - [\text{RBr}]_f$$

$$\text{we have } [\text{RH}]_f = (2.834 - 0.438) = 2.396 \text{ mmol l}^{-1}$$

$$\text{Percent conversion of RH} = \frac{[\text{RH}]_i - [\text{RH}]_f}{[\text{RH}]_i} \times 100 < 15\%$$

As this value of 15% is the maximum degree of conversion, equation (A) will not be rendered invalid by variation of the value of $[\text{RH}]$ over the course of the reaction. A more probable source of error will be the assumption that $[\text{HBr}]$ is unchanged over the course of the reaction and is equal to the initial concentration. At steady state each HBr molecule consumed by reaction (5) will yield a bromine atom. As there is no net termination involving bromine atoms (as Br_2 will readily photolyse to yield bromine atoms), this bromine will react with a molecule of propane via reaction (2) to produce another molecule of HBr.

As the concentration of HBr will be rising throughout the photolysis and as abstraction of a hydrogen atom from HBr is easier than the abstraction of hydrogen from propane, the chain length of the reaction will also be changing, thus introducing an error into equation (A).

This increase in chain length is shown by the increase in R_{CHCl_3} and decrease in $R_{\text{C}_2\text{Cl}_6}$ as the initial concentrations of HBr are increased.

Notwithstanding these deviations, equation (A) has been used to calculate a value of $k_5/k_6^{1/2}$. A graph has been plotted of

$R_{\text{CHCl}_3}/(R_{\text{C}_2\text{Cl}_6})^{1/2}$ versus hydrogen bromide initial concentration.

A straight line was obtained with a gradient of $57 \text{ l}^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}} \text{ s}^{-\frac{1}{2}}$
 (Figure 2.3) $k_5/k_6^{\frac{1}{2}} = 57 \text{ l}^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}} \text{ s}^{-\frac{1}{2}}$

As $\log k_6 = 9.7$, we have

$$\log k_5 - \frac{1}{2} \log k_6 = \log (57) = 1.76$$

$$\log k_5 = 1.76 + 4.85 \cong 6.6$$

$$\therefore k_5 = 4 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$$

Taking an average of the two values obtained at $[\text{HBr}]_i = 0$,

we have $\frac{R_{\text{CHCl}_3}}{(\text{R}_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}}} = 4.316 \times 10^{-4} \text{ mol}^{\frac{1}{2}} \text{ l}^{-\frac{1}{2}} \text{ s}^{-\frac{1}{2}}$

From equation (A) we have

$$4.316 \times 10^{-4} = \frac{k_4[\text{RH}] + k_5[\text{HBr}]}{k_6^{\frac{1}{2}}}$$

$$[\text{HBr}] = 0, [\text{RH}] = 2.834 \times 10^{-3} \text{ mol l}^{-1}$$

$$\therefore \frac{k_4}{k_6^{\frac{1}{2}}} = \frac{4.316 \times 10^{-4}}{2.834 \times 10^{-3}} = 0.152$$

$$\log k_4 - \frac{1}{2} \log k_6 = \log (0.152) = -0.817$$

$$\log k_6 = 9.7$$

$$\log k_4 = 4.85 - 0.817 \cong 4.0$$

$$k_4 = 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$$

(Using A_4 and E_4 from Section 2.7.1 we obtain $k_4 = 1.4 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ at 182°C). Hence, at the temperature employed for this series of experiments (ca 182°C) the rate of abstraction of a hydrogen atom from hydrogen bromide by a trichloromethyl radical is approximately 400 times greater than the rate of abstraction of a secondary hydrogen atom from propane by a similar radical. The rate of hydrogen abstraction from HCl by CCl_3 radicals has been measured⁴¹ by Huybrechts and De Mare

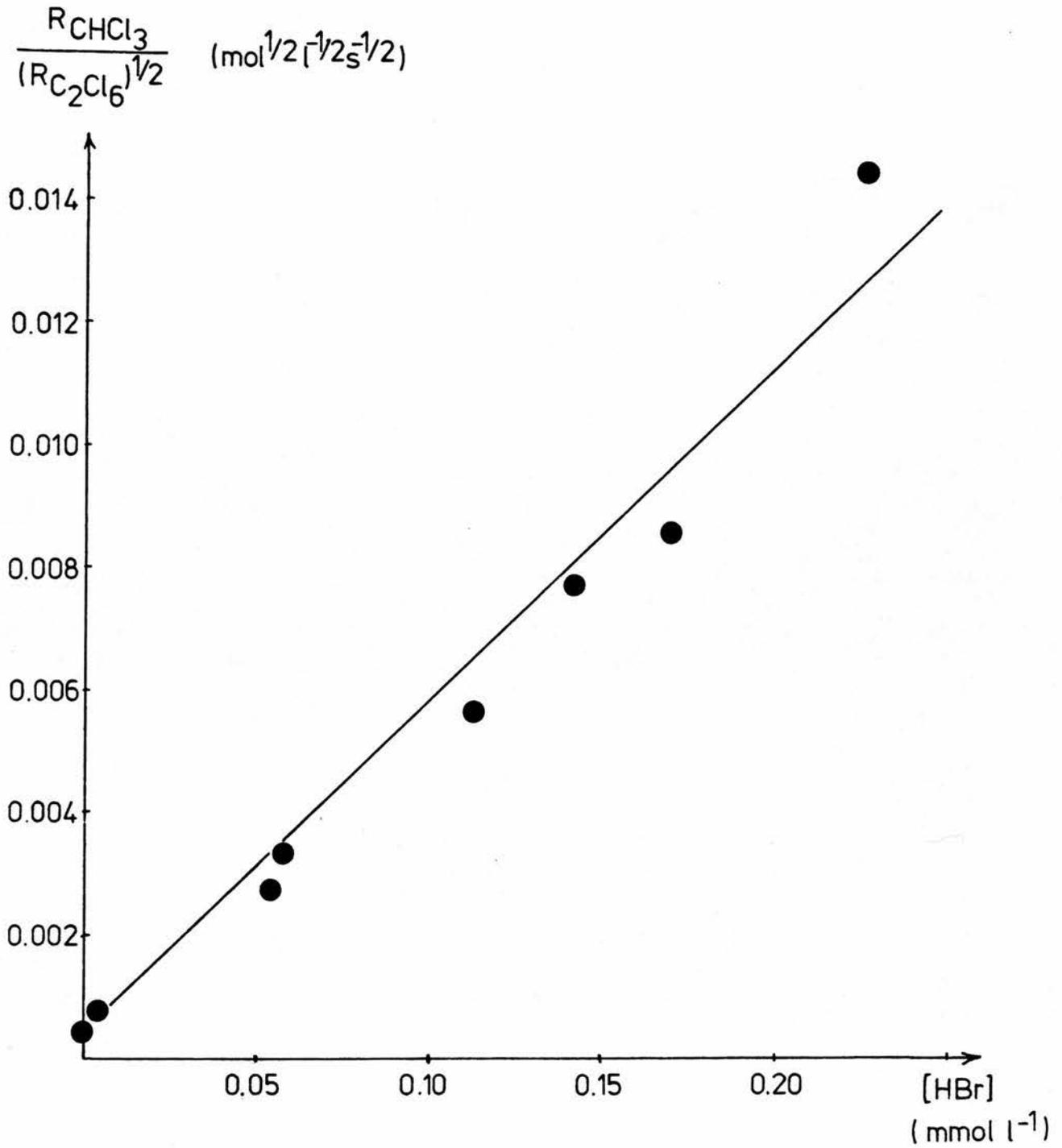


FIGURE 2.3

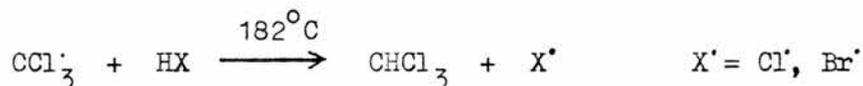
Graph of $\frac{R_{\text{CHCl}_3}}{(\text{RC}_2\text{Cl}_6)^{1/2}}$ versus concentration of added HBr

in the propane-bromotrichloromethane-hydrogen bromide system.

$$\text{as } k = 10^{8.65} \exp\left(\frac{-11,300}{RT}\right) \text{ l mol}^{-1} \text{ s}^{-1}$$

$$\text{rate at } 182^\circ\text{C} = 1.8 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$$

Therefore, for the reaction,



$$\text{we have } \frac{k_{\text{HBr}}}{k_{\text{HCl}}} = \frac{4 \times 10^6}{1.8 \times 10^3} \cong 2 \times 10^3 \text{ at } 182^\circ\text{C}$$

White and Kuntz³⁹ studied the gas phase photolysis of the carbon tetrachloride-cyclohexane system by the rotating sector method within the temperature range 112-183°C. It was proposed in Section 1.7 ($\text{CCl}_3\text{Br} + \text{c-C}_6\text{H}_{12}$) that the deviation between the results of White and Kuntz and those of this study were probably due to the participation of HBr in the system. The relative ease of hydrogen abstraction calculated above ($k_{\text{HBr}} = 2000 k_{\text{HCl}}$) shows that the HBr will be considerably more likely to participate in the $\text{CCl}_3\text{Br}-\text{C}_3\text{H}_8$ system than HCl would be in the $\text{CCl}_4-\text{C}_3\text{H}_8$ system and it is reasonable to assume that it participates to a similar extent in the $\text{CCl}_3\text{Br}-\text{c-C}_6\text{H}_{12}$ system.

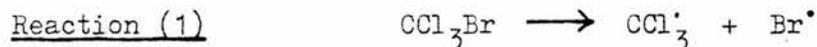
A further study of the reaction between trichloromethyl radicals and hydrogen bromide by reacting equal quantities of each ($1.417 \times 10^3 \text{ mol l}^{-1}$) in the absence of propane could not provide useful kinetic data as no C_2Cl_6 termination product could be detected. Even at 28°C, where the ratio $R_{\text{C}_2\text{Cl}_6} : R_{\text{CHCl}_3}$ would be expected to be higher than at more elevated temperatures, only chloroform was detected among the products ($R_{\text{CHCl}_3} = 1.87 \times 10^{-8} \text{ mol l}^{-1} \text{ s}^{-1}$). In view of the high rate obtained earlier for reaction (5) it would be quite surprising if the chain length was short enough to yield significant quantities of C_2Cl_6 .

A further series of experiments was carried out in which the propane concentrations were increased eightfold but the hydrogen bromide concentrations were maintained at the low level used for the earlier kinetic calculations. The results are shown in Table 2.9. It was hoped that this series may yield kinetic data at lower $\text{HBr} : \text{C}_3\text{H}_8$ ratios than the series of experiments described earlier. However the concentration of termination product C_2Cl_6 was again too low for detection under the conditions used to separate and quantitatively measure the products. The rates of formation of chloroform and isopropyl bromide were again very similar indicating that the reaction mechanism was unchanged.

2.7.3 Computer Simulation of the Propane + Bromotrichloromethane System

A computer programme, designed to simulate the progress of any gas phase chemical reaction by numerically integrating the differential equations which describe the rates of change of the reacting species, was used to model the propane + bromotrichloromethane system both with and without addition of hydrogen bromide to the reactants. Numerical integration of the differential equations is performed by an algorithm written by C.W. Gear¹¹¹⁻¹¹⁴ which is a predictor-corrector method specifically designed to solve "stiff" differential equations. (See Appendix 1). The input to the programme consists of the concentrations of the starting species, the reaction scheme to be considered with all rate data in Arrhenius form, the reaction temperature, and control data for the length of iterative step and the total reaction time. The output from the computer gives the concentrations of all chemical species included in the reaction scheme after various

reaction times. Values of Arrhenius parameters were not available for all forward and reverse reactions and consequently values were estimated or calculated for each reaction. These Arrhenius parameters were obtained as follows:-



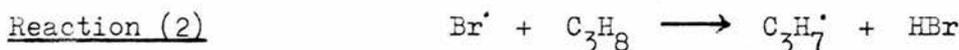
The rate of this initiation reaction will be dependent upon the intensity of the radiation within the reaction vessel, which itself would depend upon variables such as the age of the ultraviolet light source and the extent of carbon deposit on the window of the reaction flask nearest to the light source.

Thus no meaningful estimates of the preexponential term and the activation energy could be calculated from thermochemical considerations. It would have been possible to ensure some degree of consistency of initial intensity (i.e. before carbon deposit) by using a photometer to determine the required rheostat setting on the ultraviolet lamp power supply, but such an operation was not considered necessary. As the only termination reactions predicted by the mechanism proposed are reactions (-1) and (6) we can assume that the initiation rate is given by (1)-(-1) and at steady state operation this should be equal to the rate of reaction (6). The rate of reaction (-6) will be negligible because of the strength⁴⁰ of the $\text{CCl}_3\text{-CCl}_3$ bond. Consequently, the rate of reaction (1) was determined for the computer simulation as being that value which would yield a concentration of hexachloroethane similar to that obtained experimentally at the same temperature. The activation energy was fixed at zero and the preexponential term varied to yield the desired initiation rate.

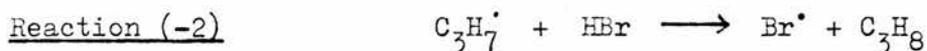
Footnote: As the units required for A-factors in the computer programme were $\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$, these units are used for the estimated A-factors obtained on pages 66-73.



As explained above, the absolute values of the Arrhenius parameters of this reaction are of minor importance in the computer simulation, as long as the net initiation rate (1)-(-1) will yield a final concentration of hexachloroethane equal to that obtained by experiment. As the only radical-radical recombinations with an activation energy are those in which steric restrictions must be overcome⁴⁴, the activation energy of this reaction was set equal to zero (there being no such steric restrictions). The pre-exponential term was estimated as $A_{-1} = 6.99 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.



The Arrhenius parameters for this equation have been determined by Fettis, Knox and Trotman-Dickenson¹¹⁵. They calculated $E_2 = 10.2 \text{ kcal mol}^{-1}$ and $A_2 = 1.585 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.



An approximate value for the activation energy can be obtained by calculating ΔH_{-2} the enthalpy change and using the relationships

$$(A) \quad E_{-2} = E_2 + \Delta H_{-2}^\circ$$

$$(B) \quad \Delta H_{-2}^\circ = \Delta H_f^\circ(\text{C}_3\text{H}_8) + \Delta H_f^\circ(\text{Br}) - \Delta H_f^\circ(\text{C}_3\text{H}_7) - \Delta H_f^\circ(\text{HBr})$$

We have $\Delta H_f^\circ(\text{C}_3\text{H}_8) = -24.9$ (Selley¹¹⁶) -24.81 (Prosen et al¹¹⁷) (in kcal mol⁻¹)

$$\Delta H_f^\circ(\text{Br}) = 26.71 \text{ kcal mol}^{-1} \text{ (Benson}^{118})$$

$$\Delta H_f^\circ(\text{Pr}^i) = 17.6 \text{ (Benson}^{119}), 18.2 \text{ (Hiatt \& Benson}^{50}) \text{ (in kcal mol}^{-1})$$

$$\Delta H_f^\circ(\text{HBr}) = 8.60 \text{ (Selley}^{116}), -8.7 \text{ (Benson}^{119}), -8.66 \text{ (Mendenhall et al}^{120}) \text{ (in kcal mol}^{-1})$$

Hence, from (B), $\Delta H_{-2}^\circ = (-24.8 + 26.7 - 17.6 + 8.7) = -7 \text{ kcal mol}^{-1}$

$$\text{from (A), } E_{-2} = 10.2 - 7 = 3.2 \text{ kcal mol}^{-1}$$

A value of 3 kcal mol^{-1} was used in the computer simulation exercises for the value of activation energy E_{-2} .

In dilute gases the measured equilibrium constant K_e is related to the standard free energy change ΔG° of a stoichiometric reaction by the relation

$$\begin{aligned}\Delta G^\circ &= RT \ln K_e \\ &= 2.303 RT \log K_e \\ K_e &= \exp\left(\frac{-\Delta G^\circ}{RT}\right)\end{aligned}$$

As $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ we have

$$K_e = e^{\left(\frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}\right)} \quad \text{-----} \quad \text{(C)}$$

The equilibrium constant K_e can be defined as the ratio of the rate of the forward reaction (k_f) to the rate of the back reaction (k_b)

$$\begin{aligned}\text{i.e. } K_e &= \frac{k_f}{k_b} = \frac{A_f e^{-E_f/RT}}{A_b e^{-E_b/RT}} \\ &= \frac{A_f}{A_b} e^{-(E_f - E_b)/RT}\end{aligned}$$

Substituting (C) in this equation, and $\Delta H^\circ = (E_f - E_b)$ from equation

$$\begin{aligned}\text{(A), we have } \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} &= \frac{A_f}{A_b} e^{(-\Delta H^\circ/RT)} \\ e^{\frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}} &= \frac{A_f}{A_b} e^{(-\Delta H^\circ/RT)} \\ S^\circ &= R \ln \frac{A_f}{A_b} \quad \text{-----} \quad \text{(D)}\end{aligned}$$

This equation can be used to determine the pre-exponential item A_{-2}

$$\log_{10} A_{-2} - \log_{10} A_2 = \frac{\Delta S^\circ}{2.303 R} = \frac{\Delta S^\circ}{4.574} \quad \text{-----} \quad \text{(E)}$$

We have

$$\begin{aligned}
 S^\ominus (\text{Br}) &= 41.8 \text{ cal mol}^{-1} \text{ K}^{-1} \quad (\text{Benson}^{118}) \\
 S^\ominus (\text{Pr}^i) &= 66.7 \text{ cal mol}^{-1} \text{ K}^{-1} \quad (\text{Hiatt \& Benson}^{50}) \\
 S^\ominus (\text{HBr}) &= 47.4 \text{ cal mol}^{-1} \text{ K}^{-1} \quad (\text{Mendenhall,} \\
 &\hspace{15em} \text{Golden \& Benson}^{120})
 \end{aligned}$$

An empirical method of determination of S^\ominus values is given by Benson¹¹⁹ as being the sum of the S^\ominus values of the component groups less a term $R \ln \sigma$ which accounts for the symmetry of the molecule. All normal alkanes shall, by this method, have an external twofold axis and two threefold axes for the terminal methyl groups. The value of σ is defined as the total number of independent permutations of identical groups within the molecule. For normal alkanes, therefore $\sigma = 2 \times 3 \times 3 = 18$

$$S^\ominus (\text{C}_3\text{H}_8) = 2 \times S^\ominus [\text{C}-(\text{H})_3\text{C}] + S^\ominus [\text{C}-(\text{H})_2(\text{C})_2] - R \ln 18$$

The values of the partial contributions of the $[\text{C}-(\text{H})_3\text{C}]$ and $[\text{C}-(\text{H})_2(\text{C})_2]$ groups are given by Benson¹¹⁹ as 30.41 and 9.42 cal mol⁻¹ C⁰⁻¹ respectively.

$$S^\ominus (\text{C}_3\text{H}_8) = 60.82 + 9.42 - 5.8 = 64.44 \text{ cal mol}^{-1} \text{ K}^{-1}$$

As the S^\ominus values have now been calculated for each component of reaction (-2) the overall ΔS^\ominus for the reaction can be calculated

$$\begin{aligned}
 \text{as:- } \Delta S_{-2}^\ominus &= S^\ominus (\text{Br}) + S^\ominus (\text{C}_3\text{H}_8) - S^\ominus (\text{HBr}) - S^\ominus (\text{Pr}^i) \\
 &= 41.8 + 64.4 - 47.4 - 66.7 \\
 &= -7.9 \text{ cal mol}^{-1} \text{ K}^{-1}
 \end{aligned}$$

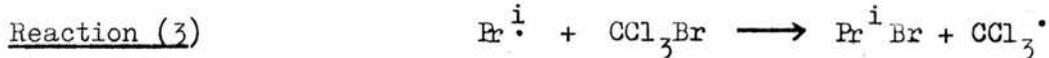
As $\log A_2 = 13.2$ we obtain from equation (E)

$$\log A_{-2} = 13.2 - \frac{7.9}{4.574} = 11.47$$

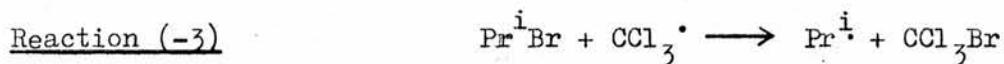
The activation energy had been rounded down to 3 kcal mol⁻¹ from a calculated estimate of 3.2 kcal mol⁻¹; the pre-exponential term was also reduced slightly to $\log A_{-2} = 11.2$ in an attempt to reduce the error in reaction rate. As the Arrhenius parameters were calculated by such an indirect route it is very difficult to

predict the magnitude of the error. We have therefore

$$E_{-2} \cong 3 \text{ kcal mol}^{-1} \text{ and } A_{-2} \cong 1.25 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$



Tomkinson and Pritchard¹²⁷ studied the equivalent reaction with methyl instead of isopropyl radicals and obtained an activation energy of $7.1 \text{ kcal mol}^{-1}$ and a pre-exponential term $\log A = 13.2 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Using this data, values of A_3 and E_3 were estimated as $E_3 = 7.1 \text{ kcal mol}^{-1}$ and $\log A_3 = 12 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (i.e. $A_3 = 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). The pre-exponential term would be reduced for steric reasons but the activation energy would not be expected to change significantly on replacing the methyl group with an isopropyl group.



The value of A_{-3} was calculated in a similar manner to the value of A_{-2} . We have

$$S^{\ominus}(\text{CCl}_3^{\cdot}) = 70.8 \text{ cal mol}^{-1} \text{ K}^{-1} \text{ (Benson}^{119})$$

$$S^{\ominus}(\text{Pr}^{\cdot i}) = 66.7 \text{ cal mol}^{-1} \text{ K}^{-1} \text{ (Hiatt \& Benson}^{50})$$

$$S^{\ominus}(\text{CCl}_3\text{Br}) = 79.8 \text{ cal mol}^{-1} \text{ K}^{-1} \text{ (Benson}^{119})$$

As the value of $S^{\ominus}(\text{Pr}^i\text{Br})$ was not available from the literature an estimated value was used. Benson¹¹⁹ quotes S^{\ominus} values of $\text{C-Br(H)}_2\text{C} = 40.8 \text{ cal mol}^{-1} \text{ K}^{-1}$ and $\text{C-Br(C)}_3 = 2.0 \text{ cal mol}^{-1} \text{ K}^{-1}$.

The value of C-BrH(C)_2 was estimated as $19.2 \text{ cal mol}^{-1} \text{ K}^{-1}$

(In the equivalent iodine and chlorine series the value of S^{\ominus} for C-XH(C)_2 was approximately midway between the values of S^{\ominus} for $\text{C-X(H)}_2\text{C}$ and C-X(C)_3). As isopropyl bromide has two internal threefold symmetry axes due to the methyl groups we obtain

$$\begin{aligned}
 S^\ominus (\text{Pr}^i\text{Br}) &= 2 \times S^\ominus [\text{C}-(\text{H})_3\text{C}] + S^\ominus [\text{C}-\text{BrH}(\text{C})_2] - R \ln (3 \times 3) \\
 &= 60.8 + 19.2 - 4.4 \\
 &= 75.6 \text{ cal mol}^{-1}\text{K}^{-1}
 \end{aligned}$$

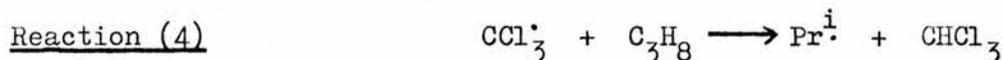
As $\log A_3 = 12 \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}$ we can calculate $\log A_{-3}$ from the equation

$$\log_{10} A_{-3} - \log_{10} A_3 = \frac{\Delta S^\ominus}{4.574}$$

This is the equivalent equation to that used to calculate $\log_{10} A_{-2}$ (i.e. equation (E)).

$$\begin{aligned}
 \Delta S^\ominus_{-3} &= S^\ominus (\text{CCl}_3\text{Br}) + S^\ominus (\text{Pr}^i) - S^\ominus (\text{Pr}^i\text{Br}) - S^\ominus (\text{CCl}_3) \\
 &= 79.8 + 66.7 - 75.6 - 70.8 \\
 &= 0.1 \text{ cal mol}^{-1}\text{K}^{-1} \\
 \therefore \log A_{-3} - \log A_3 &= \frac{0.1}{4.574} \\
 \therefore \log A_{-3} &= 12 + \frac{0.1}{4.574} \cong 12 \\
 \therefore A_{-3} &= 10^{12} \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}
 \end{aligned}$$

The value of ΔH^\ominus_{-3} was not available from published data. The activation energy was estimated at 10 kcal mol^{-1} for the purpose of computer simulation of the system. Because of the low concentrations of CCl_3 radicals and Pr^iBr molecules the value of the activation energy should not prove critical to the final product ratios obtained by computer simulation.



To obtain a value for A_4 and E_4 the first few runs of the $\text{C}_3\text{H}_8 + \text{CCl}_3\text{Br}$ system were used. A graph was plotted of $\log_{10} (R_{\text{CHCl}_3} / R_{\text{C}_2\text{Cl}_6}^{1/2} [\text{C}_3\text{H}_8])$ versus the reciprocal of temperature (as in Figure 2.2) and values of E_4 and $\log A_4$ were calculated as in the first part of this discussion. The values obtained were $E_4 = 8.57 \text{ kcal mol}^{-1}$ and $\log A_4 = 10.13 \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}$ (i.e. $A_4 = 1.35 \times 10^{10} \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}$). Although subsequent runs in the $\text{C}_3\text{H}_8 + \text{CCl}_3\text{Br}$ system resulted in some change in these Arrhenius

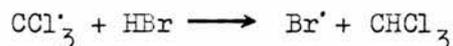
parameters, these values were used throughout the computer simulation work.

Reaction (-4)



A calculation similar to that used to determine ΔH_{-2} showed this reaction to be endothermic by approximately 1 kcal mol^{-1} . E_{-4} will therefore be approx. 1 kcal mol^{-1} greater than E_4 . A value of $E_{-4} = 10 \text{ kcal mol}^{-1}$ was used. It was assumed that the pre-exponential term would be similar to that of reaction (-2) and consequently an estimated value of $\log A_{-4} = 11.2 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was used. (i.e. $A_{-4} = 1.585 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).

Reaction (5)



It was to obtain the Arrhenius parameters of this step that the computer simulation exercise had been employed. As all experiments involving addition of HBr had been carried out at the same temperature, the most which could be obtained would be a measure of the rate constant $k_5 (=A_5 \exp(-E_5/RT))$. The calculations in part 2 of this discussion yielded an approximate value of $\log k_5(455^\circ\text{A}) = 9.6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (see calculation below for alternative value).

Reaction (-5)



Arrhenius parameters for this equation have been calculated by Sullivan & Davidson¹⁰⁹ as $\log A_{-5} = 12.4 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $E_{-5} = 9.3 \text{ kcal mol}^{-1}$. Using these values, approximate values of A_5 and E_5 could be obtained. ΔH_5° can be calculated from ΔH_f° values:- We have $\Delta H_f^\circ (\text{CCl}_3) = 18.5$ (Benson¹¹⁹), 18.7 (Benson¹¹⁸), 19.0 (Mendenhall et al¹²⁰) kcal mol^{-1} .

$$\Delta H_f^\circ (\text{HBr}) = 8.66 \text{ kcal mol}^{-1} \quad (\text{see calculation of } E_{-2})$$

$$\Delta H_f^\circ (\text{CHCl}_3) = -24.7 \text{ (Benson}^{118}), -25 \text{ (Benson}^{119}) \text{ kcal mol}^{-1}$$

$$\Delta H_f^\circ (\text{Br}) = 26.71 \text{ kcal mol}^{-1} \quad (\text{see calculation of } E_{-2})$$

$$\Delta H_5^\circ = -(18.7 - 8.66) + (26.71 - 25) \cong -8.3 \text{ kcal mol}^{-1}$$

$$E_{+5} = E_{-5} + \Delta H_5^\circ \cong 9.3 - 8.3 = 1.0 \text{ kcal mol}^{-1}$$

The pre-exponential term can be calculated in a similar manner

to A_{-2} , i.e. from the values of ΔS_5^\ddagger and A_{-5} . We have:-

$$S^\ddagger (\text{CCl}_3^\bullet) = 70.8 \text{ cal mol}^{-1} \text{ K}^{-1} \quad (\text{see calculation of } A_{-3})$$

$$S^\ddagger (\text{HBr}) = 47.4 \text{ cal mol}^{-1} \text{ K}^{-1} \quad (\text{see calculation of } A_{-2})$$

$$S^\ddagger (\text{CHCl}_3) = 70.7 \text{ cal mol}^{-1} \text{ K}^{-1} \quad (\text{JANAF tables}^{122})$$

$$S^\ddagger (\text{Br}^\bullet) = 41.8 \text{ cal mol}^{-1} \text{ K}^{-1} \quad (\text{see calculation of } A_{-2})$$

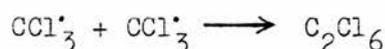
$$\Delta S_5^\ddagger = -(70.8 + 47.44) + (70.7 + 41.8) = -5.74 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$\log A_5 - \log A_{-5} = \frac{5.74}{4.574} = -1.25$$

$$\log A_5 = 9.4 - 1.25 = 8.15 \text{ l mol}^{-1} \text{ s}^{-1} = 11.15 \text{ cm}^3 \text{ mol}^{-1} \text{ l}^{-1}$$

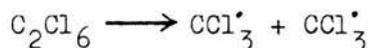
Using the approximate Arrhenius parameters calculated here ($E_5 = 1 \text{ kcal mol}^{-1}$, $\log A_5 = 11.15 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) we obtain $\log k_5^{455^\circ \text{A}} = 10.6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (cf value calculated from experimental results, $\log k_5^{455^\circ \text{A}} = 9.6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). These values are not inconsistent considering the many assumptions and approximations employed in their derivation.

Reaction (6)



Arrhenius parameters for this combination reaction have been obtained from other work carried out in this laboratory⁴¹. These values were used in the computer simulation viz. $\log A_6 = 12.7 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $E_6 = 0 \text{ kcal mol}^{-1}$.

Reaction (-6)



Kuntz and White⁴⁰ calculated an activation energy of 68 kcal mol^{-1} and a pre-exponential of $\log A(-6) = 17.7 \text{ s}^{-1}$. The values of the Arrhenius parameters obtained from the previous calculations were used to simulate the progress of the reaction. As no figure was obtained for a reaction time of exactly 1200s., the concentrations at times before and

after 1200s were calculated and, by graphical interpolation (Figures 2.4,2.5,2.7,2.8) values of $[\text{CHCl}_3]$ and $[\text{C}_2\text{Cl}_6]$ were obtained for $t=1200\text{s}$. By variation of the initiation rate A_1 a C_2Cl_6 final concentration was estimated equivalent to that obtained experimentally. This was also done graphically (Figures 2.6.2,2.9.2) and by comparison with the R_{CHCl_3} vs A_1 graph (figures 2.6.1,2.9.1), corresponding values of R_{CHCl_3} and $R_{\text{C}_2\text{Cl}_6}$ could be calculated for a given set of reaction conditions and Arrhenius parameters. From these values the ratio $R_{\text{CHCl}_3}/(R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}}$ could be calculated and compared with the values obtained experimentally. It was found that the rate of reaction 5 ($\text{CCl}_3 + \text{HBr}$) had a very significant effect on the results. At a reaction rate $k_5 = 5.1 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ ($E_5 = 3.55 \text{ kcal mol}^{-1}$, $A_5 = 2.5 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$, $\text{temp} = 455.5^\circ\text{K}$) a reasonably good fit was obtained between simulated and experimental data. As the plot of $R_{\text{CHCl}_3}/(R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}}$ was linear it was felt necessary to match only two points on the line. The points selected were $[\text{HBr}]_i = 5.67 \times 10^{-2} \text{ mmol l}^{-1}$ and $[\text{HBr}]_i = 1.70 \times 10^{-1} \text{ mmol l}^{-1}$. As two experiments were carried out at the lower HBr concentration, i.e. at 5.38×10^{-2} and $5.67 \times 10^{-2} \text{ mmol l}^{-1}$, the values of R_{CHCl_3} and $R_{\text{C}_2\text{Cl}_6}$ taken were the arithmetic means of those obtained from experiment. The results are shown in Table 2.10. This yielded a $R_{\text{CHCl}_3}/(R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}}$ vs. $[\text{HBr}]$ plot as shown in Figure 2.10. It can be seen that the gradient of the line from the computer simulation is slightly less than that of the experimental data suggesting that the reaction rate of $k_5 = 5.1 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ may be somewhat less than the actual value. However, since not all Arrhenius parameters in the simulation were absolute values

FIGURE 2.4.1

$$A_1 = 5.40 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

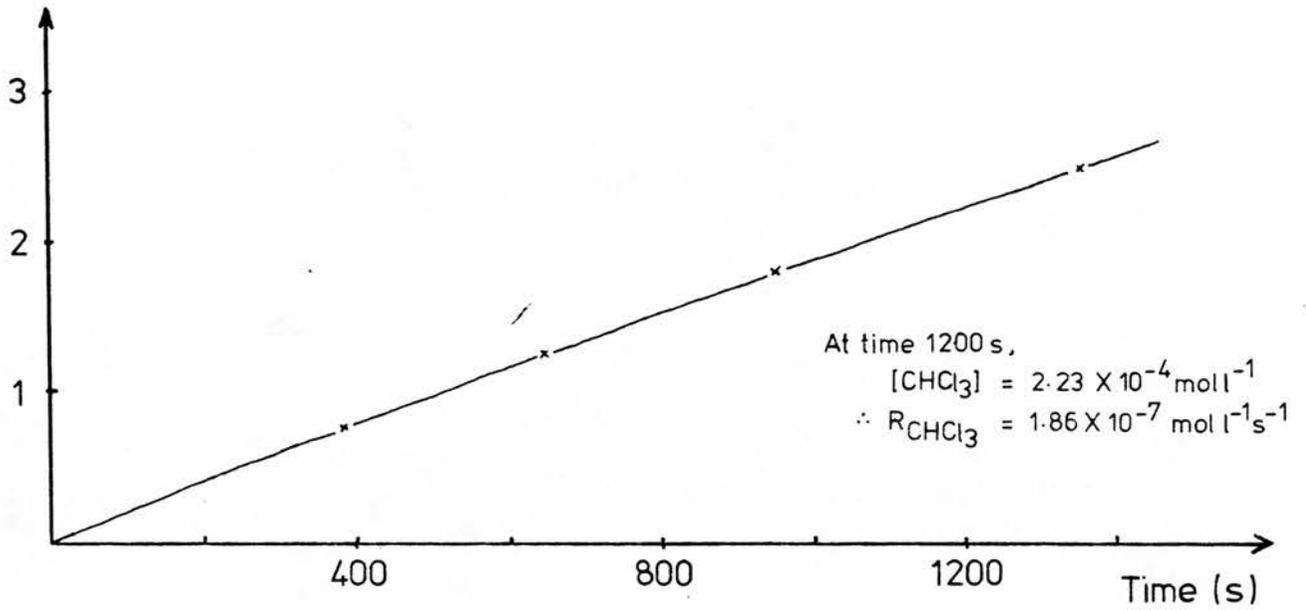
 $10^4 [\text{CHCl}_3] \text{ in mol l}^{-1}$


FIGURE 2.4.2

$$A_1 = 5.85 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

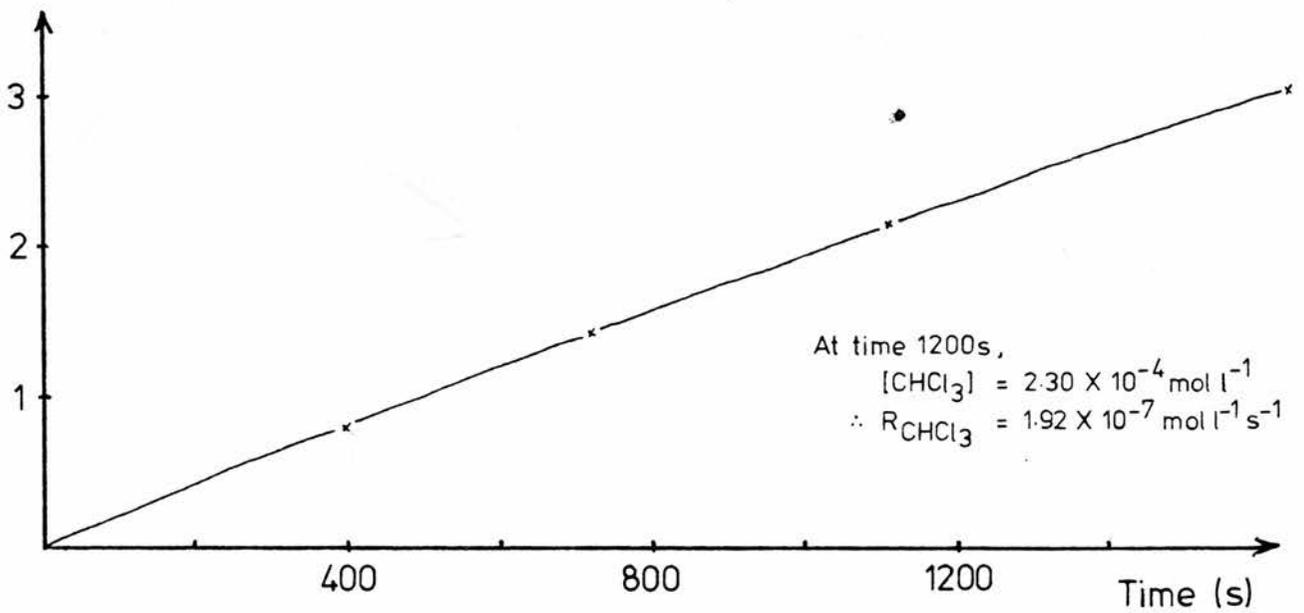
 $10^4 [\text{CHCl}_3] \text{ in mol l}^{-1}$


FIGURE 2.4.3

$$A_1 = 7.5 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

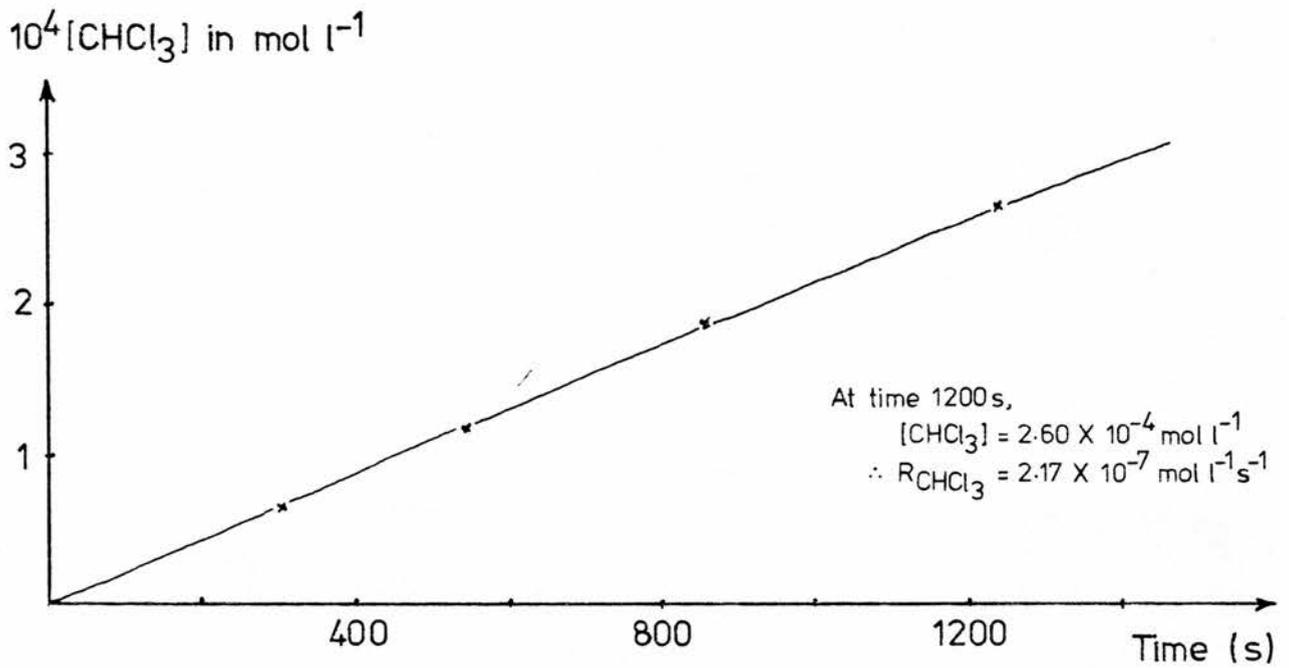


FIGURE 2.4.4

$$A_1 = 8.25 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

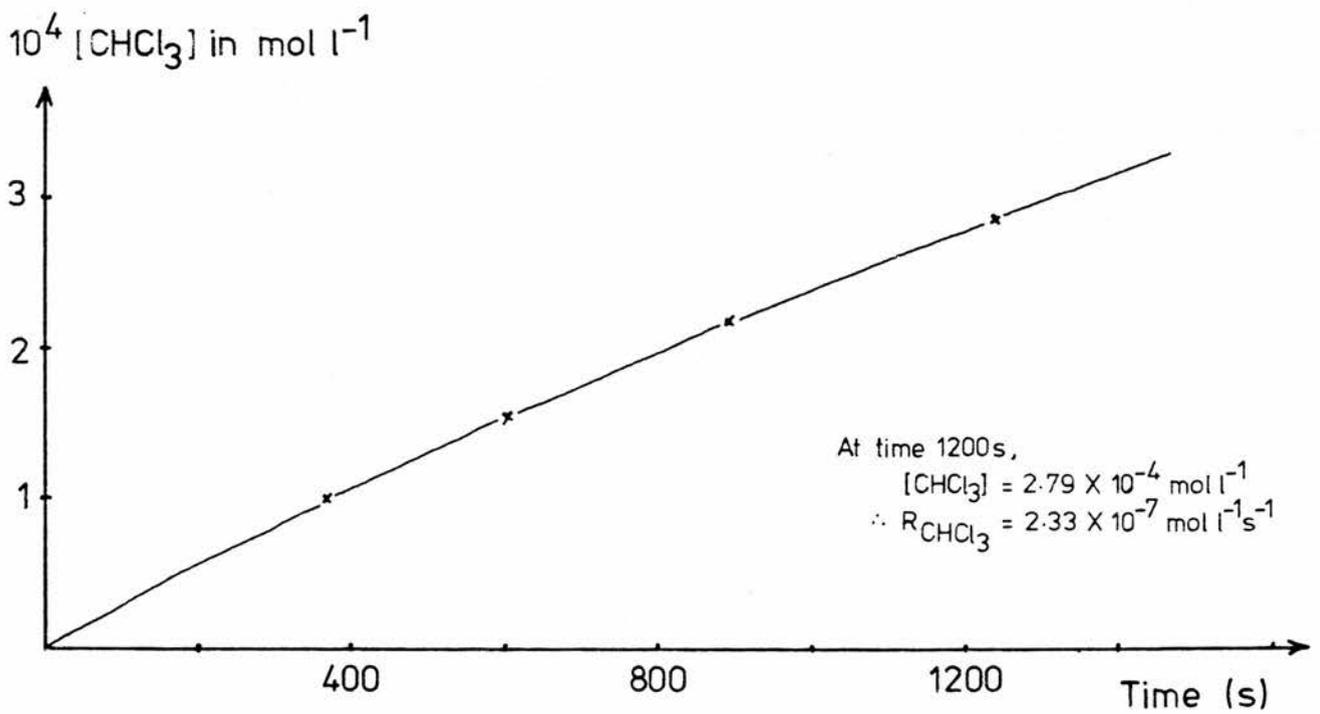


FIGURE 2.5.1

$$A_1 = 5.40 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

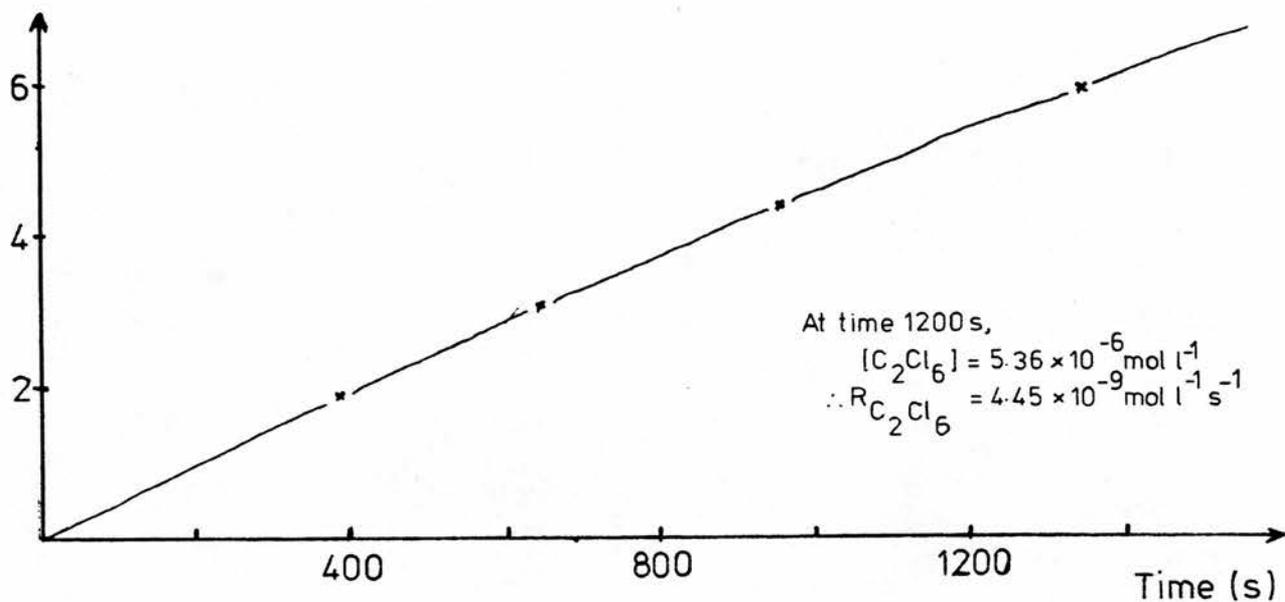
 $10^6 [\text{C}_2\text{Cl}_6] \text{ in mol l}^{-1}$


FIGURE 2.5.2

$$A_1 = 5.85 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

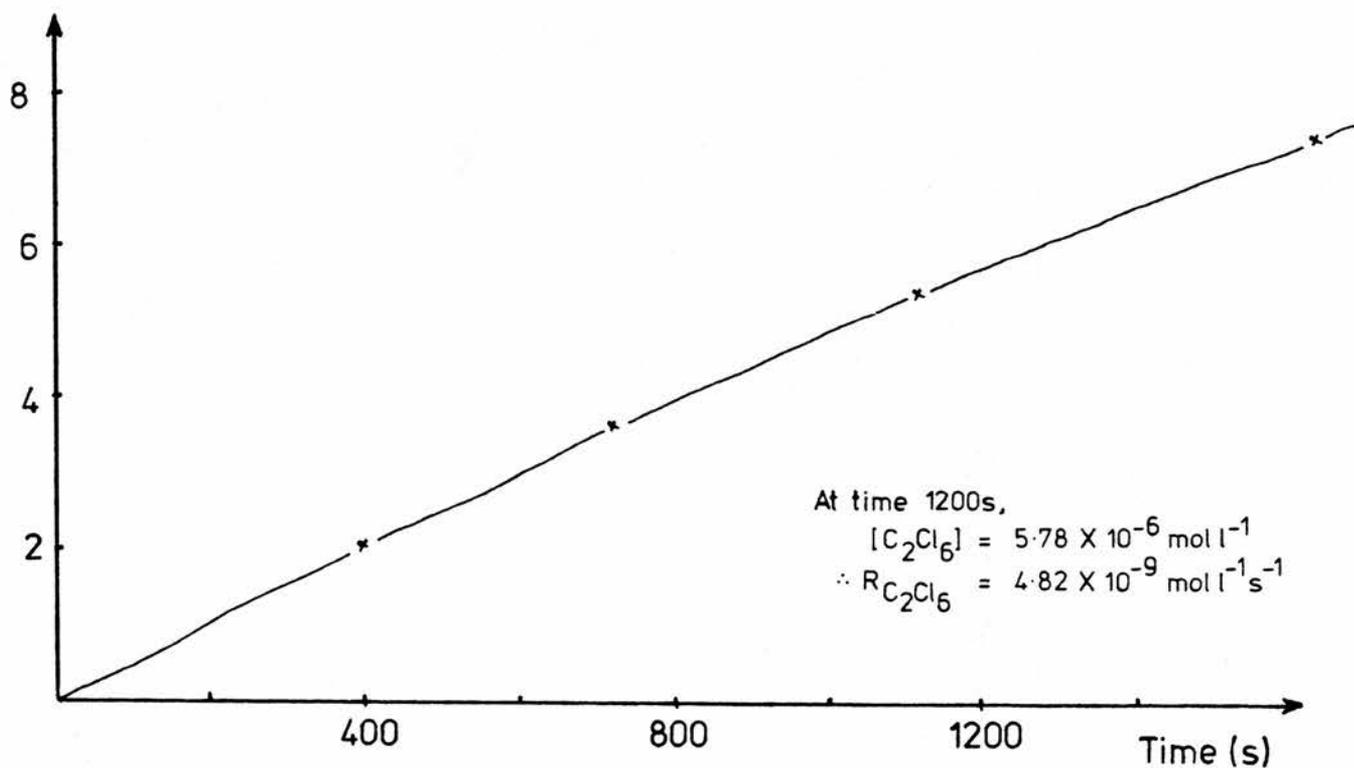
 $10^6 [\text{C}_2\text{Cl}_6] \text{ in mol l}^{-1}$


FIGURE 2.5.3 $A_1 = 7.5 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

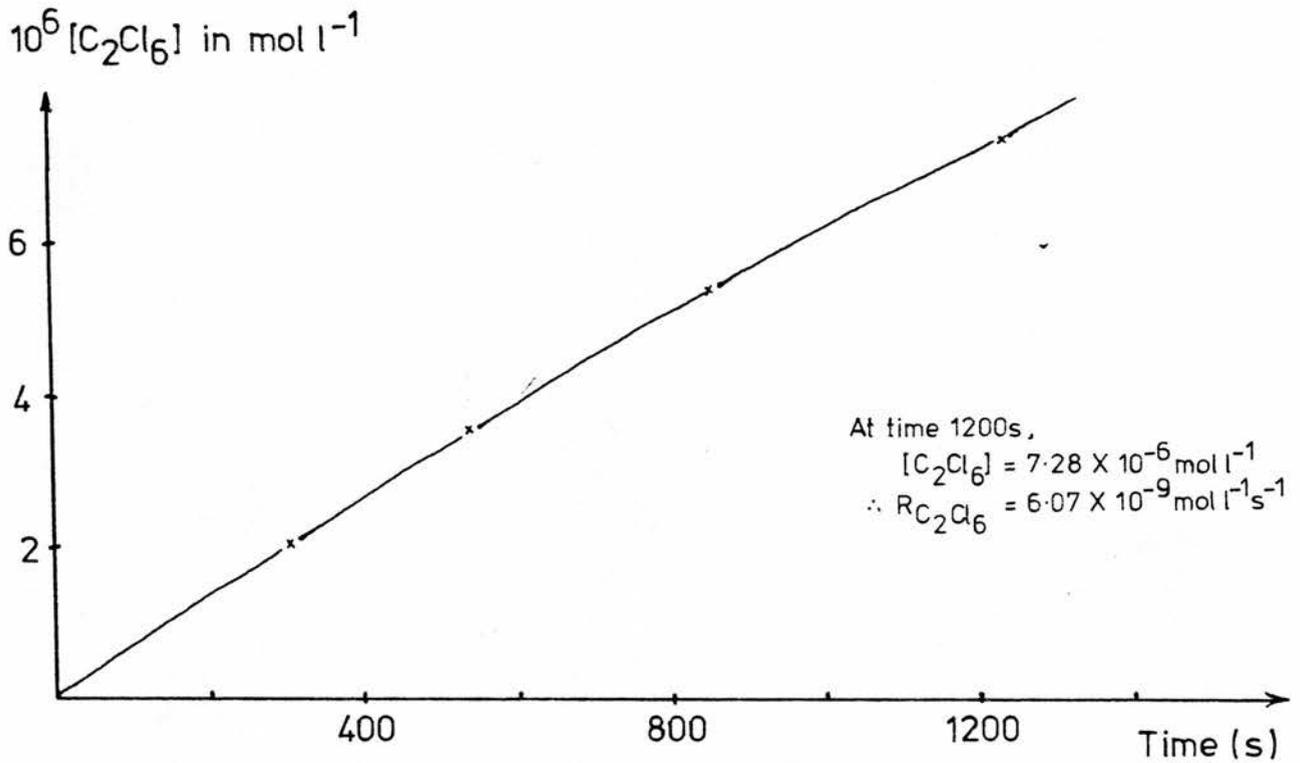


FIGURE 2.5.4 $A_1 = 8.25 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

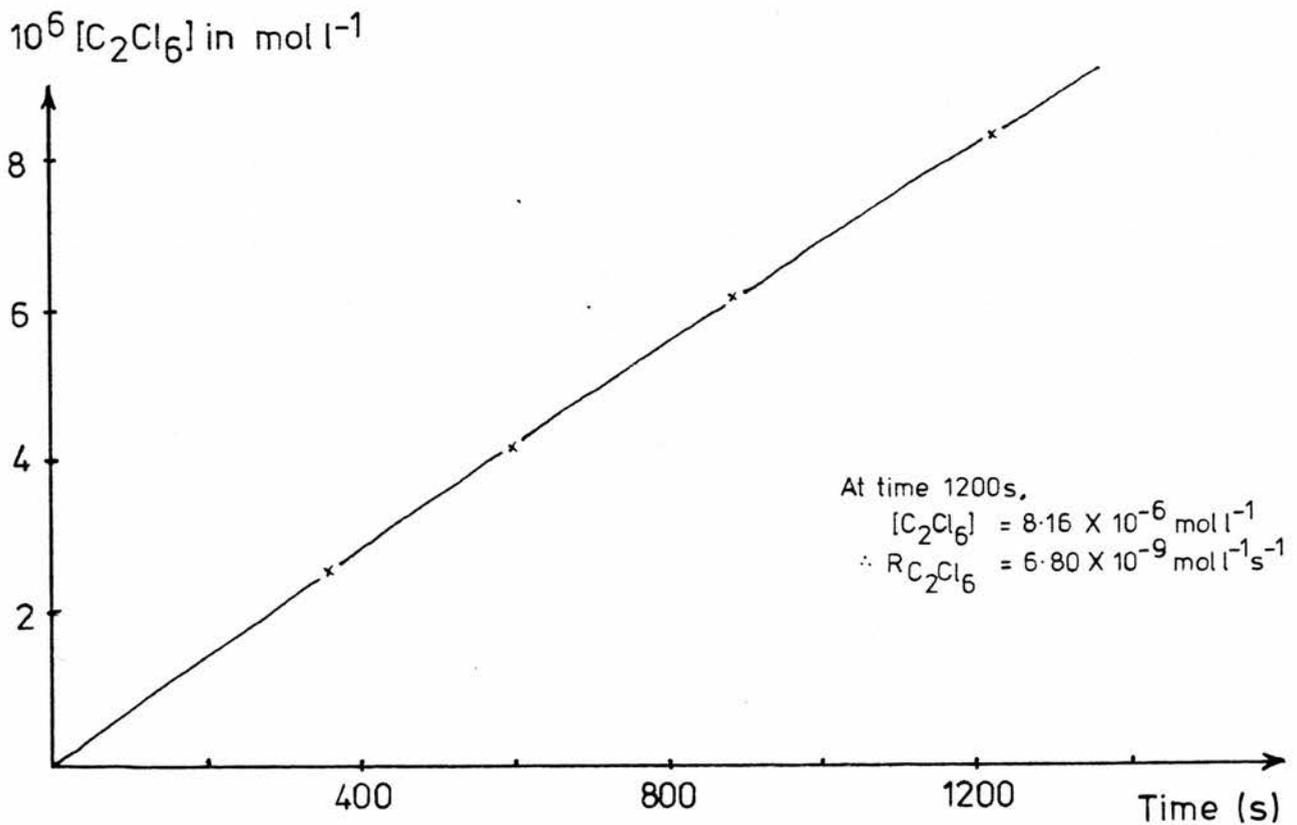


FIGURE 2.6.1 The Effect of Changing A_1 on the Rate of CHCl_3 Formation. (in mol/l/s)

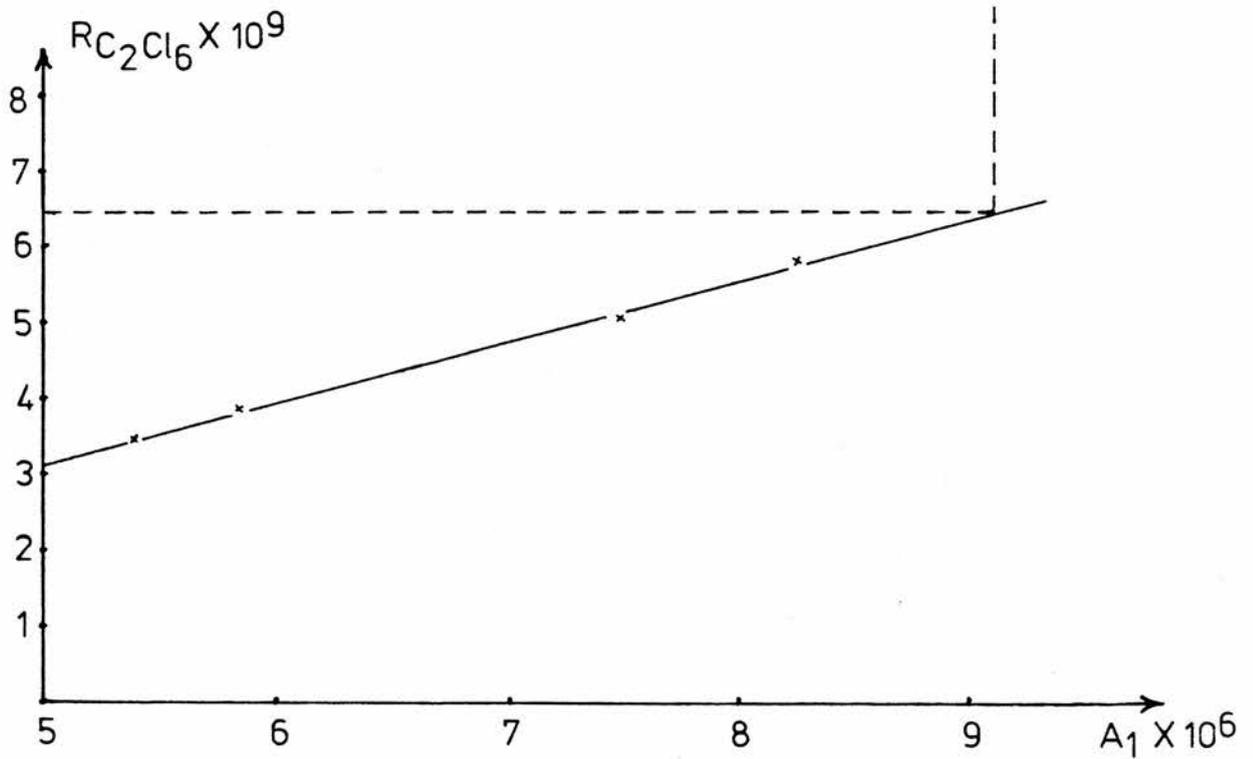
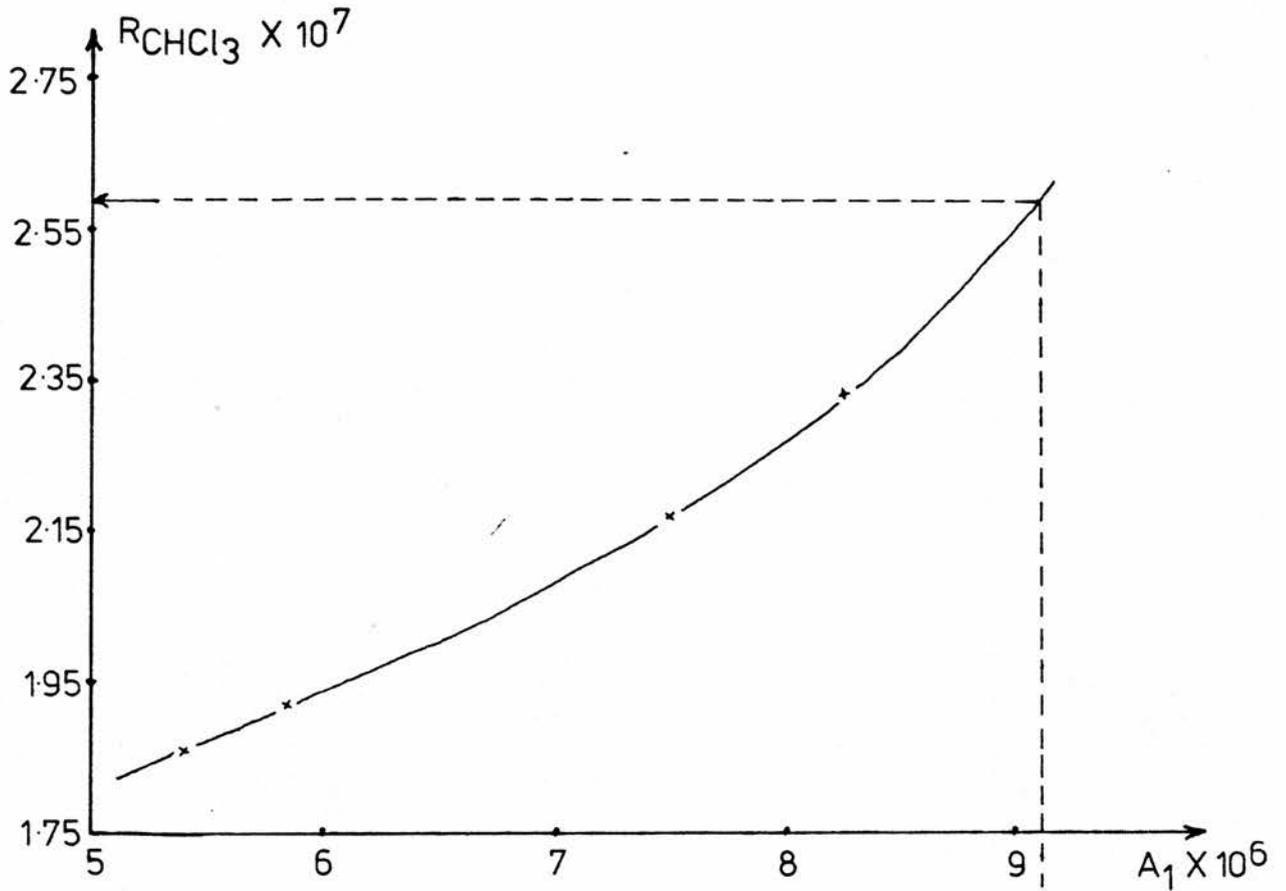


FIGURE 2.6.2 The Effect of Changing A_1 on the Rate of C_2Cl_6 Formation (in mol/l/s)

FIGURE 2.7.1

$$A_1 = 3.0 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

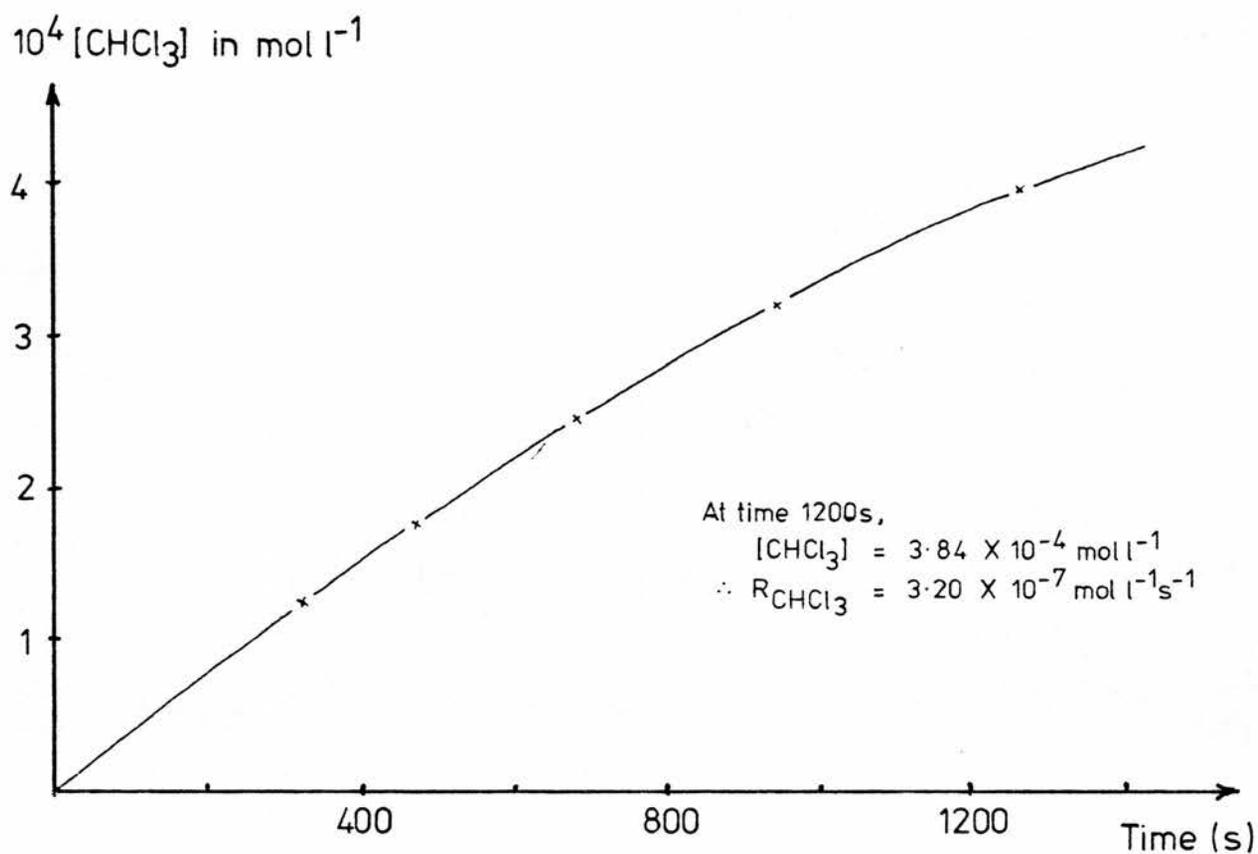


FIGURE 2.7.2

$$A_1 = 4.3 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

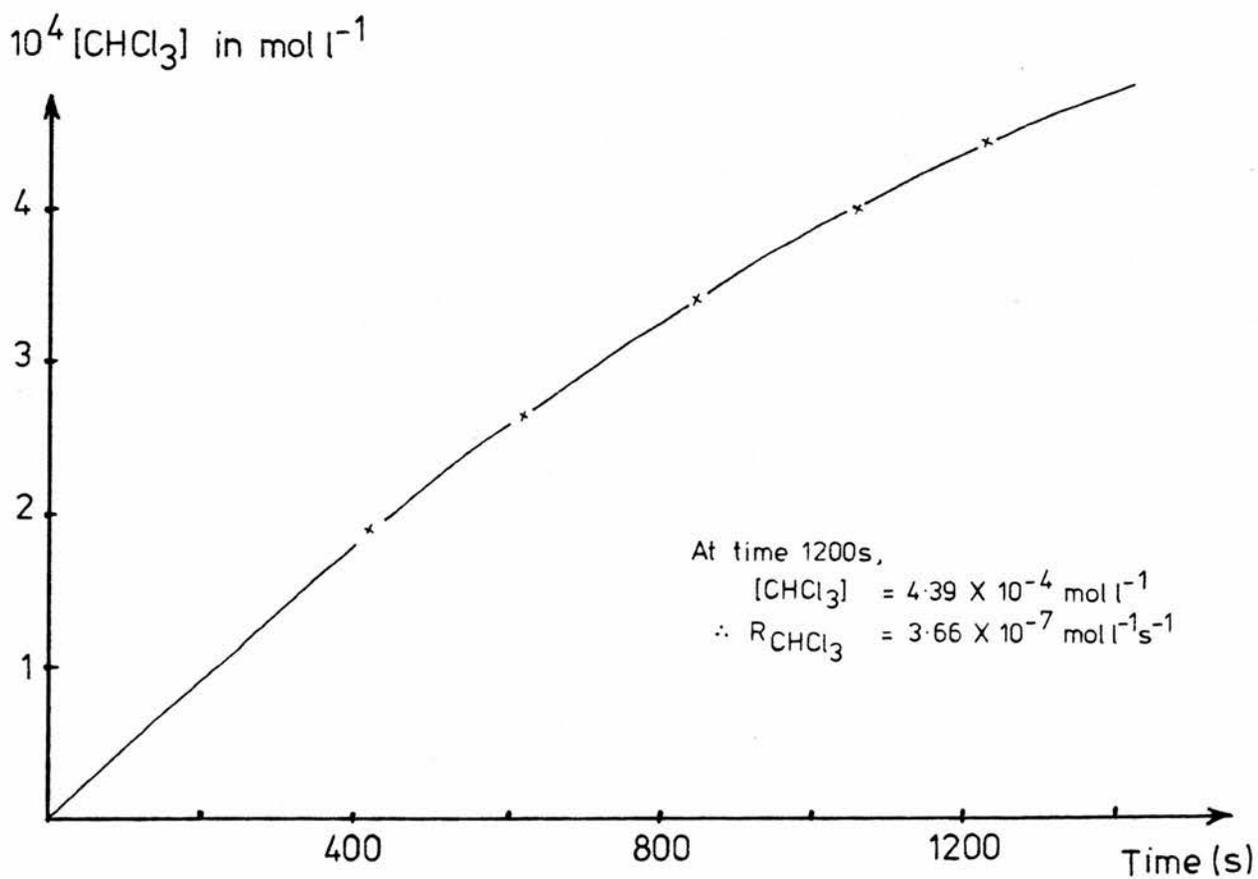


FIGURE 2.7.3

$$A_1 = 5.0 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

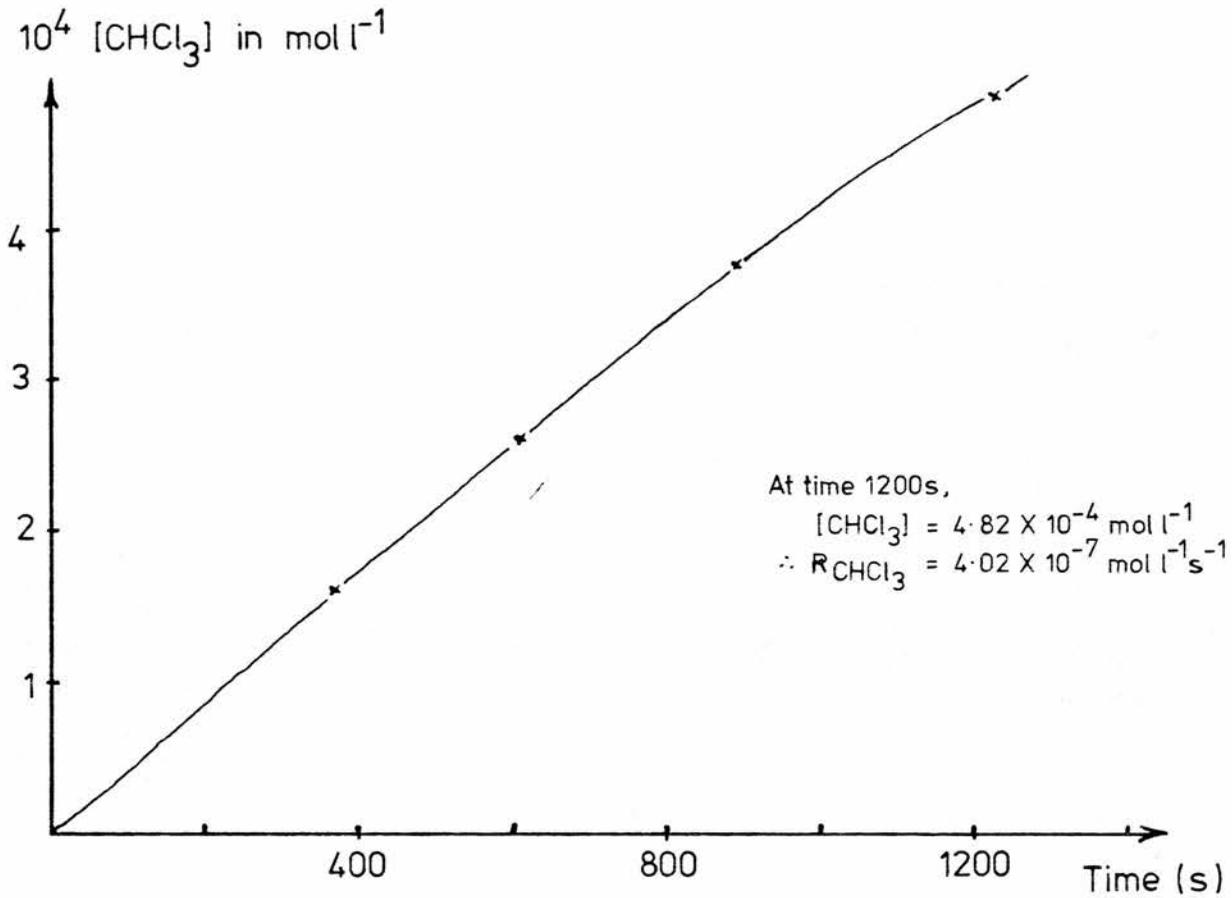


FIGURE 2.8.1

$$A_1 = 3.0 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

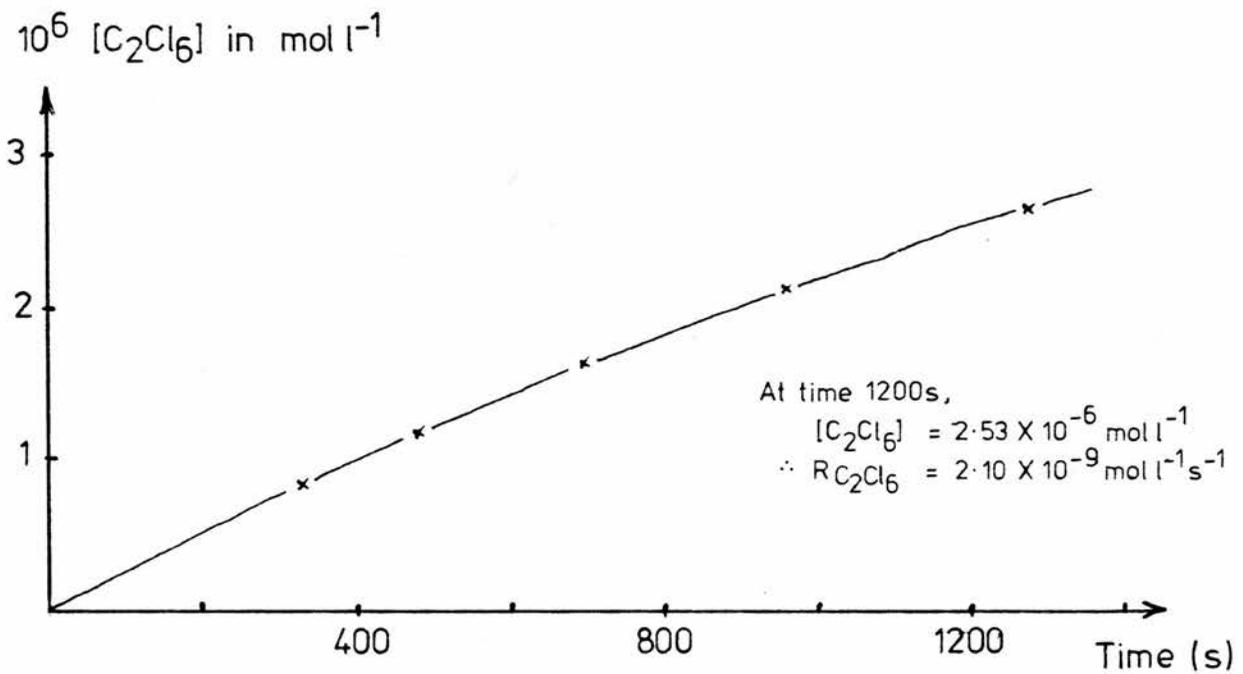


FIGURE 2.8.2

$$A_1 = 4.3 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

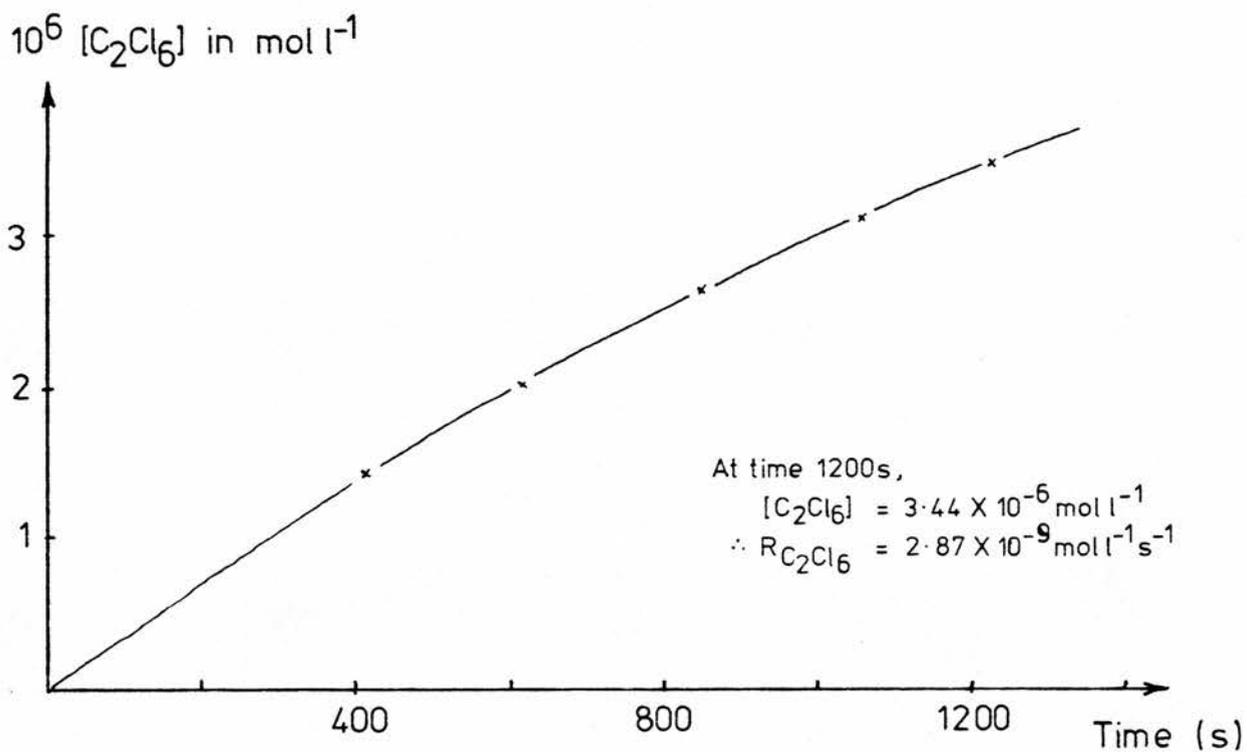


FIGURE 2.8.3

$$A_1 = 5.0 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

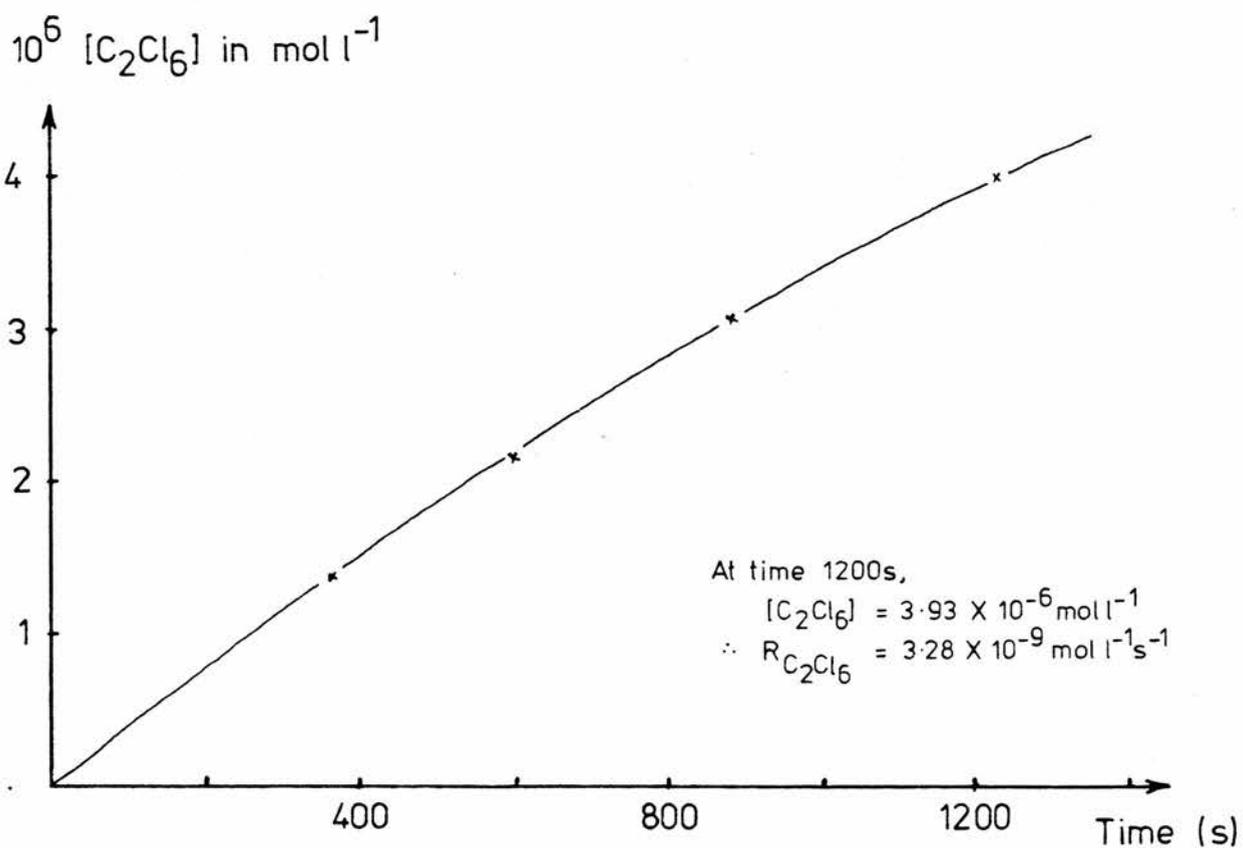


FIGURE 2.9.1 The Effect of Changing A_1 on the Rate of CHCl_3 Formation (in mol/l/s).

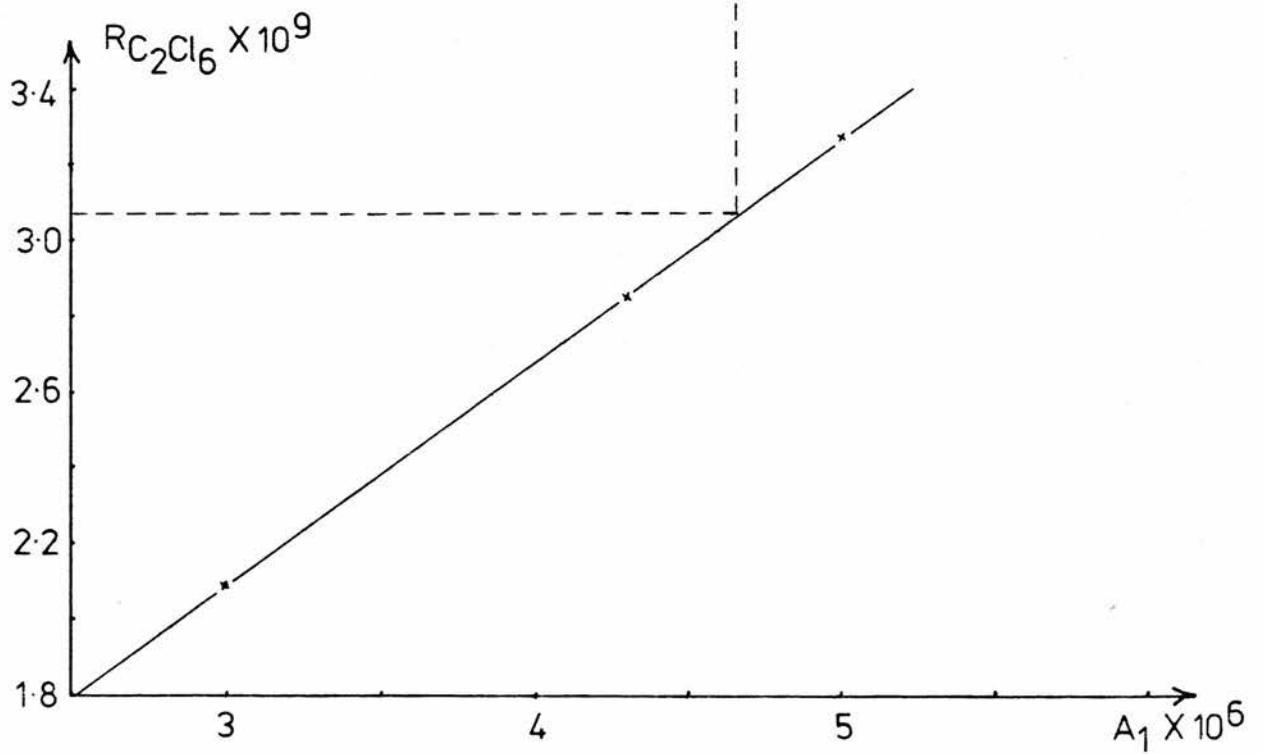
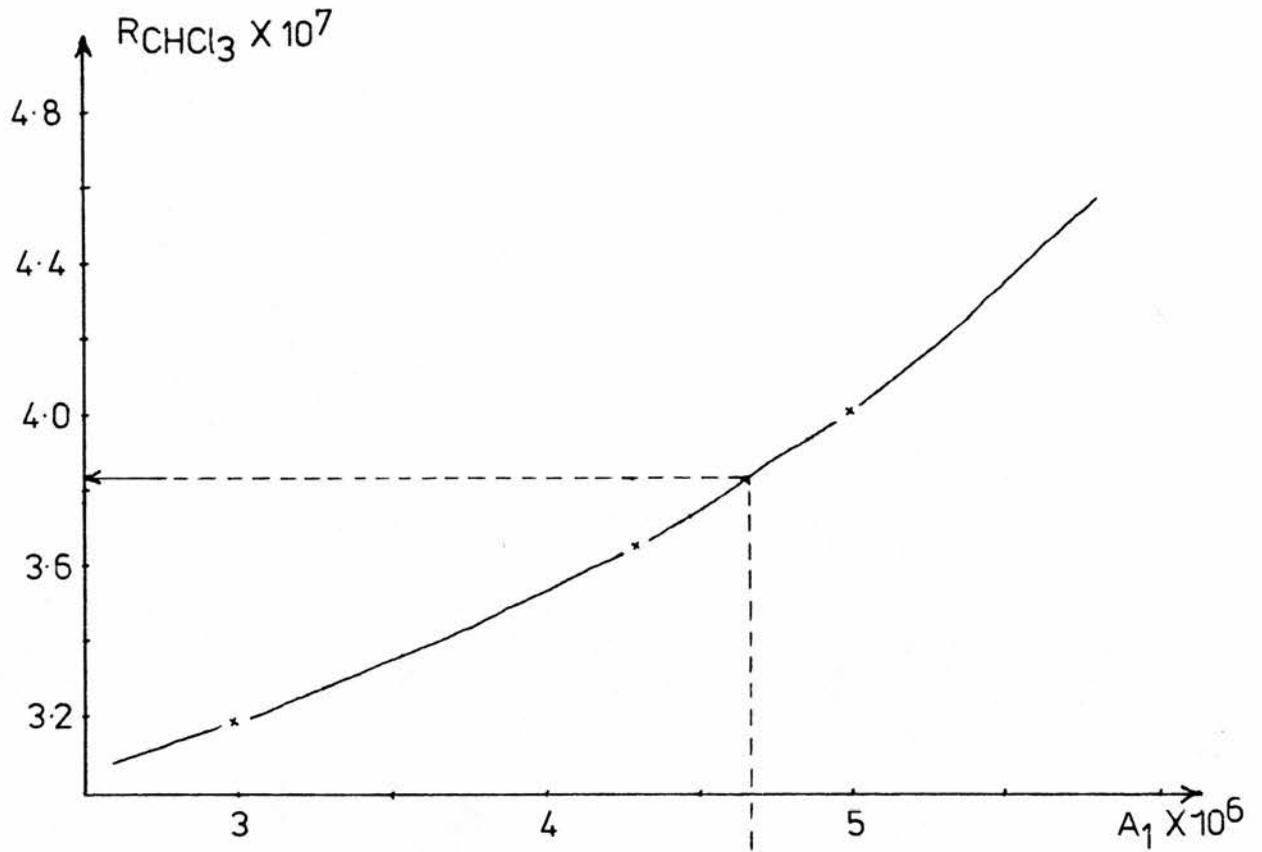


FIGURE 2.9.2 The Effect of Changing A_1 on the Rate of C_2Cl_6 Formation (in mol/l/s)

TABLE 2.10

Comparison of Computer Simulated and Experimental Results from the
 $\text{HBr}/\text{CCl}_2\text{Br}/\text{C}_2\text{H}_6$ System

$[\text{HBr}]_i$ (in mmol l^{-1})	Mean experimental value of $R_{\text{C}_2\text{Cl}_6}$ ($\text{mol l}^{-1} \text{s}^{-1}$)	Value of $R_{\text{C}_2\text{Cl}_6}$ used for simulation ($\text{mol l}^{-1} \text{s}^{-1}$)	Mean experimental value of R_{CHCl_3} ($\text{mol l}^{-1} \text{s}^{-1}$)	Value of R_{CHCl_3} ex simulation ($\text{mol l}^{-1} \text{s}^{-1}$)	$\frac{R_{\text{CHCl}_3}}{(R_{\text{C}_2\text{Cl}_6})^{1/2} \text{ exp}}$	$\frac{R_{\text{CHCl}_3}}{(R_{\text{C}_2\text{Cl}_6})^{1/2} \text{ sim}}$
5.38×10^{-2}	7.49×10^{-9}	7.49×10^{-9}	2.61×10^{-7}	2.59×10^{-7}	2.730×10^{-3}	2.99×10^{-3}
5.67×10^{-2}					3.342×10^{-3}	
1.70×10^{-1}	3.08×10^{-9}	3.08×10^{-9}	4.77×10^{-7}	3.85×10^{-7}	8.595×10^{-3}	6.94×10^{-3}

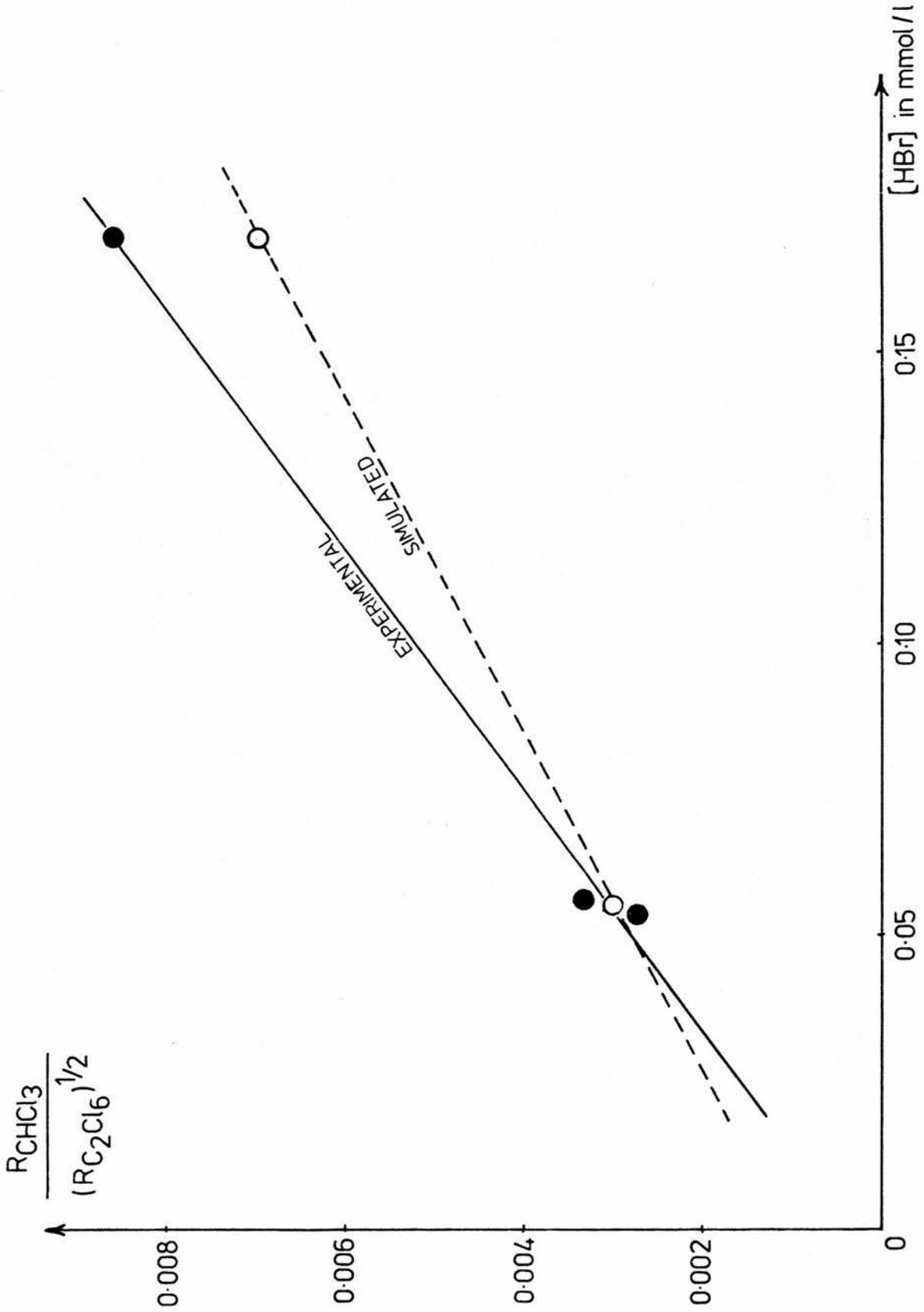


FIGURE 2.10 Comparison of Experimental and Computer Simulated Results for the $CCl_3Br / C_3H_8 / HBr$ System.

there will be many intrinsic errors in this system. Furthermore, the errors inherent in the experimental work are sufficiently great to preclude a more accurate estimation of k_5 . It is interesting to note that the approximate value of k_5 calculated from the experimental data in Section 2.7.2 was $4 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$, in excellent agreement with the rate calculated above. This would appear to give confirmation to the assumptions and discussion made in this section regarding mechanism and relative reaction rates.

As all experiments in this simulation study were carried out at the same temperature it is not possible to obtain values of A_5 and E_5 . To calculate these values it is necessary to use the same Arrhenius parameters for all reactions except Reaction (5) and to simulate the runs carried out in the absence of added HBr at various temperatures. The values of A_5 and E_5 corresponding to experimental data should indicate actual values.

For this simulation runs were selected from the beginning, centre, and end of the linear section of Figure 2.2, the plot of

$$\log_{10} \frac{R_{\text{CHCl}_3}}{(R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}} [\text{C}_3\text{H}_8]_{\text{av}}} \quad \text{versus the reciprocal of time.}$$

Runs at 101°C , 138°C and 245°C were used. As in the HBr simulation earlier, the initiation rate A_1 was adjusted to yield a value of $R_{\text{C}_2\text{Cl}_6}$ which corresponded to the experimentally found value and A_5 and E_5 varied to obtain a good fit for the value of

$$\log_{10} \frac{R_{\text{CHCl}_3}}{(R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}} [\text{C}_3\text{H}_8]_{\text{av}}}$$

A reasonable fit was obtained at $A_5 = 2.75 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ and $E_5 = 4.25 \text{ kcal mol}^{-1}$. The results are shown on Figure 2.11 and in Table 2.11.1. Table 2.11.2 shows that the computer simulated system also illustrates the decrease in R_{PrBr} relative to R_{CHCl_3} as temperature is raised. The sensitivity of R_{CHCl_3} to A_5 and E_5 is shown by the data in Table 2.12. The reaction rates have been determined at 182°C for direct comparison with the HBr series.

An interesting observation from the computer results is that the concentration of HBr in the reaction mixture increases at exactly the same rate as the concentration of C_2Cl_6 . This occurs because the system has no termination reaction involving Br radicals, and each Br radical will form a molecule of HBr by Reaction (2). Although this HBr molecule is a source of easily abstractable H via Reaction (5), the HBr is regenerated again via Reaction (2) and the number of HBr molecules present cannot therefore diminish but will increase for every molecule of CCl_3Br photolysed. As the initiation rate = termination rate, $\frac{d}{dt} [\text{HBr}] = \frac{d}{dt} [\text{C}_2\text{Cl}_6]$. This applies whether HBr is added to the reaction or not. As an increased $[\text{HBr}]$ has been shown to result in an increased R_{CHCl_3} it is found that the value of $\log_{10} R_{\text{CHCl}_3} / (R_{\text{C}_2\text{Cl}_6})^{1/2} [\text{C}_3\text{H}_8]_{\text{av}}$ also increases with time. This is illustrated by Figure 2.12, the results being obtained from the computer simulation of the run at 138°C . The concentrations of CCl_3^{\cdot} and Pr^{\cdot} were also plotted against time (Figure 2.13) and give further evidence that steady state is never achieved.

The lowest temperature run in Table 2.2 was continued for 6000s whereas the other runs in the series were continued for

TABLE 2.11.1

Comparison of Experimental and Computer Simulated Results in the
 $\text{C}_7\text{H}_8/\text{CCl}_2\text{Br}$ System

Temp. (°C)	Experimental $\text{R}_{\text{C}_2\text{Cl}_6}$ (mol l ⁻¹ s ⁻¹)	$\text{R}_{\text{C}_2\text{Cl}_6}$ used for simulation (mol l ⁻¹ s ⁻¹)	Experimental R_{CHCl_3} (mol l ⁻¹ s ⁻¹)	Simulated R_{CHCl_3} (mol l ⁻¹ s ⁻¹)	Simulated $[\text{C}_7\text{H}_8]_{\text{av}}$ (mmol l ⁻¹)	R_{CHCl_3} $\log(\text{R}_{\text{C}_2\text{Cl}_6})^2 [\text{C}_7\text{H}_8]_{\text{av}}$ (experimental)	R_{CHCl_3} $\log(\text{R}_{\text{C}_2\text{Cl}_6})^2 [\text{C}_7\text{H}_8]_{\text{av}}$ (simulated)
101	1.294×10^{-8}	1.294×10^{-8}	1.009×10^{-8}	1.073×10^{-8}	1.89	-1.502	-1.30
138	1.201×10^{-8}	1.201×10^{-8}	2.173×10^{-8}	1.805×10^{-8}	1.88	-1.151	-1.06
245	2.438×10^{-8}	2.438×10^{-8}	2.505×10^{-7}	1.439×10^{-7}	1.83	-0.280	-0.30

TABLE 2.11.2

Comparison of Experimental and Computer Simulated Results in the
 $\text{C}_7\text{H}_8/\text{CCl}_2\text{Br}$ System

Temp. (°C)	$\text{R}_{\text{Pr-Br}}:\text{R}_{\text{CHCl}_3}$ (experimental)	$\text{R}_{\text{Pr-Br}}:\text{R}_{\text{CHCl}_3}$ (simulated)
101	1.57	1.97
138	1.23	1.54
245	0.91	1.13

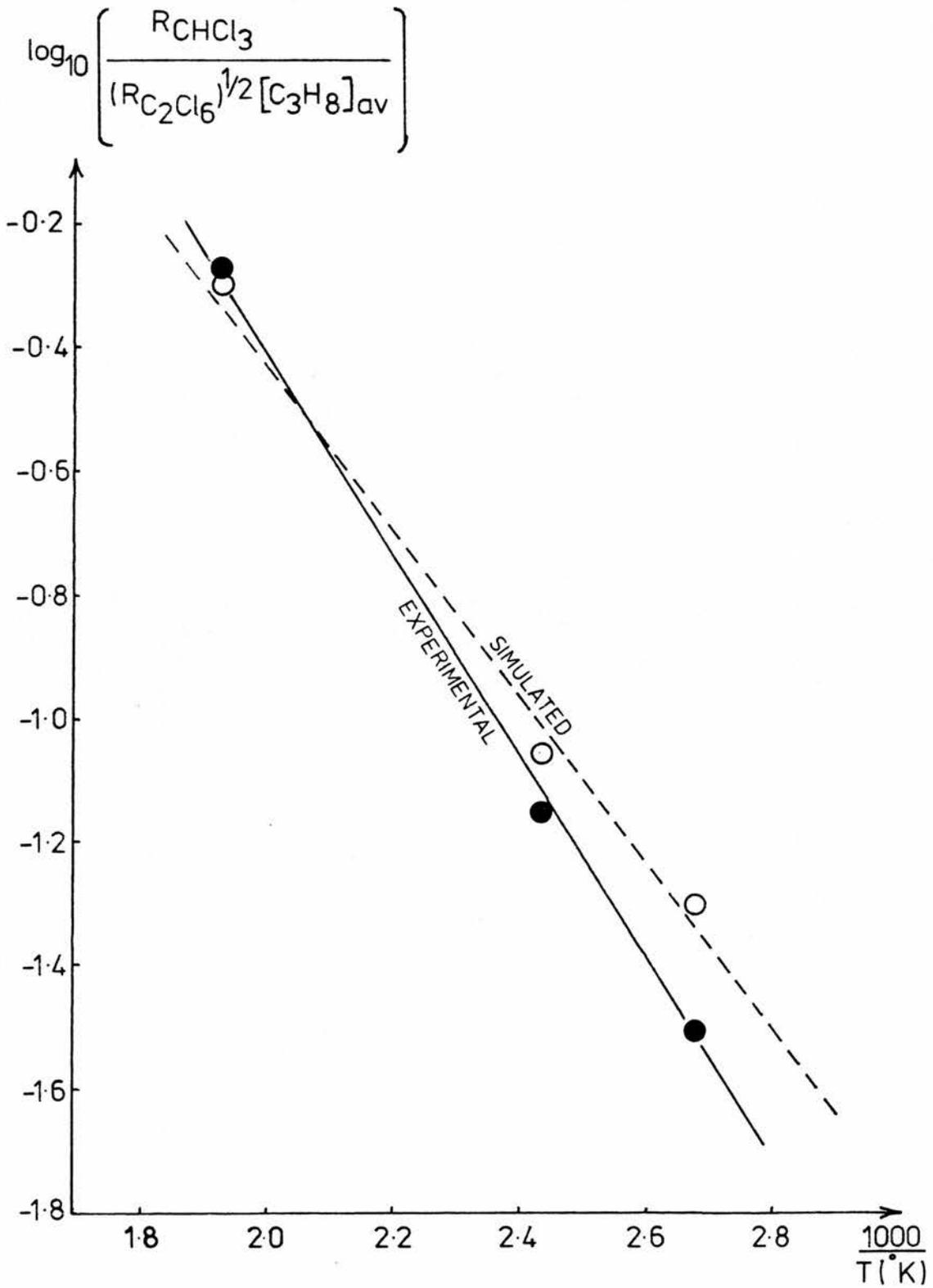


FIGURE 2.11

Comparison of Experimental and Computer Simulated Results for the $\text{CCl}_3\text{Br} / \text{C}_3\text{H}_8$ System.

TABLE 2.12

The Effect of Variation of A_5 and E_5 on R_{CHCl_3}

(Reaction Temp. = 138°C)

A_5 $1 \text{ mol}^{-1} \text{ s}^{-1}$	E_5 (kcal mol ⁻¹)	$\log k_5$ at 182°C	Simulated R_{CHCl_3} mol l ⁻¹ s ⁻¹	$\log_{10} \frac{R_{\text{CHCl}_3}}{(R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}} [\text{C}_3\text{H}_8]^{\frac{1}{2}}}$
2.75×10^8	4.25	6.4	1.805×10^{-8}	-1.06
2.55×10^8	3.75	6.6	3.089×10^{-8}	-0.82
5.53×10^8	4.25	6.7	3.749×10^{-8}	-0.73
3.36×10^8	3.80	6.7	3.869×10^{-8}	-0.72

$$R_{\text{CHCl}_3} \text{ (experimental)} = 2.173 \times 10^{-8} \text{ mol l}^{-1} \text{ s}^{-1}$$

$$\log_{10} \frac{R_{\text{CHCl}_3}}{(R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}} [\text{C}_3\text{H}_8]_{\text{av}}} \text{ (experimental)} = -1.15$$

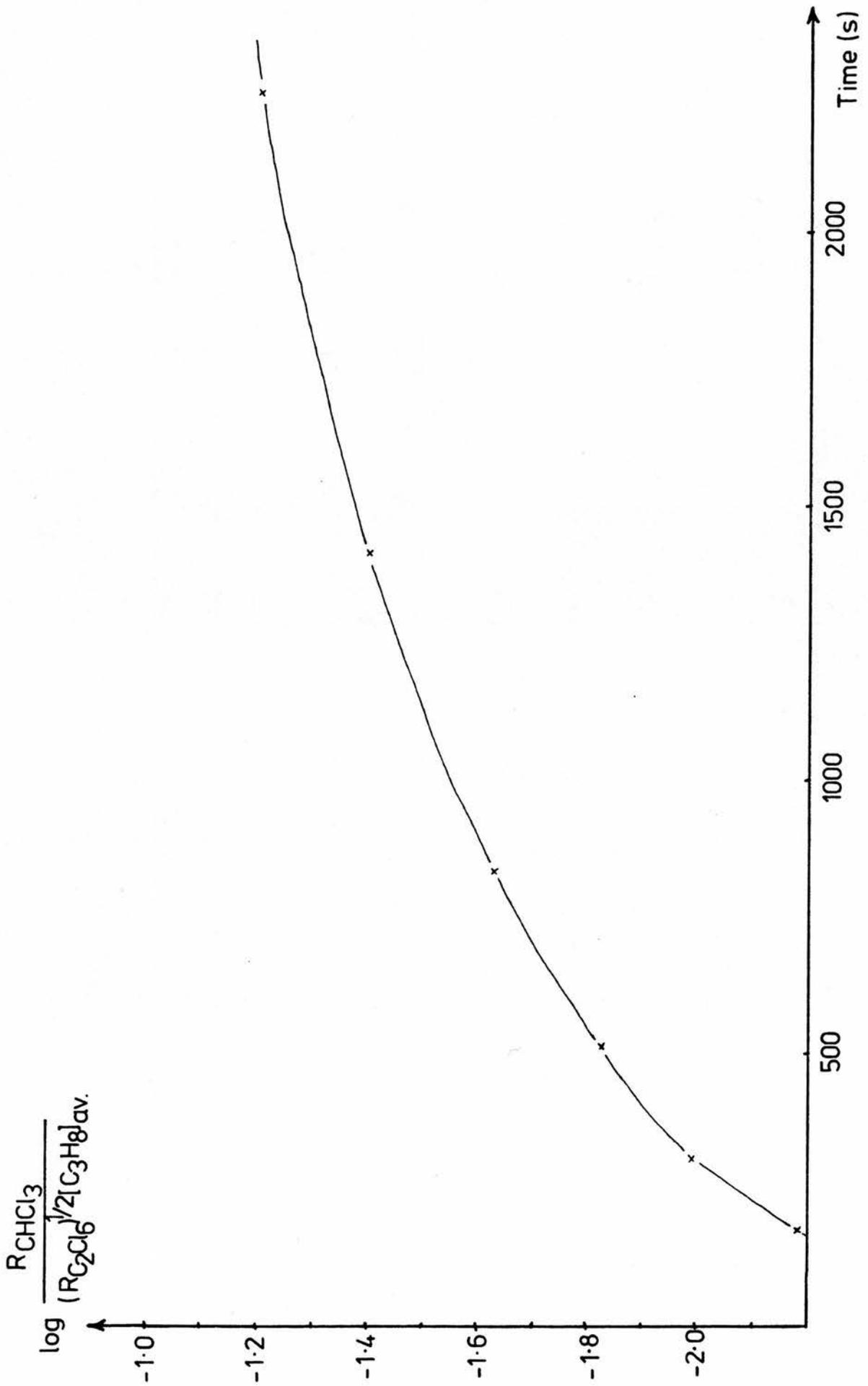


FIGURE 2.12 Time Dependence of $\log_{10} (R_{\text{CHCl}_3} / (R_{\text{C}_2\text{Cl}_6})^{1/2} [\text{C}_3\text{H}_8]_{\text{av.}})$

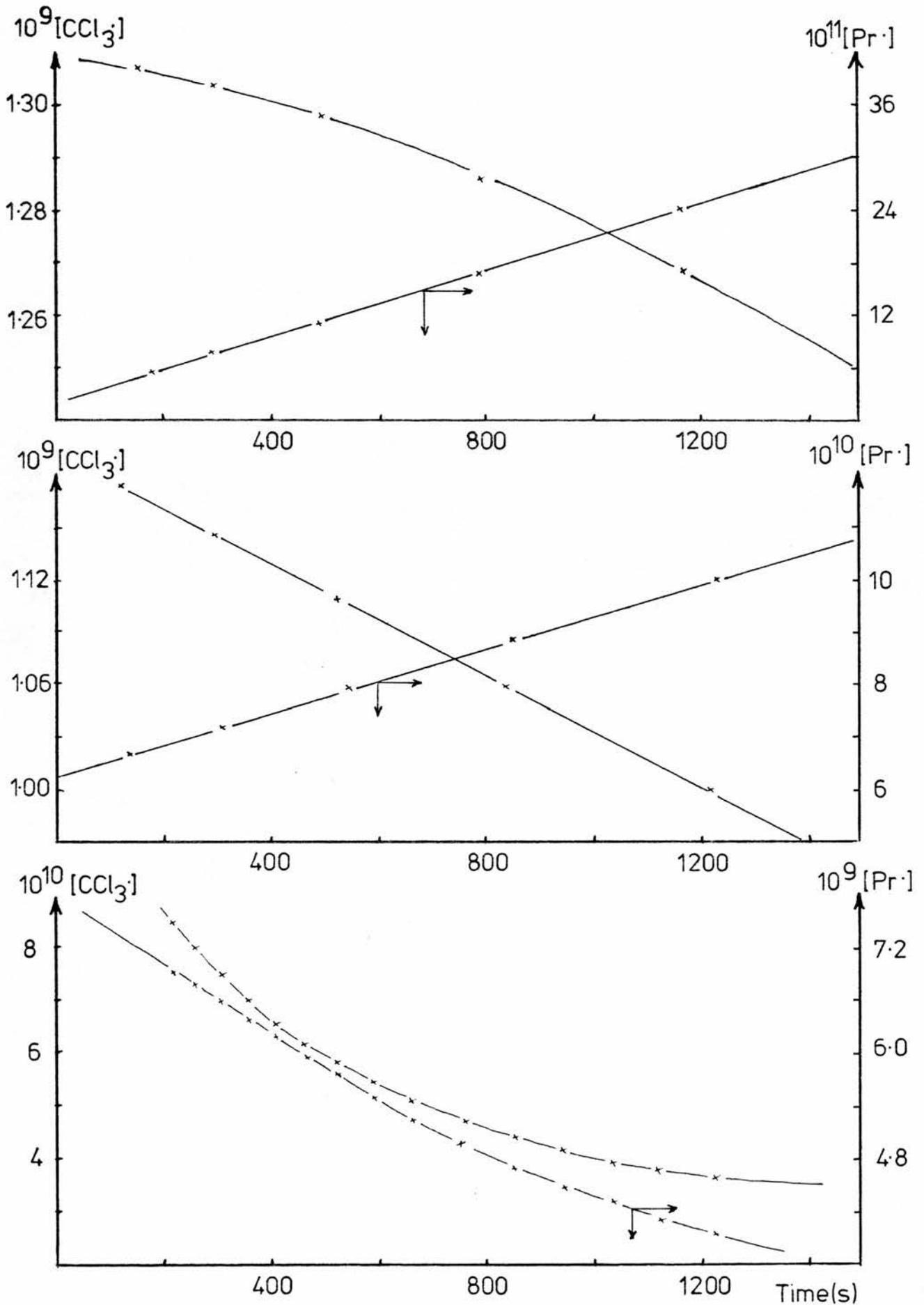


FIGURE 2.13

Time Dependence of Radical Concentrations (in mol/l) for Propane + Bromotrichloromethane with 0 (top), 5.67×10^{-5} (centre), and 1.70×10^{-4} mol/l (bottom) hydrogen bromide added.

only 1800s. The value of $\log_{10} R_{\text{CHCl}_3} / (R_{\text{C}_2\text{Cl}_6})^{1/2} [\text{C}_3\text{H}_8]_{\text{av}}$ would thus be expected to be greater than it would for an 1800s run at the same temperature. This was indeed the case, as can be seen in Figure 2.2. The deviations from linearity at the high temperature end of this graph have been attributed earlier in this discussion to over-conversion of the reactants.

This discussion has shown that by suitable selection of Arrhenius parameters a photolytic reaction of moderate complexity can be simulated using a computer programme. Factors such as time dependence, temperature dependence and concentration dependence can be adjusted and the effects on rates of product formation observed. By comparison with experimental data the validity of any kinetic or mechanistic assumptions can be assessed.

In this section the computer simulation of the $\text{CCl}_3\text{Br}/\text{C}_3\text{H}_8/\text{HBr}$ has provided good agreement with experimental data and has yielded much useful data about the concentrations of radical and molecular species as the reaction progressed.

SECTION 3

The Photolysis of Carbon Tetrachloride With Propane

INTRODUCTION

In sections 1 and 2 of this thesis the photolysis of bromotrichloromethane in the presence of saturated hydrocarbons was examined. The major problem encountered in these studies was attributed to the presence of hydrogen bromide with its readily abstractable hydrogen atom.

In this section a similar system to that of the previous section is examined - the photolysis of carbon tetrachloride in the presence of propane. The results of the previous sections indicated that the presence of hydrogen chloride in the system should have a less dramatic effect than the hydrogen bromide which appears in the bromotrichloromethane system. However, as the primary initiation step involves formation of a chlorine atom, and as this radical will readily react with one of the large number of hydrocarbon molecules present to yield HCl, the steady state concentration of HCl will be significantly greater than that of HBr in Sections 1 and 2. Kerr and Trotman-Dickenson²³ report rates of hydrogen abstraction from alkanes by chlorine atoms as $\log k(\text{primary H})$

$$= 10.2 - \frac{1000 \text{ cal}}{2.303 RT}, \quad \log k(\text{secondary H}) = 10.3 - \frac{300 \text{ cal}}{2.303 RT},$$

$\log k(\text{tertiary H}) = 10.2 \text{ l mol}^{-1} \text{ s}^{-1}$. Only by examining the experimental data obtained in this system can the effect of the HCl present be estimated.

Carbon tetrachloride is a long established source of trichloromethyl radicals although earlier workers did not obtain the radicals by fission of the $\text{CCl}_3\text{-Cl}$ bond as the initiation step.

Smyser and Smallwood¹²³ studied the reaction between hydrogen atoms and CCl_4 . They found that a chlorine atom

was readily abstracted to yield trichloromethyl radicals and HCl; the hydrogen atoms could also abstract a further chlorine atom to yield dichlorocarbene and a further molecule of HCl. The carbene then polymerised explosively to yield polytetrachloroethylene. Several years later Vance and Baumann¹²⁴ studied the system under more controlled conditions and found that at low carbon tetrachloride concentrations $[HCl] \gg 2 [CCl_4]$ confirming that the second chlorine atom was readily abstracted.

The related system, $Cl \cdot + CCl_4$, has also been studied by several workers^{125,126}. There are no reports of dichlorocarbene formation in these studies.

The reaction between CCl_4 and alcohols has been studied¹²⁷ using benzoyl peroxide as the radical initiating species, and the reaction between CCl_4 and hydrocarbons has been initiated^{53,128,129} using a variety of peroxy and azo initiators.

In this section however, the initiating trichloromethyl radicals are obtained from fission of the CCl_3-Cl bond. This has been used as an initiation step by many workers who used various techniques to rupture the bond.

CCl_4 and CCl_3Br have both been shown to yield trichloromethyl radicals¹³⁰ from pyrolysis or electric discharge, the CCl_3 radicals having been trapped in argon and nitrogen matrices at 14°K.

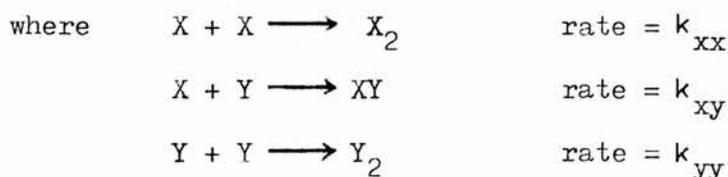
Gamma radiation has been used to produce CCl_3 radicals from carbon tetrachloride^{63,86} and chloroform⁶², the radicals being used as initiators for the telomerisation of ethylene. Katz and coworkers⁸⁸⁻⁹⁰ have studied the reactions of n-hexane and cyclohexane with trichloromethyl radicals produced by γ -radiation of carbon tetrachloride in solution phase.

The reaction between ethanol and carbon tetrachloride has been studied using both thermal and photolytic fission¹³¹ of the $\text{CCl}_3\text{-Cl}$ bond.

Pfordte¹³² has studied the photolysis of CCl_4 and proposed a radical mechanism to account for the products. More recently Rebbert and Ausloos¹³³ studied the photolysis of CCl_4 more thoroughly at several wavelengths and in the presence of HCl , HBr and C_2H_6 . They report a quantum yield of CCl_3 radicals of > 0.9 at 213.9 nm, whereas at 163.3 nm they detected CCl_2 as the major product of the initiation reaction, the quantum yield being ca.0.75. The dichlorocarbene participated in insertion reactions with the hydrogen halides (i.e. $\text{CCl}_2 + \text{HCl} \longrightarrow \text{CHCl}_3$) and in several combination reactions.

Wijnen and coworkers¹³⁴⁻⁶ photolysed carbon tetrachloride in the presence of ethane and ethylene and observed hexachloroethane, 1,1,1-trichloropropane and n-butane among the termination products. They showed that the rates of combination of pairs of radicals X and Y are governed by the expression:-

$$k_{xy} / k_{xx}^{\frac{1}{2}} k_{yy}^{\frac{1}{2}} = 2$$



They also measured the disproportionation:combination rate ratios for the pairs of radicals present in the system. In the present section the k_d/k_c ratio is estimated for the combination of isopropyl and trichloromethyl radicals and the results compared with those of Wijnen. The differences in k_d/k_c are rationalised in terms of the number of abstractable hydrogen atoms available

for disproportionation.

Tomkinson and coworkers¹³⁷ photolysed carbon tetrachloride, hexachloroethane and hexachloroacetone in the presence of saturated hydrocarbons. They observed no reaction when CCl_4 was photolysed in the presence of propane at 313.0 nm but at 253.7 nm they detected C_2Cl_6 , CHCl_3 , HCl , $\text{CH}_3\text{CHClCH}_3$ and $\text{CH}_2\text{ClCH}_2\text{CH}_3$, the ratio of isopropyl chloride to n-propyl chloride being ca. 50. In sections 1 and 2 of this thesis the abstraction of hydrogen from HBr by CCl_3 radicals prevented useful Arrhenius data being obtained. Tomkinson et al. claim that CCl_3 radicals will not abstract a hydrogen atom from HCl at less than 250°C. If this is the case then the results of the present section should not be affected in the same way as those from the CCl_3Br photolyses.

Using the rotating sector technique White and Kuntz³⁹ have photolysed carbon tetrachloride in the presence of cyclohexane over the rather narrow temperature range 112-183°C and obtained Arrhenius parameters for the hydrogen abstraction from cyclohexane by CCl_3 . They also estimated the rate of combination of trichloromethyl radicals $k = 3.9 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. This work was followed up by Wampler and Kuntz⁹⁹ who examined the photolysis of CCl_4 in the presence of several other saturated hydrocarbons in the temperature range 89-173°C.

Recent work in this laboratory by Currie⁵³ showed that the rate of photoinitiation of carbon tetrachloride was temperature dependent. He also showed that under his photolysis conditions (250 nm) a secondary initiation reaction yielded dichlorocarbene which had a significant effect on product ratios. Subsequently azocyclohexane was used as radical initiator in the cyclohexane/carbon tetrachloride system.

The propane/bromotrichloromethane system was investigated in the last section and as a continuation of the study this present section describes the propane/carbon tetrachloride system and the results are evaluated in the light of those of previous workers on related systems.

SECTION 3

The Photolysis of Carbon Tetrachloride With Propane

EXPERIMENTAL

3.1 REACTANTS

(a) Carbon Tetrachloride:- was Fisons spectrograde reagent, and was tested and found to be chromatographically pure.

(b) Propane:- was Matheson Gas Products research grade as described in Section 2.

Both the above reagents were used without further purification.

3.2 APPARATUS

The vacuum system has already been extensively described in Sections 1 and 2. The reaction vessel was cylindrical with planar ends, and was made of quartz. It was connected to the vacuum line by a "Pyrex" capillary tube which passed through the top of the oven. The volume of the reaction vessel was 198 ml, measured by completely filling it with distilled water and observing the increase in weight. The light sources used were either the full arc from a Hanovia UVS 220 medium pressure arc lamp as described in the first section, or a 200W super high pressure mercury arc coupled to a Bausch and Lomb high intensity monochromator, yielding a monochromatic source at 250 nm (10 nm bandwidth).

3.3 EXPERIMENTAL PROCEDURE

Both reagents were stored on the vacuum line; propane was kept in a large storage bulb as described in Section 2, and carbon tetrachloride was stored in a tube on the line. It was not considered necessary to blacken the outside of this tube as the Pyrex glass would absorb any radiation necessary for decomposition of the CCl_4 . Experimental procedure was similar to that described in earlier sections. The pressures of propane and carbon tetrachloride in bulb A were 50 torr and 25 torr respectively before distillation into the reaction vessel.

3.4 ANALYSIS

The gas liquid chromatography apparatus was described in Section 1. The conditions employed for separation were: temperature 80°C., flow rate 35 mlmin⁻¹ and chartspeed 48 inh⁻¹ for peaks up to and including carbon tetrachloride and 24 inh⁻¹ thereafter. Samples were injected using 4 µl stainless steel capillary needles. The same column was used as in the previous sections.

3.5 IDENTIFICATION OF PRODUCTS

A typical chromatogram of the products showed nine peaks, as shown in Fig.3.1. Most were identified by a comparison of retention times with authentic samples, and confirmed by gas-liquid chromatography coupled mass spectrometry. One peak was not well identified by either method but was deduced from its magnitude and position to be 1,1,1-trichloro-2-methylpropane. The mass spectrograph obtained from this compound was not decipherable as the peak occurred in the tails of both carbon tetrachloride and tetrachloroethylene.

3.6 RESULTS

Three separate series of experiments were carried out. Initially, the medium pressure arc lamp was placed 25 cm from the nearest window of the reaction vessel. In an attempt to increase the chain length of the reaction at lower temperatures the lamp was moved to a position 40 cm from the reaction vessel. In the third series of experiments a Bausch and Lomb monochromator light source (as described earlier in this section) was used. The rates of formation of the different observed products are shown in Table 3.1. Values for the rates of formation of the termination product 2,3-dimethylbutane have been included. It was found however that this peak occurred between the relatively larger chloroform and propyl

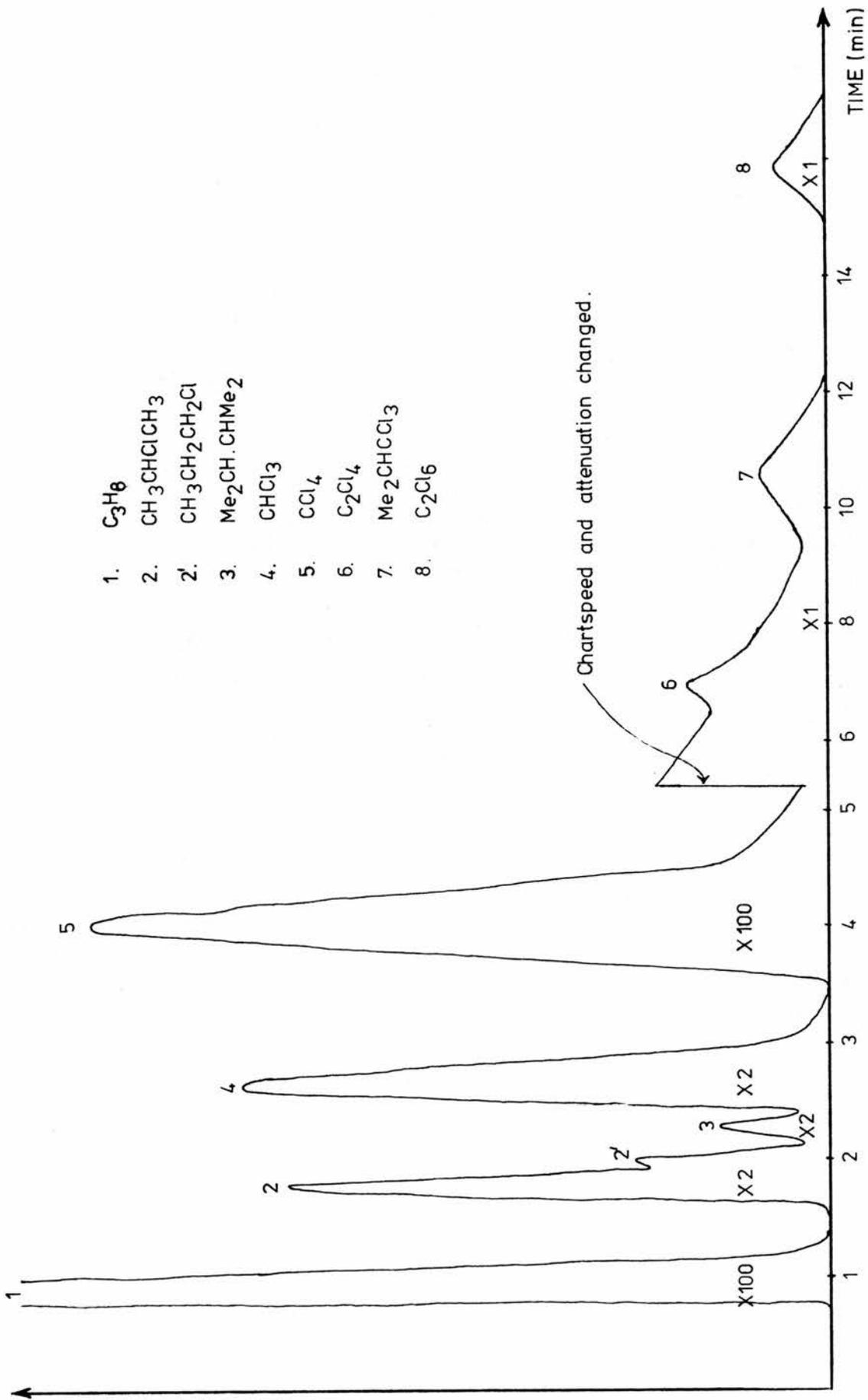


FIGURE 3.1 G.c. Analysis of the Products of Carbon Tetrachloride Photolysis in the Presence of Propane.

TABLE 3.1

Rates of Product Formation in the Propane-Carbon Tetrachloride System

Temp (°C)	1000/T(°K)	Time (s)	R_{CHCl_3} (mol l ⁻¹ s ⁻¹)	R_{PrCl} (mol l ⁻¹ s ⁻¹)	$R_{(\text{iPr})_2}$ (mol l ⁻¹ s ⁻¹)	R_{iPrCCl_3} (mol l ⁻¹ s ⁻¹)	$R_{\text{C}_2\text{Cl}_6}$ (mol l ⁻¹ s ⁻¹)
Series A							
45	3.145	5400	5.810 x 10 ⁻¹⁰	9.292 x 10 ⁻¹⁰	-	1.248 x 10 ⁻⁹	5.810 x 10 ⁻¹⁰
71	2.907	3900	7.438 x 10 ⁻¹⁰	1.681 x 10 ⁻⁹	-	1.763 x 10 ⁻⁹	1.299 x 10 ⁻⁹
90	2.755	3600	6.392 x 10 ⁻¹⁰	1.376 x 10 ⁻¹⁰	3.502 x 10 ⁻¹⁰	-	6.933 x 10 ⁻¹⁰
118	2.588	7380	2.343 x 10 ⁻¹⁰	5.630 x 10 ⁻⁹	1.543 x 10 ⁻¹⁰	1.767 x 10 ⁻¹⁰	1.965 x 10 ⁻¹⁰
147	2.381	5400	5.062 x 10 ⁻¹⁰	1.418 x 10 ⁻⁹	-	2.867 x 10 ⁻¹⁰	1.655 x 10 ⁻¹⁰
153	2.347	7200	3.931 x 10 ⁻¹⁰	1.285 x 10 ⁻⁹	1.592 x 10 ⁻¹⁰	1.660 x 10 ⁻¹⁰	2.615 x 10 ⁻¹⁰
205	2.092	9000	6.572 x 10 ⁻¹⁰	1.160 x 10 ⁻⁹	1.520 x 10 ⁻¹⁰	1.010 x 10 ⁻¹⁰	5.345 x 10 ⁻¹¹
224	2.012	7500	1.041 x 10 ⁻⁹	1.151 x 10 ⁻⁹	1.821 x 10 ⁻¹⁰	6.824 x 10 ⁻¹¹	1.863 x 10 ⁻¹⁰
277	1.818	7200	2.405 x 10 ⁻⁹	2.068 x 10 ⁻⁹	1.529 x 10 ⁻¹⁰	8.173 x 10 ⁻¹¹	1.169 x 10 ⁻¹¹
Series B							
91	2.747	27900	2.279 x 10 ⁻¹⁰	4.719 x 10 ⁻¹⁰	7.697 x 10 ⁻¹¹	4.189 x 10 ⁻¹⁰	1.855 x 10 ⁻¹⁰
96	2.710	31800	1.452 x 10 ⁻¹⁰	3.854 x 10 ⁻¹⁰	5.525 x 10 ⁻¹¹	1.859 x 10 ⁻¹⁰	1.439 x 10 ⁻¹⁰
98	2.695	17400	1.387 x 10 ⁻¹⁰	5.514 x 10 ⁻¹⁰	7.470 x 10 ⁻¹¹	9.778 x 10 ⁻¹¹	8.656 x 10 ⁻¹¹
112	2.597	22500	3.068 x 10 ⁻¹⁰	1.125 x 10 ⁻⁹	-	3.192 x 10 ⁻¹⁰	2.932 x 10 ⁻¹⁰
146	2.387	24600	2.767 x 10 ⁻¹⁰	8.293 x 10 ⁻¹⁰	3.815 x 10 ⁻¹¹	2.772 x 10 ⁻¹⁰	1.899 x 10 ⁻¹⁰
154	2.342	37800	3.564 x 10 ⁻¹⁰	1.052 x 10 ⁻⁹	5.017 x 10 ⁻¹¹	2.298 x 10 ⁻¹⁰	1.601 x 10 ⁻¹⁰
167	2.273	18900	3.402 x 10 ⁻¹⁰	8.987 x 10 ⁻¹⁰	1.992 x 10 ⁻¹¹	-	8.633 x 10 ⁻¹¹
179	2.212	15000	1.231 x 10 ⁻⁹	4.713 x 10 ⁻⁹	1.115 x 10 ⁻¹¹	6.834 x 10 ⁻¹⁰	2.231 x 10 ⁻¹⁰
Series C							
68.5	2.928	55500	2.022 x 10 ⁻¹¹	5.532 x 10 ⁻¹¹	1.477 x 10 ⁻¹¹	1.101 x 10 ⁻¹¹	2.790 x 10 ⁻¹¹
118	2.558	51300	2.866 x 10 ⁻¹¹	7.747 x 10 ⁻¹¹	1.666 x 10 ⁻¹¹	6.062 x 10 ⁻¹²	3.207 x 10 ⁻¹¹
176	2.227	56700	9.393 x 10 ⁻¹¹	1.995 x 10 ⁻¹⁰	1.006 x 10 ⁻¹¹	3.960 x 10 ⁻¹²	4.083 x 10 ⁻¹¹
223	2.016	55800	2.717 x 10 ⁻¹⁰	3.626 x 10 ⁻¹⁰	8.322 x 10 ⁻¹²	4.073 x 10 ⁻¹²	3.949 x 10 ⁻¹¹
227	2.000	47400	2.792 x 10 ⁻¹⁰	4.237 x 10 ⁻¹⁰	1.951 x 10 ⁻¹¹	1.168 x 10 ⁻¹¹	5.179 x 10 ⁻¹¹

$$[\text{C}_3\text{H}_8]_i = 2.851 \times 10^{-3} \text{ mol l}^{-1}$$

$$[\text{CCl}_4]_i = 1.425 \times 10^{-3} \text{ mol l}^{-1}$$

Values omitted were not measurable due to practical problems with the GLC apparatus

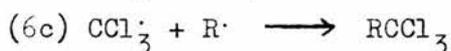
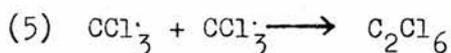
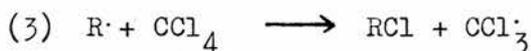
chloride peaks and measurement was very inaccurate indeed. However, no other stationary phase was discovered which even showed the presence of this peak, so the results, as measured, were used in the subsequent calculations.

SECTION 3

The Photolysis of Carbon Tetrachloride With Propane

DISCUSSION

The photolysis of ethane-ethylene mixtures with carbon tetrachloride has been studied by Wijnen and coworkers¹³⁴⁻¹³⁶; Kuntz^{39,99} has studied further alkane-carbon tetrachloride systems and although bromotrichloromethane has been used primarily, studies have been made in this laboratory⁵³ photolysing cyclohexane with carbon tetrachloride. The basic mechanism has been shown to be



where, in this study, R represents the isopropyl radical and R_{-H} represents propylene. It has been shown in a previous study⁷⁸ that $\text{CCl}_3\cdot$ will not abstract a primary hydrogen if a secondary hydrogen is available. Consequently the formation of n-propyl radicals will not be significant.

In the reactions of propane with bromotrichloromethane described earlier, no trace of the products of reactions (6) and (7) was observed. In this study however, both 2,3-dimethylbutane and 1,1,1-trichloro-2-methylpropane were observed and measured. Edwards and Mayo⁸ found that at 100°C the rate of hydrogen abstraction from cyclohexane by methyl radicals was 4.8 times faster than the rate of chlorine abstraction from carbon tetrachloride. Reaction (3) would thus be expected to be somewhat slower than reaction (4) in this system. This contrasts with the bromotrichloromethane-propane system discussed in the previous chapter where, because of the relative

bond strengths $D(\text{CCl}_3-\text{Cl}) = 72 \text{ kcal mol}^{-1}$ ⁹³⁻⁹⁵ and $D(\text{CCl}_3-\text{Br}) = 49.5 \text{ kcal mol}^{-1}$ ^{93,138} the bromine abstraction from CCl_3Br is more facile than the chlorine abstraction from CCl_4 is in this system. Hence the steady state concentration of isopropyl radicals is greater for this system and the termination products are detectable.

The combination of isopropyl radicals has been studied by several workers. Metcalf and Trotman-Dickenson ¹³⁹ calculated a value of $\log k_7 = 10.8 \text{ l.mol}^{-1}\text{s}$, Huybrechts and coworkers have reported a value of $\log k_7 = 11.1 \text{ l.mol}^{-1}\text{s}^{-1}$ ¹⁴⁰, and more recently Walker ¹⁴¹ quotes a value of $\log k_7 = 9.5 \text{ l.mol}^{-1}\text{s}^{-1}$, where k_7 is the rate of both disproportionation and combination reactions together. Hiatt and Benson ⁵⁰ have calculated that $k_{7c} = 10^{8.6} \text{ l.mol}^{-1}\text{s}^{-1}$. The relative rates of the combination and disproportionation reactions have been reported as $k_d/k_c \cong 0.66$ ¹⁴²⁻¹⁴⁶. Using this value, the area of propylene peak arising from reaction (7d) in the glc analysis can be calculated as

$$\text{Area} = \frac{\text{mol.wt } \text{C}_3\text{H}_6 - \text{mol.wt } \text{N}_2}{\text{mol.wt } \text{C}_6\text{H}_{14} - \text{mol.wt } \text{N}_2} \times 0.66 \times \text{Area } \text{R}_2 \text{ peak} = 0.16 \times \text{Area } \text{R}_2 \text{ peak}$$

The 2,3 dimethylbutane peak was the smallest measurable peak and its area is somewhat difficult to measure accurately. (The propylene peak will thus be impossible to measure). Propylene is also formed from reaction (6d). Using a value of $k_d/k_c = 0.45$ (estimated later in this discussion) and applying similar calculations, the area can be calculated to be only 0.19 of the area of cross-termination product peak $\text{C}_3\text{H}_7\text{CCl}_3$. Hence although combination/disproportionation reactions (6) and (7) may take place to an appreciable extent the amount of propylene formed will be very difficult indeed to measure. No propylene peak was observed.

In the experiments with bromotrichloromethane, the only source of chloroform was from hydrogen abstraction from the alkane by the trichloromethyl radical. Reaction (6d), however, constitutes another possible source of chloroform. No values have been published regarding the relative disproportionation and combination rates of trichloromethyl and isopropyl radicals. Kraus and Calvert¹⁴⁷ and Sheldon and Kochi¹⁴⁸ looked at the k_d/k_c values for several alkyl radicals and found that a reasonably consistent normalisation of the published values could be obtained by dividing the k_d/k_c value by the number of β -hydrogen atoms available for disproportionation. This yielded normalised values of 0.06 for primary radicals, 0.2 for secondary radicals and 0.8 for tertiary radicals. They explained that deviations from these mean values represented degrees of steric hindrance or stress. Gibian and Corley¹⁴⁹ however, quoted more recent values of the k_d/k_c ratios and concluded that there was no basis for this purely statistical generalisation, even for simple alkyl radicals in the gas phase.

As the propylene peak was not measurable and chloroform was produced from both reactions (4) and (6d) it was not possible to make a thorough study of the k_d/k_c ratios for the cross-combination reaction. Nevertheless an estimate can be made from the lower temperature runs. As the activation energy for reaction (4) will be considerably greater than the assumed zero value for reaction (6d), it can be assumed that at sufficiently low temperatures all chloroform will have come from the disproportionation step.

Table 3.2 shows values of $R_{\text{CHCl}_3}/R_{\text{iPrCCl}_3}$ and these values are plotted in Fig 3.2.

TABLE 3.2

Rates of Formation Obtained by
Photolysis of the C₃H₈ - CCl₄ System

Temperature (°C)	1000/T(°K)	R _{CHCl₃} (mol.l ⁻¹ s ⁻¹)	R _{PrCCl₃} (mol.l ⁻¹ s ⁻¹)	$\frac{R_{CHCl_3}}{R_{PrCCl_3}}$
45	3.145	5.810x10 ⁻¹⁰	1.248x10 ⁻⁹	0.466
71	2.907	7.438x10 ⁻¹⁰	1.763x10 ⁻⁹	0.422
118	2.588	2.343x10 ⁻¹⁰	1.767x10 ⁻¹⁰	1.326
147	2.381	5.062x10 ⁻¹⁰	2.867x10 ⁻¹⁰	1.766
153	2.347	3.931x10 ⁻¹⁰	1.660x10 ⁻¹⁰	2.368
205	2.092	6.572x10 ⁻¹⁰	1.010x10 ⁻¹⁰	6.507
224	2.012	1.041x10 ⁻⁹	6.824x10 ⁻¹¹	15.255
277	1.818	2.405x10 ⁻⁹	8.173x10 ⁻¹¹	29.426

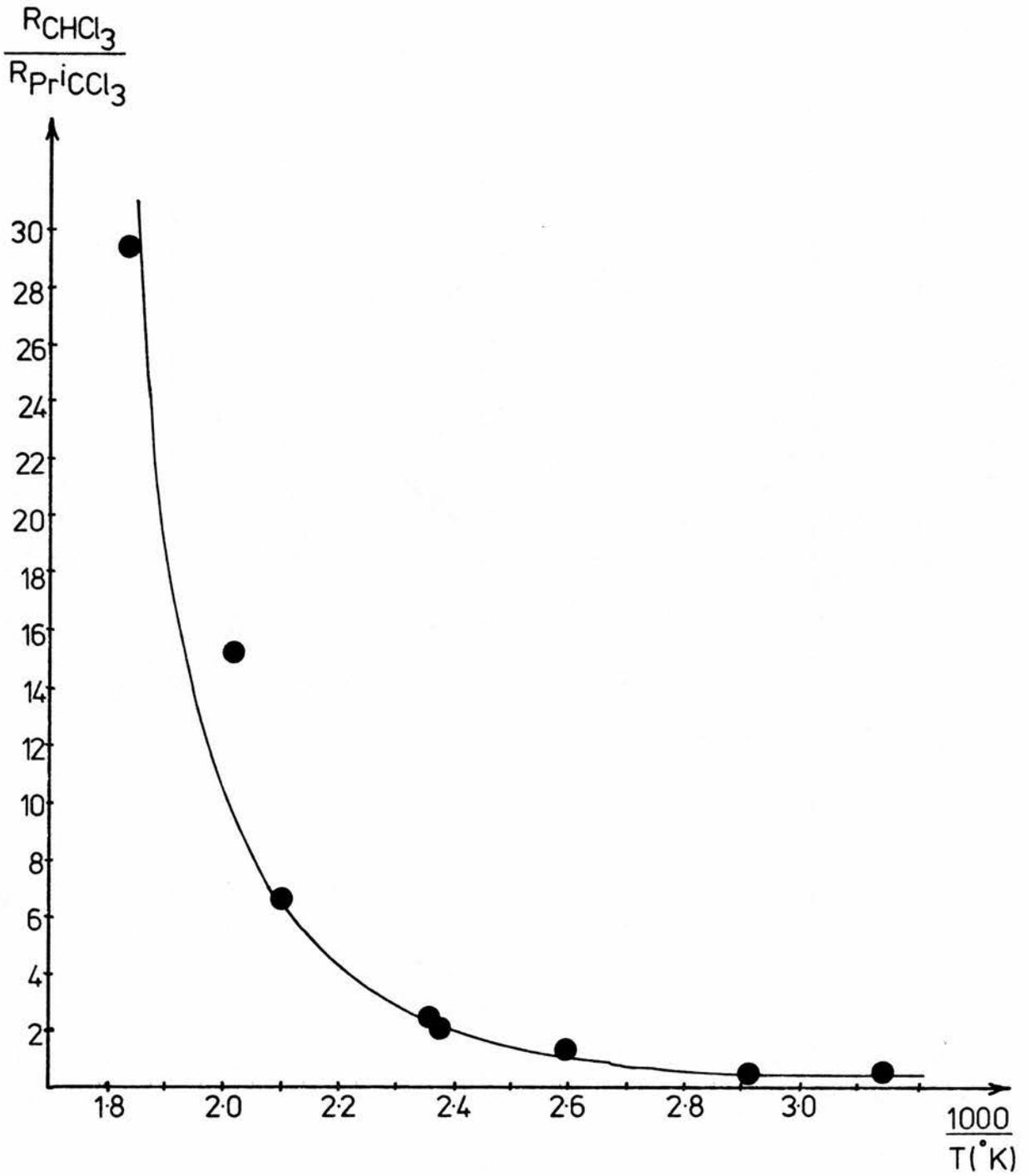


FIGURE 3.2

Graph of $\frac{R_{CHCl_3}}{R_{Pr^iCCl_3}}$ versus the reciprocal of temperature for the propane-carbon tetrachloride system.

The values calculated are from series A where the light source was 25 cm from the nearest window of the reaction vessel i.e. conditions favourable for relatively high rates of formation of termination products. The experiments in series B and C yield similar points but the scatter is considerably greater. The shape of the graph is a curve as expected; at lower temperatures the graph levels off and chloroform production is relatively consistent, all of it being presumably formed by disproportionation step (6d). The value of $R_{\text{CHCl}_3} / R_{\text{i-PrCCl}_3}$ at this stage is about 0.45 ± 0.05 . This is compared with other related values in Table 3.3 for termination reactions:-

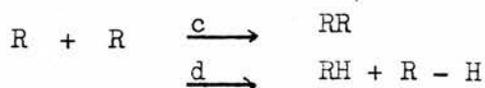


TABLE 3.3

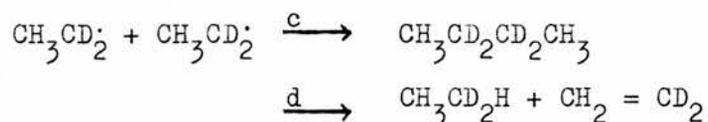
Disproportionation and Combination of
Radicals - Relative Rates

R	R	k_d/k_c	Ref.	k_d/k_c
CCl_3	C_2H_5	0.22, 0.24, 0.25	135, 136 150	0.079
CCl_3	$\text{i-C}_3\text{H}_7$	0.45	this work	0.075
CCl_3	$\text{c-C}_6\text{H}_{11}$	very low	53	-
CCl_3	$\text{C}_2\text{H}_4\text{Cl}^a$	$0.14, (0.11)^b$	134, 150	0.070
$\text{C}_2\text{H}_4\text{Cl}^a$	C_2H_5	0.22	150	0.073

(a) The radical was $\text{CH}_2\text{CH}_2\text{Cl}$

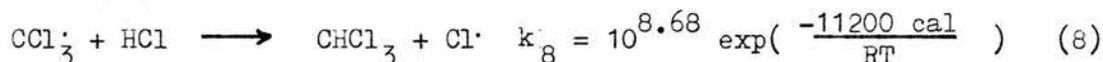
(b) An approximate calculation

The last column shows the normalised value, where N represents the number of β -hydrogen atoms present. These values are in good agreement with the normalisation proposals of Sheldon and Kochi. Wijnen and Steacie¹⁵¹ and M^cNesby et al¹⁵² photolysed $\alpha, \alpha, \alpha', \alpha'$ -tetradeuteriodiethyl ketone and confirmed that the β -hydrogen was abstracted. They showed that



and did not observe any deuterium migration during disproportionation. Consequently it is not unreasonable to suppose that there should be a statistical relationship governing these cross-combinations within a particular series of related compounds. The above results show however that there is not necessarily a direct relationship for primary, secondary or tertiary radicals, primary ethyl and secondary isopropyl yielding the same normalised value.

In the bromotrichloromethane studies it was shown that hydrogen abstraction from hydrogen bromide by trichloromethyl radicals constituted an important source of chloroform. It has, however, been shown in this laboratory⁴¹ that the rate of the corresponding reaction (8) is



slower than values for abstraction of secondary hydrogen atoms from alkanes^{39,99} and consequently the greater concentration of alkane than hydrogen chloride should ensure that reaction (8) would never occur to a significant extent.

Approximating the value of k_d/k_c for the cross-termination reaction (6) as 0.5 we have

$$(R_{\text{CHCl}_3})_4 = (R_{\text{CHCl}_3})_{\text{total}} - \frac{1}{2} (R_{\text{PrCCl}_3})$$

where $(R_{\text{CHCl}_3})_4$ represents the rate of formation of chloroform by reaction (4).

If the reaction is not permitted to progress beyond 5%

$$\begin{aligned} \text{conversion i.e. } [\text{PrH}]_i &\approx [\text{PrH}]_f && \text{where } i \text{ and } f \text{ denote initial} \\ \text{and } [\text{CCl}_4]_i &\approx [\text{CCl}_4]_f && \text{and final concentrations} \end{aligned}$$

the normal steady state assumptions can be made. We have

$$0 = \frac{d[\text{Cl}]}{dt} = \phi I_a - k_2 [\text{Cl}] [\text{RH}] \quad (\text{where } \phi \text{ is the primary quantum yield, } I_a \text{ is the light absorbed,}$$

$$\begin{aligned} \therefore [\text{Cl}] &= \phi I_a / k_2 [\text{RH}] && I_a = 2.303 \epsilon_{\text{CCl}_4} [\text{CCl}_4] l \cdot I_0 \\ &&& I_0 = \text{incident light intensity} \\ &&& l = \text{path length through cell)} \end{aligned}$$

$$\text{Also } 0 = \frac{d[\text{R}]}{dt} = \phi I_a + k_4 [\text{CCl}_3] [\text{RH}] - k_3 [\text{R}] [\text{CCl}_4] - k_6 [\text{CCl}_3] [\text{R}] - 2k_7 [\text{R}]^2 \quad (\text{A})$$

$$\text{and } 0 = \frac{d[\text{CCl}_3]}{dt} = \phi I_a + k_3 [\text{R}] [\text{CCl}_4] - k_4 [\text{CCl}_3] [\text{RH}] - k_6 [\text{CCl}_3] [\text{R}] - 2k_5 [\text{CCl}_3]^2 \quad (\text{B})$$

Subtraction of B from A yields

$$\begin{aligned} 0 &= k_4 [\text{CCl}_3] [\text{RH}] - k_3 [\text{R}] [\text{CCl}_4] - k_7 [\text{R}]^2 + k_5 [\text{CCl}_3]^2 \\ \therefore k_4 [\text{CCl}_3] [\text{RH}] + k_5 [\text{CCl}_3]^2 &= k_3 [\text{R}] [\text{CCl}_4] + k_7 [\text{R}]^2 \\ (R_{\text{CHCl}_3})_4 + R_{\text{C}_2\text{Cl}_6} &= R_{\text{RCl}} + (R_{\text{R}_2})_{\text{c+d}} \end{aligned} \quad (\text{C})$$

R is the isopropyl radical in this series of runs, and $(R_{\text{R}_2})_{\text{c+d}}$ represents the total rate of both reactions (7c) and (7d)

$$\text{i.e. } (R_{\text{R}_2})_{\text{c+d}} = 1.66 (R_{\text{R}_2})_{\text{measured}}$$

If the mechanism proposed earlier was correct and complete then equation (C) should hold through the whole temperature range.

The left and right hand sides of this equation have been

calculated and are shown in Table 3.4. It is obvious from

these results that equation (C) is only held at high temperatures

(> 220°C) where the chain length is reasonably long, and $(R_{\text{CHCl}_3})_4 \approx R_{\text{i-PrCl}}$.

TABLE 3.4

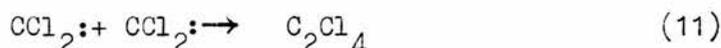
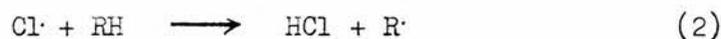
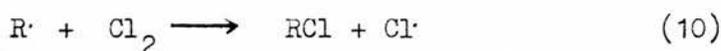
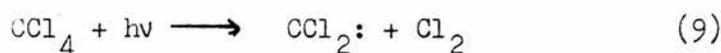
Rates of Formation Obtained by Photolysis

of the $\text{CCl}_4 - \text{C}_3\text{H}_8$ System (in $\text{mol.l}^{-1}\text{s}^{-1}$)

Temp (°C)	$(R_{\text{CHCl}_3})_4$	$R_{\text{C}_2\text{Cl}_6}$	$R_{i\text{PrCl}}$	$(R_{R_2})_{c+d}$	LHS of Equation C	RHS of Equation C
90	6.392×10^{-10}	6.933×10^{-10}	1.376×10^{-10}	5.813×10^{-10}	1.333×10^{-9}	7.189×10^{-10}
118	1.460×10^{-10}	1.965×10^{-10}	5.630×10^{-9}	2.561×10^{-10}	3.425×10^{-10}	5.886×10^{-9}
153	3.101×10^{-10}	2.615×10^{-10}	1.285×10^{-9}	2.643×10^{-10}	5.716×10^{-10}	1.549×10^{-9}
205	6.067×10^{-10}	5.345×10^{-11}	1.160×10^{-9}	2.523×10^{-10}	6.602×10^{-10}	1.412×10^{-9}
224	1.007×10^{-9}	1.863×10^{-10}	1.151×10^{-9}	3.023×10^{-10}	1.193×10^{-9}	1.453×10^{-9}
277	2.364×10^{-9}	1.169×10^{-11}	2.068×10^{-9}	2.538×10^{-10}	2.376×10^{-9}	2.322×10^{-9}
91	1.845×10^{-11}	1.855×10^{-10}	4.719×10^{-10}	1.278×10^{-10}	2.040×10^{-10}	5.997×10^{-10}
96	5.225×10^{-11}	1.439×10^{-10}	3.854×10^{-10}	9.172×10^{-11}	1.962×10^{-10}	4.771×10^{-10}
98	8.981×10^{-11}	8.656×10^{-11}	5.514×10^{-10}	1.240×10^{-10}	1.764×10^{-10}	6.754×10^{-10}
146	1.381×10^{-10}	1.899×10^{-10}	8.293×10^{-10}	6.333×10^{-11}	3.280×10^{-10}	8.926×10^{-10}
154	2.415×10^{-10}	1.601×10^{-10}	1.052×10^{-9}	8.328×10^{-11}	4.016×10^{-10}	1.135×10^{-9}
167	3.402×10^{-10}	8.633×10^{-11}	8.987×10^{-10}	3.307×10^{-11}	4.265×10^{-10}	9.318×10^{-10}
179	8.893×10^{-10}	2.231×10^{-10}	4.713×10^{-9}	1.851×10^{-11}	1.112×10^{-9}	4.732×10^{-9}
685	1.472×10^{-11}	2.790×10^{-11}	5.532×10^{-11}	2.452×10^{-11}	4.262×10^{-11}	7.984×10^{-11}
118	2.563×10^{-11}	3.207×10^{-11}	7.747×10^{-11}	2.766×10^{-11}	5.770×10^{-11}	1.051×10^{-10}
176	9.195×10^{-11}	4.083×10^{-11}	1.995×10^{-10}	1.670×10^{-11}	1.328×10^{-10}	2.162×10^{-10}
223	2.697×10^{-10}	3.949×10^{-11}	3.626×10^{-10}	1.381×10^{-11}	3.092×10^{-10}	3.764×10^{-10}
227	2.734×10^{-10}	5.179×10^{-11}	4.237×10^{-10}	3.239×10^{-11}	3.252×10^{-10}	4.561×10^{-10}

The chloroform and 2,3-dimethylbutane terms have been suitably corrected and there have been no reports of disproportionation of trichloromethyl radicals¹⁵³ to affect the overall rate of formation of hexachloroethane. The inference from the data is therefore that excess isopropyl chloride is formed at lower temperatures without the associated production of chloroform.

Currie, Sidebottom and Tedder⁵³ also observed this excess of alkyl chloride at lower temperatures in the CCl_4 -cyclohexane system, and proposed a carbene mechanism to account for it. To study this mechanism, more reactions (9) - (11), must be considered -

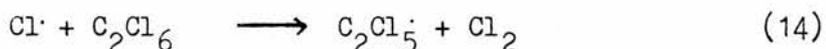
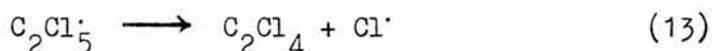
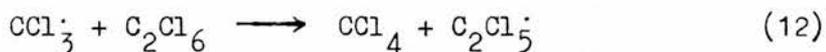


Using the values of Benson¹¹⁹ we have

	ΔH_f^\ddagger (kcal mol ⁻¹)	S° (cal mol ⁻¹)		ΔH_f^\ddagger (kcal mol ⁻¹)	S° (cal mol ⁻¹)
CCl_4	-24.0	74.2	Cl_2	0	53.3
CCl_3	18.5	70.8	Cl	28.9	39.5
CCl_2	45	63.7			

As $\Delta G = \Delta H - T\Delta S$ we have ΔH values for reaction (1) and (9) of 71.4 and 69 kcal mol⁻¹ respectively and ΔG values of 54.2 and 50.8 kcal mol⁻¹ respectively at 100°C. Although the presence of a small activation energy in reverse reaction (-9) (compared with zero activation energy for reaction (-1)) will reduce the tendency for reaction (9) to occur by increasing E_g , it can be seen from the similarity in energy requirements from each initiation reaction that both are likely under the conditions employed.

Tetrachloroethylene was observed in Fig 3.1 and was also reported in the results of Currie and coworkers. Reaction (11) is the only reasonable explanation for its presence, unless further reactions of hexachloroethane are studied. In studies of the pyrolysis of hexachloroethane⁴⁰ over the temperature range 340-400°C, White and Kuntz proposed



As the steady state concentrations of trichloromethyl radicals and chlorine atoms would be low in these propane studies and final concentrations of hexachloroethane were always low it is unlikely that reactions (12) and (14) would lead to detectable concentrations of tetrachloroethylene.

It should have been possible to calculate the relative extents of reactions (1) and (9) by considering

$$R_1 \equiv R_{\text{C}_2\text{Cl}_6} + (R_{\text{CCl}_3\text{Pr}})_{\text{c+d}} + (R_{\text{R}_2})_{\text{c+d}}$$

$$R_9 \equiv R_{\text{RCl}} - (R_{\text{RCl}})_{\text{eq(c)}}$$

where $(R_{\text{RCl}})_{\text{eq(c)}}$ is the rate of formation of isopropyl chloride calculated from equation (C). Unfortunately, an experimental error of only a few percent in the measurement of the chloroform or isopropyl chloride rates leads to a very significant error in the final ratio R_1/R_9 and no general trends could be deduced regarding the extent or the possible temperature dependence of the initiation reactions. Nevertheless this mechanism offered a satisfactory explanation of the deviations from equation (C) at lower temperatures. From the mechanism proposed in reactions (1) to (7) a reaction chain is obtained, reaction (1) being the only initiation step, reactions (2)-(4) being the propagation steps and (5)-(7) the termination stages.

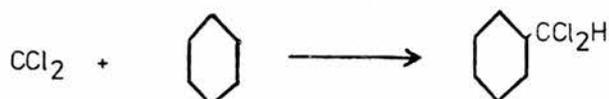
As the temperature of reaction is increased the rates of the propagation steps will also increase but the termination reactions, having no activation energy will have unchanged rate constants. This will not affect equation (C) but it will increase the quantum yields of isopropyl chloride and chloroform, (i.e the number of molecules produced per quantum of light absorbed by CCl_4). However, from the additional reaction steps resulting from photolysis to dichlorocarbene the result is different. No reaction chain is present and each quantum of light absorbed will yield one molecule of dichlorocarbene and one molecule of chlorine. This molecule of chlorine will yield one molecule of isopropyl chloride and one of hydrogen chloride by reactions (10) and (2) or it can photolyse as in reaction (15) to give



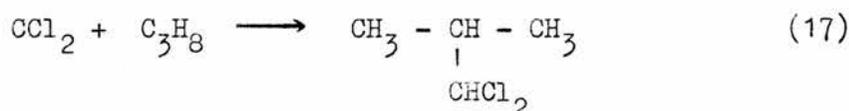
two chlorine atoms which will, by reactions (2) and (10), yield a further one molecule of isopropyl chloride. The isopropyl radicals from reaction (2) could also participate in termination reactions (6) and (7).

Thus the overall effect of this secondary initiation step would be to increase the value of the right hand side of equation (C) but not to affect the left hand side. As temperature of reaction increases, this equation tends to equate chloroform and isopropyl chloride, the termination products being relatively unimportant. As the chain length (i.e. number of propagation cycles per initiation (or termination) step) increases, the quantum yield of CHCl_3 and $i\text{-C}_3\text{H}_7\text{Cl}$ by initiation reaction (1) increases, whereas the quantum yield of $i\text{-C}_3\text{H}_7\text{Cl}$ from initiation reaction (9) cannot exceed 1. Hence the effect of this secondary initiation step on equation (C) diminishes as temperature is increased; this is borne out by experimental results.

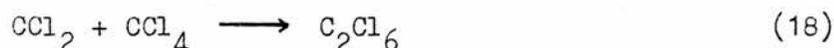
Another problem can arise from this carbene mechanism. It has been assumed that all the dichlorocarbene terminated by reaction (11) to yield tetrachloroethylene. One of the most common reactions of carbenes is the "insertion" type whereby the carbene inserts itself in another molecule. White and Kuntz³⁹ report dichloromethylcyclohexane from their studies of the reaction between carbon tetrachloride and cyclohexane.



The analogous reaction with propane would yield 1,1-dichloro-2-methylpropane. (reaction (17)) which was not identified among the reaction products.



Another insertion reaction could result from the reaction with CCl_4 (reaction (18)). This would not be detectable, as hexachloro-



ethane is also produced by reaction (5). If this occurred to any significant extent the calculations involving the rate of formation of C_2Cl_6 would be invalidated.

A suitable check to discover whether hexachloroethane was produced by reaction (5) alone or by both reactions (5) and (18) would be to measure the ratio $k_6/(k_5k_7)^{\frac{1}{2}}$. It has been often shown by many workers^{142,154} that this ratio yields a value of about 2 in all but a minority of cases (e.g. $\text{CH}_3 + \text{CH}_3\text{COCH}_2$; ratio = 1.0¹⁵⁵). Although the specific case of isopropyl and trichloromethyl radicals has hitherto not been reported, the combination of isopropyl radicals with methyl,¹⁵⁶ ethyl¹⁴⁴ and t-butyl¹⁴⁴ radicals and the combination of trichloromethyl radicals with both ethyl¹³⁵ and chloroethyl¹³⁴ radicals have been studied and in each case the value of the ratio was about 2. The rates of formation of the three termination products

in this reaction system however were not great enough for accurate gas-chromatograph areas to be measured and as a consequence the spread of values for the ratio is too great to draw any useful conclusions.

Early work^{78,79} carried out to measure absolute rate constants and Arrhenius parameters for the abstraction of a hydrogen atom by the trichloromethyl radical as in reaction (4) used trichlorobromomethane as the source of CCl_3 radicals. It has since been shown^{68,100} that these calculations were not valid as the rate of initiation by photolysis of CCl_3Br , which had been assumed to be constant over the temperature range employed, in fact increased with rising temperature. Recalculation of the same experimental results¹⁰⁰ has aligned the rate constants with those obtained by Wampler and Kuntz⁹⁹ for alkanes in the C_5 to C_8 range. As the Arrhenius factors can be calculated without reference to the initiation rate ϕIa , any temperature dependence of this value should not affect the calculated values.

$$(R_{\text{CHCl}_3})_4 = k_4 [\text{CCl}_3] [\text{RH}]$$

$$R_{\text{C}_2\text{Cl}_6} = k_5 [\text{CCl}_3]^2$$

where $(R_{\text{CHCl}_3})_4 = R_{\text{CHCl}_3} - \frac{1}{2} R_{\text{RCCl}_3}$ represents, as

explained earlier, the rate of formation of chloroform by reaction

(4) alone. Combination of these two equations yields

$$\frac{(R_{\text{CHCl}_3})_4}{(R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}}} = \frac{k_4 [\text{RH}]}{k_5^{\frac{1}{2}}}$$

$$\log_e \left(\frac{(R_{\text{CHCl}_3})_4}{(R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}}} [\text{RH}] \right) = \log_e A_4^{-\frac{1}{2}} \log_e A_5 + \frac{\frac{1}{2}E_5 - E_4}{RT}$$

or, since $E_5=0$

$$\log_{10} \left(\frac{(R_{\text{CHCl}_3})_4}{(R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}} [\text{RH}]} \right) = \log_{10} A_4^{-\frac{1}{2}} \log_{10} A_5 - \frac{E_4}{2.303 RT}$$

Hence a graph plotting the left hand side against the reciprocal of temperature should yield a gradient of $(-E_4/2.303R)$ and an intercept on the y-axis of $(\log_{10} A_4 - \frac{1}{2} \log_{10} A_5)$. These values are shown in Table 3.5 and illustrated in Fig 3.3.

This graph has a gradient of -1.88 ± 0.55 and a y-axis intercept of 2.23 ± 0.23 . Assuming that $\log_{10} A_5 = 9.7 \text{ l mol}^{-1} \text{ s}^{-1}$ this gives:-

$$E_4 = 8.60 \pm 2.53 \text{ kcal mol}^{-1}$$

$$\log A_4 = 7.1 \pm 0.2 \text{ l mol}^{-1} \text{ s}^{-1}$$

Wampler and Kuntz⁹⁹ have studied the hydrogen abstraction from alkanes by the trichloromethyl radical. They obtained activation energies between $8.2 \text{ kcal mol}^{-1}$ (tertiary hydrogen abstraction from 2,3-dimethylbutane) and $10.8 \text{ kcal mol}^{-1}$ (hydrogen abstraction from n-hexane) and pre-exponential terms between $7.88 \text{ l mol}^{-1} \text{ s}^{-1}$ (2,3-dimethylbutane) and $9.11 \text{ l mol}^{-1} \text{ s}^{-1}$ (cyclooctane).

The activation energy calculated above is slightly lower than would be expected from Kuntz's values. The A-factor however is also lower so the overall rate k_4 is in reasonable agreement with the previous results. We have $k_4 = 10^{-7.1} e^{-8.6/RT}$. At 150°C and setting $A_4 = 10^{8.4}$, we obtain $E_4 = 11.2 \text{ kcal mol}^{-1}$, consistent with results obtained by other workers on related systems.

A similar calculation to the above can be made to measure A_3 and E_3 .

$$(R_{\text{RCl}})_3 = k_3 [\text{R}] [\text{CCl}_4]$$

$$(R_{\text{R}_2})_{\text{c+d}} = k_7 [\text{R}]^2$$

where $(R_{\text{RCl}})_3$ is the rate of formation of isopropylchloride from reaction (3) alone and $(R_{\text{R}_2})_{\text{c+d}}$ is the combined rate of combination and disproportionation. $(R_{\text{RCl}})_3$ is calculated from equation (C), discussed earlier, and $(R_{\text{R}_2})_{\text{c+d}} = 1.66 (R_{\text{R}_2})$ as measured. Combination of the two equations above yields.

TABLE 3.5

Rates of Formation Obtained by Photolysis
of the $\text{CCl}_4 - \text{C}_2\text{H}_6$ System (in $\text{mol l}^{-1} \text{s}^{-1}$)

Temp($^{\circ}\text{C}$)	$(R_{\text{CHCl}_3})_4$	$(R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}}$	$1000/T(^{\circ}\text{K})$	$\log_{10} \frac{(R_{\text{CHCl}_3})_4}{(R_{\text{C}_2\text{Cl}_6})^{\frac{1}{2}} [\text{RH}]}$
118	1.460×10^{-10}	1.402×10^{-5}	2.556	-2.437
153	3.101×10^{-10}	1.617×10^{-5}	2.346	-2.172
205	6.067×10^{-10}	7.311×10^{-6}	2.091	-1.536
224	1.007×10^{-9}	1.365×10^{-5}	2.011	-1.587
277	2.364×10^{-9}	3.419×10^{-6}	1.818	-0.615
91	1.845×10^{-11}	1.362×10^{-5}	2.746	-3.323
96	5.225×10^{-11}	1.200×10^{-5}	2.709	-2.816
98	8.981×10^{-11}	9.304×10^{-6}	2.694	-2.470
146	1.381×10^{-10}	1.378×10^{-5}	2.385	-2.454
154	2.415×10^{-10}	1.265×10^{-5}	2.341	-2.174
167	3.402×10^{-10}	9.291×10^{-6}	2.272	-
179	8.893×10^{-10}	1.494×10^{-5}	2.211	-1.680
68.5	1.472×10^{-11}	5.282×10^{-6}	2.927	-3.010
118	2.563×10^{-11}	5.663×10^{-6}	2.556	-2.799
176	9.195×10^{-11}	6.390×10^{-6}	2.226	-2.297
223	2.697×10^{-10}	6.284×10^{-6}	2.015	-1.822
227	2.734×10^{-10}	7.197×10^{-6}	1.999	-1.875

$$[\text{RH}]_i = 2.851 \times 10^{-3} \text{ mol l}^{-1}$$

$$[\text{CCl}_4]_i = 1.425 \times 10^{-3} \text{ mol l}^{-1}$$

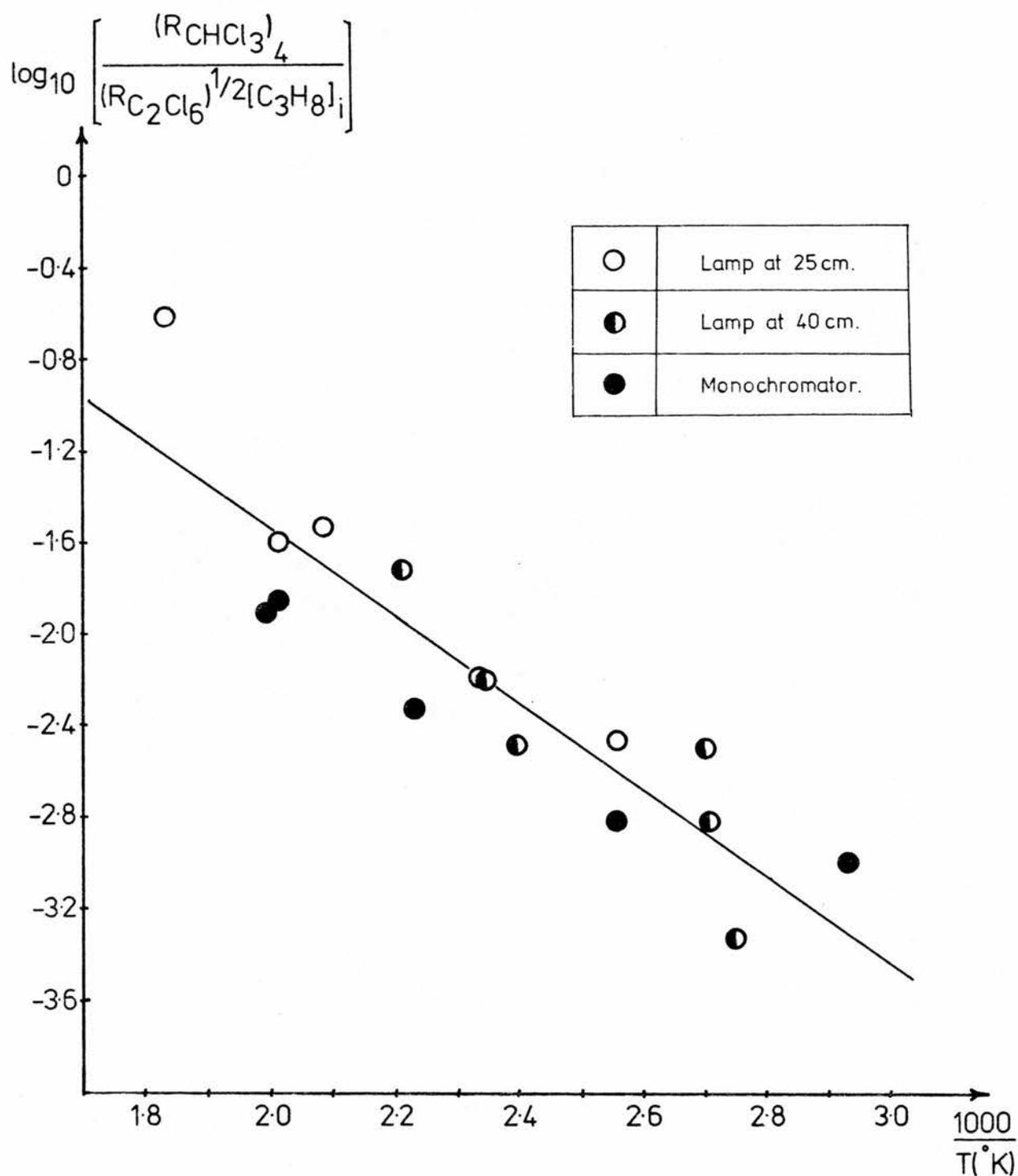


FIGURE 3.3

Graph of $\log_{10} \left[\frac{(RCHCl_3)_4}{(RC_2Cl_6)^{1/2} [C_3H_8]_i} \right]$ versus the reciprocal of temperature for the propane-carbon tetrachloride system.

$$\frac{(R_{\text{RCl}})_3}{(R_{\text{R}_2})_{\text{c+d}}^{\frac{1}{2}}} = \frac{k_3 [\text{CCl}_4]}{k_7^{\frac{1}{2}}}$$

$$\log_{10} \left(\frac{(R_{\text{RCl}})_3}{(R_{\text{R}_2})_{\text{c+d}}^{\frac{1}{2}} [\text{CCl}_4]} \right) = \log A_3^{-\frac{1}{2}} \log A_7 - \frac{E_3 - \frac{1}{2}E_7}{2.303RT}$$

As $E_7 = 0$, a plot of the left hand side against the inverse of temperature should yield a gradient of $\frac{E_3}{2.303R}$ and an intercept on the y-axis of $(\log A_3^{-\frac{1}{2}} \log A_7)$. The points are listed in Table 3.6 and plotted on Fig. 3.4. This graph has a gradient of 1.38 ± 0.39 and an intercept on the y-axis of 1.43 ± 0.16 . This gives:-

$$E_3 = 6.30 \pm 1.78 \text{ kcal mol}^{-1}$$

$$\log A_3 = (1.43 \pm 0.16) + \frac{1}{2} \log A_7$$

Using the value¹³⁹ of $k_7 = 10^{10.8} \text{ l.mol}^{-1} \text{ s}^{-1}$ we have $\log A_3 = 6.8 \pm 1.6 \text{ l.mol}^{-1} \text{ s}^{-1}$

The Arrhenius parameters for chlorine abstraction from carbon tetrachloride by methyl, ethyl and cyclohexyl radicals have recently been determined in this laboratory⁵³, $k_3(\text{R=Me}) = 10^{8.6} \exp(-9100 \text{ cal/RT})$, $k_3(\text{R=Et}) = 10^{8.4} \exp(-8900 \text{ cal/RT})$ and $k_3(\text{R=c-C}_6\text{H}_{11}) = 10^{8.6} \exp(-11800 \text{ cal/RT})$. Although the A-factor obtained in this work is somewhat lower than these values, the activation energy, E_3 , is correspondingly lower and the overall reaction rate, k_3 is comparable at the temperatures employed.

We have $k_3 = 10^{6.8} \exp(-6300 \text{ cal/RT})$. At 150°C and setting $A_3 = 10^{8.5}$, we obtain $E_3 = 9.7 \text{ kcal mol}^{-1}$ - in good agreement with values for ethyl radicals etc. quoted above.

These Arrhenius parameters calculated for reactions (3) and (4) can be confirmed by considering also reaction (6).

TABLE 3.6

Rates of Formation Obtained by Photolysis
of the $\text{CCl}_4\text{-C}_3\text{H}_8$ System ($\text{mol.l}^{-1}\text{s}^{-1}$)

Temperature (°C)	$(R_{\text{RCl}})_3$	$(R_{\text{R}_2})_{\text{c+d}}$	$1000/T(^{\circ}\text{K})$	$\log_{10} \frac{(R_{\text{RCl}})_3}{(R_{\text{R}_2})_{\text{c+d}}} [\text{CCl}_4]$
90	1.972×10^{-10}	5.778×10^{-10}	2.755	-2.239
118	8.790×10^{-11}	2.546×10^{-10}	2.588	-2.413
153	3.089×10^{-10}	2.627×10^{-10}	2.347	-1.874
205	4.094×10^{-10}	2.508×10^{-10}	2.092	-1.741
224	9.608×10^{-10}	3.005×10^{-10}	2.012	-1.410
277	2.123×10^{-9}	2.523×10^{-10}	1.818	-1.028
91	7.695×10^{-11}	1.270×10^{-10}	2.747	-2.320
96	1.050×10^{-10}	9.116×10^{-11}	2.710	-2.113
98	5.311×10^{-11}	1.233×10^{-10}	2.695	-2.474
146	2.651×10^{-10}	6.295×10^{-11}	2.387	-1.630
154	3.188×10^{-10}	8.278×10^{-11}	2.342	-1.609
167	3.642×10^{-10}	3.287×10^{-11}	2.273	-1.351
179	9.284×10^{-10}	1.840×10^{-10}	2.212	-1.318
68.5	1.825×10^{-11}	2.437×10^{-11}	2.928	-2.586
118	3.021×10^{-11}	2.749×10^{-11}	2.558	-2.393
176	1.029×10^{-10}	2.987×10^{-11}	2.227	-1.879
223	2.955×10^{-10}	1.373×10^{-11}	2.016	-1.252
227	2.930×10^{-10}	3.219×10^{-11}	2.000	-1.441

$$[\text{CCl}_4]_i = 1.425 \times 10^{-3} \text{ mol.l.}^{-1}$$

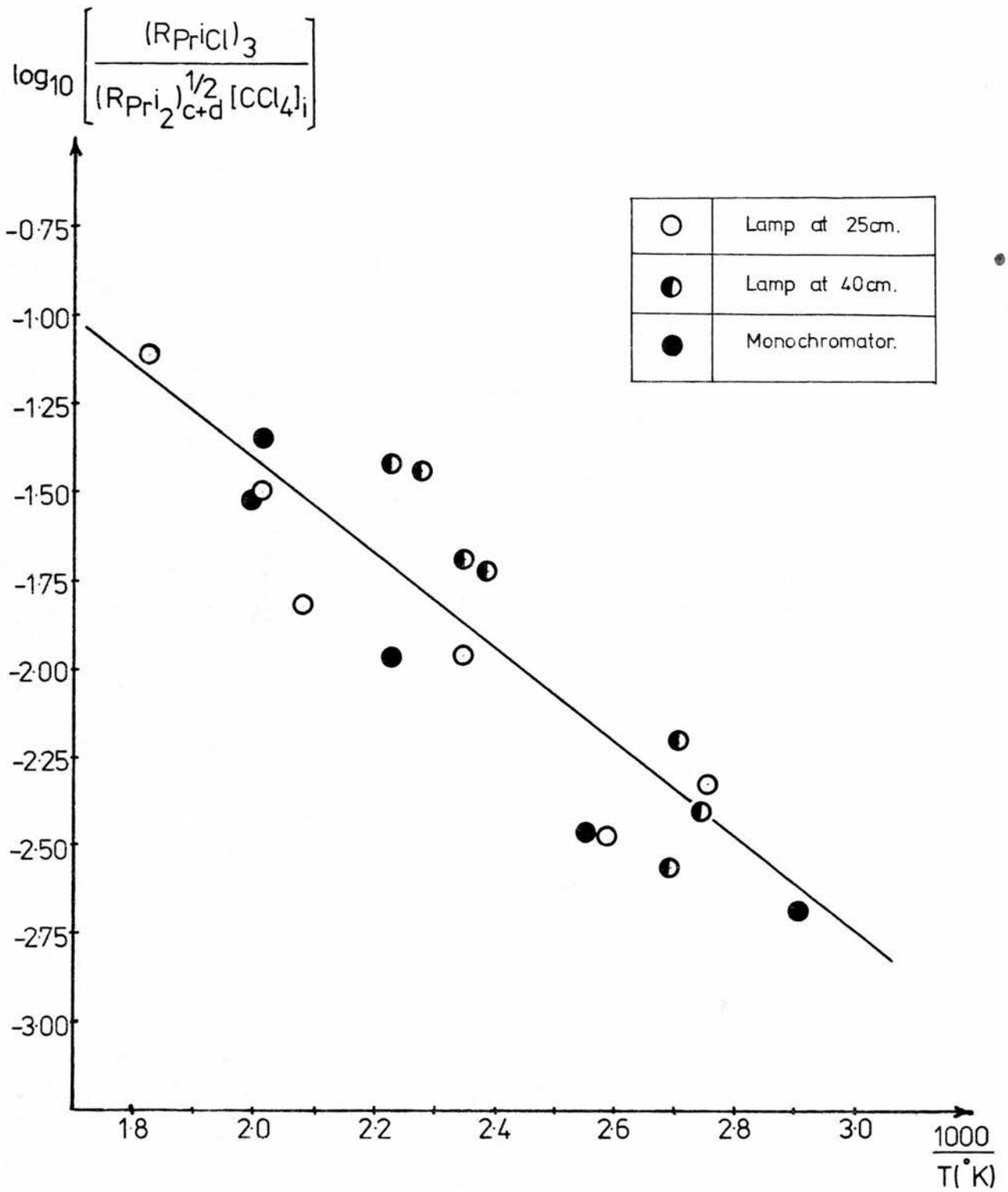


FIGURE 3.4 Graph of $\log_{10} \left[\frac{(R_{PrCl})_3}{(R_{Pr_2})_{c+d}^{1/2} [CCl_4]_i} \right]$ versus the reciprocal of temperature for the propane-carbon tetrachloride system.

$$\begin{aligned} (R_{\text{RCCl}_3})_{\text{c+d}} &= k_6 [\text{R}] [\text{CCl}_3] \\ (R_{\text{RCl}})_3 &= k_3 [\text{R}] [\text{CCl}_4] \\ (R_{\text{CHCl}_3})_4 &= k_4 [\text{CCl}_3] [\text{RH}] \end{aligned}$$

where $(R_{\text{RCCl}_3})_{\text{c+d}}$ is the combined rate of combination and disproportionation and $(R_{\text{RCl}})_3$ and $(R_{\text{CHCl}_3})_4$ are as described earlier.

Combination of these three equations yields

$$\frac{(R_{\text{RCl}})_3 (R_{\text{CHCl}_3})_4}{(R_{\text{RCCl}_3})_{\text{c+d}}} = \frac{k_3 k_4}{k_6} [\text{CCl}_4] [\text{RH}]$$

Hence
$$\log_{10} \left(\frac{(R_{\text{RCl}})_3 (R_{\text{CHCl}_3})_4}{(R_{\text{RCCl}_3})_{\text{c+d}} [\text{RH}] [\text{CCl}_4]} \right) = \log A_3 + \log A_4 - \log A_6 - \frac{E_3 + E_4 - E_6}{2.303 RT}$$

As $E_6 = 0$, a plot of the left hand side against the inverse of temperature should yield a straight line of gradient $-(E_3 + E_4)/2.303R$ and a y-axis intercept of $(\log A_3 + \log A_4 - \log A_6)$. The coordinates are shown in Table 3.7 and the graph is plotted on Figure 3.5. The graph has a gradient of 3.56 ± 0.68 and a y-axis intercept of 4.48 ± 0.29 . This gives:-

$$E_3 + E_4 = 16.28 \pm 3.11 \text{ kcal mol}^{-1}$$

$$\log A_3 + \log A_4 = (4.48 \pm 0.29) + \log A_6 \text{ l.mol}^{-1} \text{s}^{-1}$$

Using a value of $\log A_5 = 9.7 \text{ l.mol}^{-1} \text{s}^{-1}$ and $\log A_7 = 10.8 \text{ l.mol}^{-1} \text{s}^{-1}$ 139

the value of the preexponential term for the cross-combination, $\log A_6$ can be assumed to be between these values. Using the approximation

$$\log A_6 = (\log A_5 \log A_7)^{\frac{1}{2}} \text{ we obtain } \log A_6 = 10.2 \text{ l.mol}^{-1} \text{s}^{-1}$$

Substituting this value in the above equation we get:-

$$\log A_3 + \log A_4 = 14.7 \pm 0.3 \text{ l.mol}^{-1} \text{s}^{-1}$$

TABLE 3.7

Rates of Formation Obtained by Photolysis
of the $\text{CCl}_4\text{-C}_2\text{H}_6$ System

Temperature (°C)	$(R_{\text{CHCl}_3})_4$	$(R_{\text{PrCl}})_3$	$R_{\text{Pr}^i\text{CCl}_3}$	$1000/T(^{\circ}\text{K})$	$\log \frac{(R_{\text{CHCl}_3})_4 (R_{\text{PrCl}})_3}{[\text{CCl}_4][\text{Pr}^i\text{H}][\text{Pr}^i\text{CCl}_3]}$
118	1.460×10^{-10}	8.790×10^{-11}	1.767×10^{-10}	2.588	-4.749
153	3.101×10^{-10}	3.089×10^{-10}	1.660×10^{-10}	2.347	-3.849
205	6.067×10^{-10}	4.094×10^{-10}	1.010×10^{-10}	2.092	-3.219
224	1.007×10^{-9}	9.608×10^{-10}	6.824×10^{-11}	2.012	-2.458
277	2.364×10^{-9}	2.123×10^{-9}	8.173×10^{-11}	1.818	-1.822
91	1.845×10^{-11}	7.695×10^{-11}	4.189×10^{-10}	2.747	-6.080
96	5.225×10^{-11}	1.050×10^{-10}	1.859×10^{-10}	2.710	-5.140
98	8.981×10^{-11}	5.311×10^{-11}	9.778×10^{-11}	2.695	-4.922
146	1.381×10^{-10}	2.651×10^{-10}	2.772×10^{-10}	2.387	-4.489
154	2.415×10^{-10}	3.188×10^{-10}	2.298×10^{-10}	2.342	-4.085
179	8.893×10^{-10}	9.284×10^{-10}	6.834×10^{-10}	2.212	-3.528
68.5	1.472×10^{-11}	1.825×10^{-11}	1.101×10^{-11}	2.928	-5.223
118	2.563×10^{-11}	3.021×10^{-11}	6.062×10^{-12}	2.558	-4.504
176	9.195×10^{-11}	1.029×10^{-10}	3.960×10^{-12}	2.227	-3.232
223	2.697×10^{-10}	2.955×10^{-10}	4.073×10^{-12}	2.016	-2.319
227	2.734×10^{-10}	2.930×10^{-10}	1.168×10^{-11}	2.000	-2.774

$$[\text{CCl}_4]_i = 1.425 \times 10^{-3} \text{ mol/l}$$

$$\text{Gradient} = 3.56 \pm 0.68$$

$$[\text{RH}]_i = 2.851 \times 10^{-3} \text{ mol/l}$$

$$\text{Intercept} = 4.48 \pm 0.29$$

$(R_{\text{CHCl}_3})_4$ = Formation rate of CHCl_3 from reaction 4.

$(R_{\text{Pr}^i\text{Cl}})_3$ = Formation rate of Pr^iCl from reaction 3.

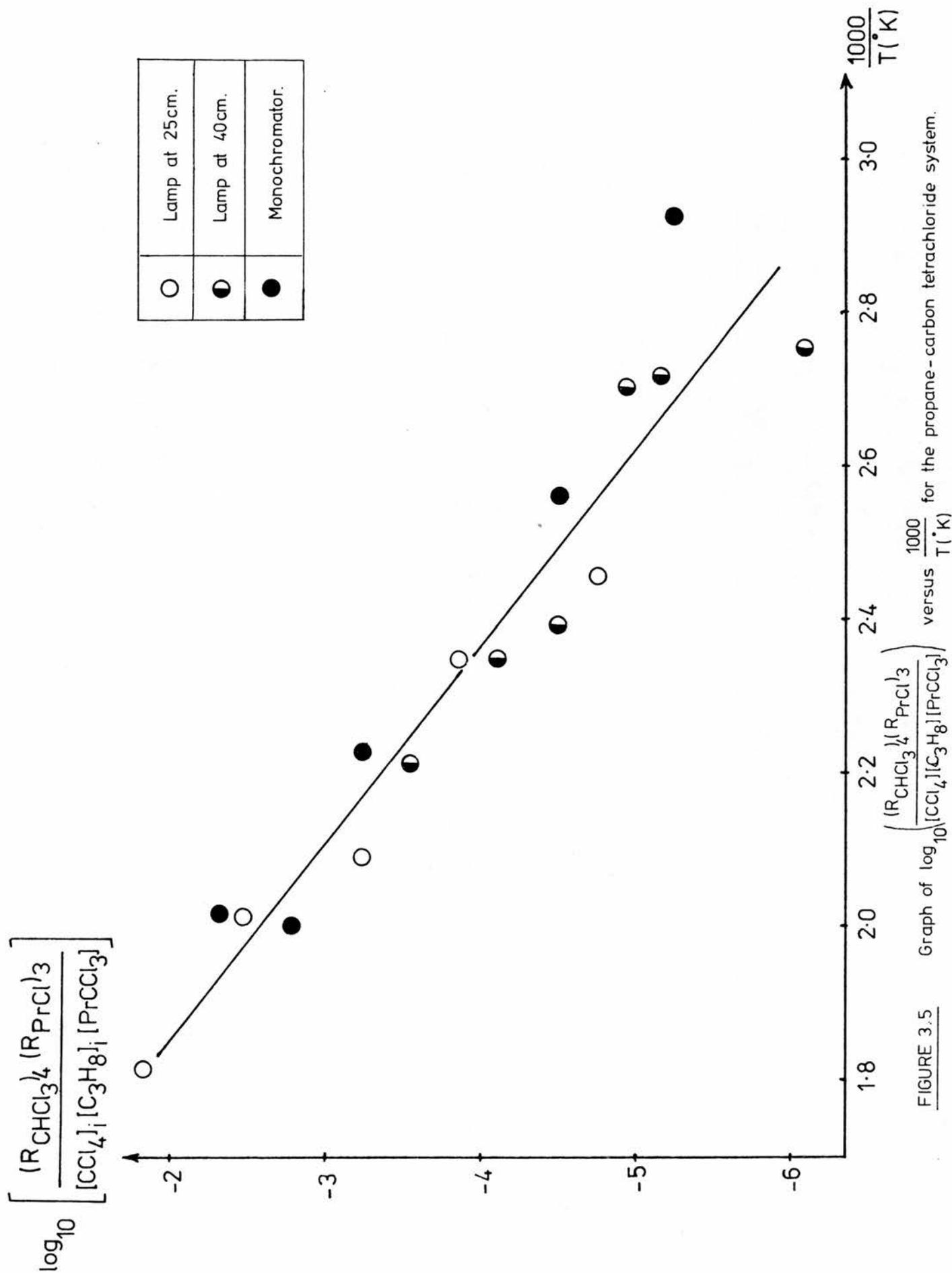


FIGURE 3.5 Graph of $\log_{10} \left(\frac{(R_{\text{CHCl}_3})_4 (R_{\text{PrCl}_3})_3}{[\text{CCl}_4]_4 [\text{C}_3\text{H}_8]_4 [\text{PrCCl}_3]_3} \right)$ versus $\frac{1000}{T} (\text{K})$ for the propane-carbon tetrachloride system.

The combination values of (E_3+E_4) and $(\log A_3 + \log A_4)$ are in good agreement with the rate constants calculated earlier for reactions (7) and (4).

We have:-

$$k_3 k_4 = A_3 \exp(-E_3/RT) A_4 \exp(-E_4/RT)$$

$$\log(k_3 k_4) = (\log A_3 + \log A_4) - (E_3 + E_4 / 2.303 RT) \quad (D)$$

At 150°C the values of $\log A_3$ and $\log A_4$ were set at 8.5 and 8.4 $\text{l.mol}^{-1} \text{s}^{-1}$ respectively in the calculations earlier in this discussion, and activation energies E_3 and E_4 were calculated as 9.7 and 11.2 kcal mol^{-1} respectively (i.e. $E_3+E_4 = 20.9 \text{ kcal mol}^{-1}$)

Using the results of Figure 3.5 we obtain (at 150°C):-

$$\log(k_3 k_4) = 14.7 - \frac{16280}{1936} = 6.3$$

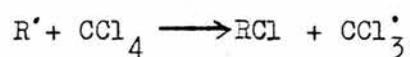
Substituting $\log(k_3 k_4) = 6.3$ and $(\log A_3 + \log A_4) = 16.9$ in equation D we obtain $E_3+E_4 = 20.5 \text{ kcal.mol}^{-1}$, very similar to the value of $20.9 \text{ kcal mol}^{-1}$ calculated from Figures 3.3 and 3.4.

The kinetic data obtained from this study of the photolysis of propane-carbon tetrachloride mixtures is therefore in very good agreement with the work of other workers in the centre of the temperature range examined i.e. around 150°C. It would appear that the discrepancy with the results of previous workers lies in the low temperature data causing the gradients of Figures 3.3, 3.4 and 3.5 to be too low. In this temperature range the carbene mechanism will assume a more significant role, the chain length of the systems under study will be very short and the products of disproportionation reactions can be expected to make up a more significant proportion of the reaction products.

Tables 3.8 and 3.9 show a comparison of the results of this study with those of other workers.

TABLE 3.8Arrhenius Parameters for the Reaction

RH	$\log_{10} A (1. \text{mol}^{-1} \text{s}^{-1})$	$E (\text{kcal mol}^{-1})$	Reference
Methane	9.8	17.9	189
Ethane	9.0	14.1	190
Propane	8.4 (estimate)	11.2	This work
Hexane	8.8	10.8	99
Cyclohexane	8.8	10.7	40
2,3-dimethylbutane	7.9	8.2	99

TABLE 3.9Arrhenius Parameters for the Reaction

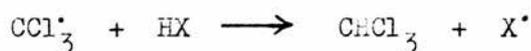
R	$\log_{10} A (1. \text{mol}^{-1} \text{s}^{-1})$	$E (\text{kcal mol}^{-1})$	Reference
Methyl	8.6	9.1	53
Methyl	10.2	13.4	137
Ethyl	8.4	8.9	53
Isopropyl	8.5 (estimate)	9.7	This work
Cyclohexyl	8.6 (estimate)	11.8	53

SECTION 4

The Photolysis of Carbon Tetrachloride With Cyclopentane

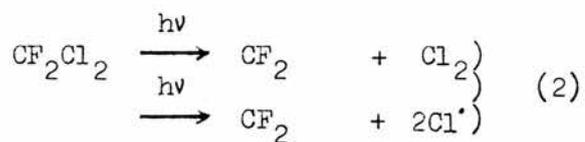
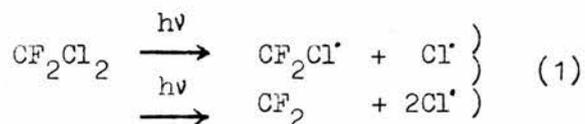
INTRODUCTION

In section 3 the reactions present in the photolysis of carbon tetrachloride in the presence of propane were described. Unlike the systems described in section 1 and 2, the reaction:-



did not appear to affect this system. However there was evidence to suggest that a secondary initiation process was taking place yielding dichlorocarbene and chlorine which had a significant effect on the balance of products. The presence of this secondary initiation process in the photolysis of carbon tetrachloride was shown by Davis and coworkers¹⁵⁷ to play an important role at wavelengths shorter than 253.7 nm. In this laboratory Currie⁵³ detected tetrachloroethylene among the products in the photolysis of carbon tetrachloride in the presence of cyclohexane, and deduced that this was the termination product of two dichlorocarbene molecules (diradicals).

Rebbert and Ausloos¹⁵⁸ studied the analogous photodecomposition of CF_2Cl_2 and suggested two pathways leading to the carbene.



In the photolysis of carbon tetrachloride the low concentration of CCl_3^{\cdot} radicals would render the first pathway unlikely. In the second pair of reactions the Cl_2 formed from the first stage could undergo either photolysis or chlorine transfer to another radical in the system, CCl_3^{\cdot} or R. It is most probable that the CCl_2^{\cdot} radicals present originated from direct photolysis of CCl_4 as in the first reaction of (2).

The thermolysis of perhalomethanes to yield radical or carbene products has also been examined¹⁵⁹ but would not occur in the temperature range of the present investigation.

A recent study of radical combination/disproportionation reactions in solution by Griller and Ingold¹⁶⁰ suggests that the combination rates of both isopropyl and cyclopentyl radicals are very similar. The paper also compares liquid and gas phase combination rates and indicates that the trends in gas phase should be very similar.

It might therefore be expected that the cyclopentane/ CCl_4 system should yield similar results on photolysis to the propane/ CCl_4 system, the alkyl radicals having similar reactivities. In this section the system is examined and the results compared with those obtained in section 3.

SECTION 4

The Photolysis of Carbon Tetrachloride With Cyclopentane

EXPERIMENTAL

4.1 REACTANTS

(a) Carbon tetrachloride was Fisons "spectrograde" reagent as used in the last section.

(b) Cyclopentane was Fisons "Laboratory Reagent" grade and was used without further purification.

4.2 APPARATUS

The vacuum system has been described earlier. The reaction vessel used was a quartz cylindrical vessel as described in Section 3. The light source was a Hanovia UVS 200 medium pressure arc lamp as described in Section 1. The lamp was situated 40 cm from the nearest face of the reaction vessel.

4.3 PROCEDURE

The procedure was identical to that described for the propane-carbon tetrachloride system. The pressures of cyclopentane and carbon tetrachloride in bulb A were 60 τ and 25 τ respectively before distillation into the reaction vessel.

4.4 ANALYSIS

The gas liquid chromatography apparatus was described in Section 1. The more volatile products were separated at 25°C with a nitrogen carrier gas flow rate of 35 mlmin⁻¹ and a chart speed of 48 inhr⁻¹. The less volatile termination products were separated on the same column at 100°C with a carrier gas flow rate of 30 mlmin⁻¹ and a chart speed of 24 inhr⁻¹. The samples were injected using a 10 μ l Hamilton syringe and 10 μ l aliquots were used for each chromatogram. The column used was a 6ft x 3/8in column with 20% by weight silicone oil supported on 60-100 mesh "Embacel".

4.5 IDENTIFICATION OF PRODUCTS

A typical chromatogram of the lighter products showed five peaks as illustrated in Fig. 4.1. Three further products were observed on separation at higher temperature; these are shown in Fig. 4.2. Other trace products were detected at the higher temperature but their concentration was too low for any positive identification. Most of the peaks were identified by a comparison of retention times with authentic samples, and confirmed by gas liquid chromatography coupled mass spectroscopy. Residual chlorine from the hexachloroethane peak was noticed in the bicyclopentyl peak and in the 1,1,1-trichloromethylcyclopentane peak. A sample of bicyclopentyl was prepared in the laboratory (See Appendix 2) and the retention time measured and compared with the chromatogram (Fig. 4.2). The last peak observed was thus identified as bicyclopentyl. The cross-combination product 1,1,1-trichloromethylcyclopentane would be expected to occur between hexachloroethane and bicyclopentyl. Measurement of the area of the peak between these two yielded values which indicated that

$$\frac{(R_{C_2Cl_6} \times R_{R_2})^{\frac{1}{2}}}{R_{RCCl_3}} \cong 0.5$$

which was in good agreement with many similar systems^{142,154}.

The peak identified as tetrachloroethylene was too small for mass spectroscopic analysis but the retention time was the same as that of an authentic sample and, in the light of the conclusions of the previous chapter, some tetrachloroethylene would be expected.

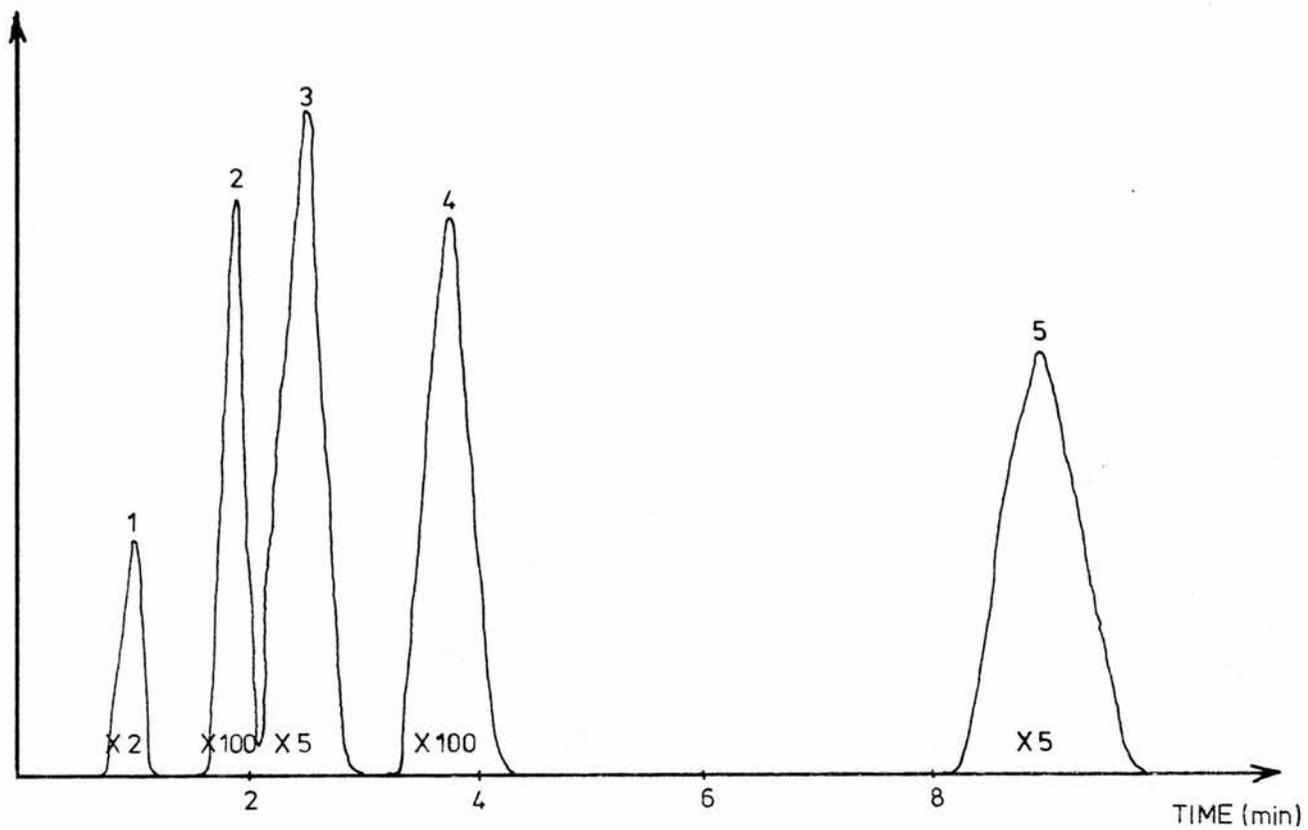


FIGURE 4.1 Low Temperature GLC Analysis of Products of CCl_4 - Cyclopentane Photolysis.

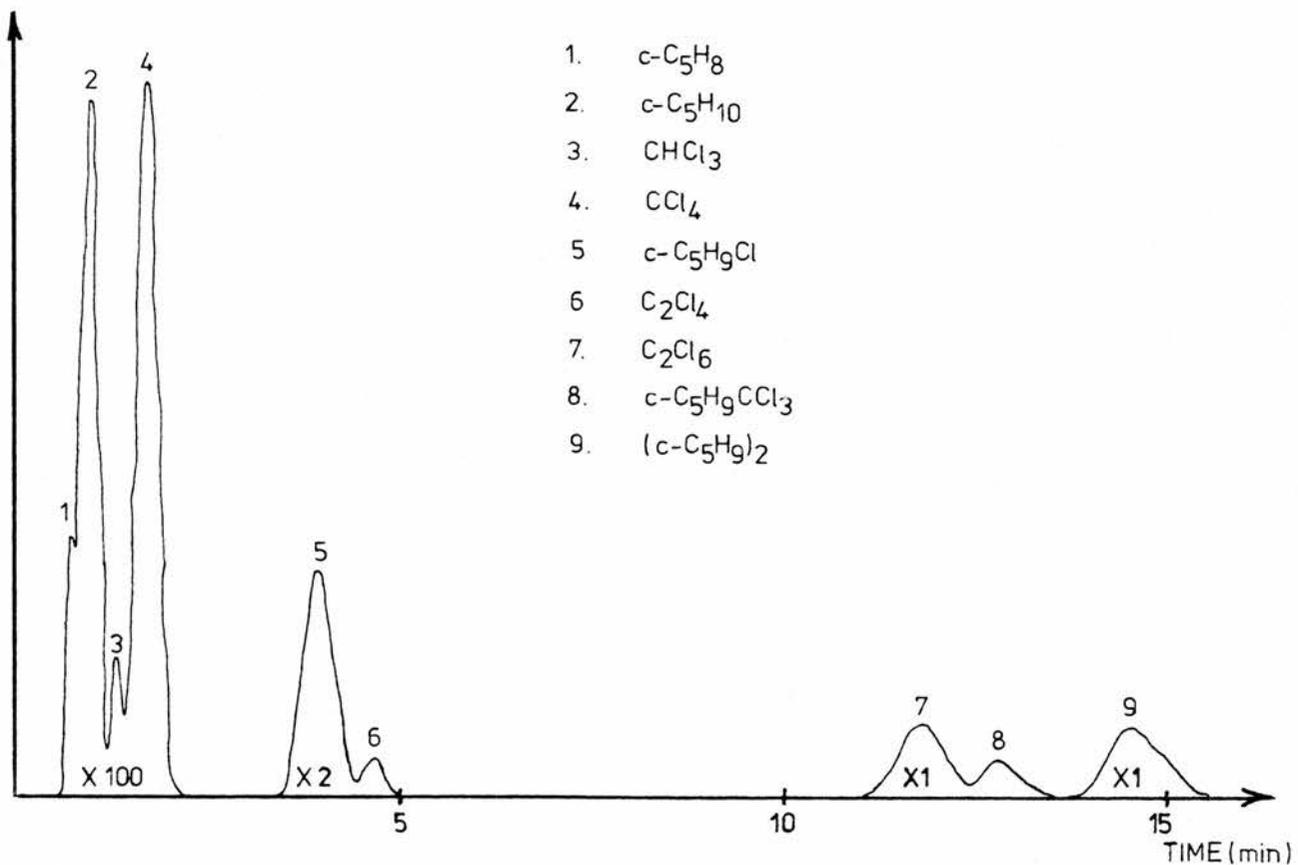


FIGURE 4.2 High Temperature GLC Analysis of Products of CCl_4 - Cyclopentane Photolysis.

4.6 RESULTS

Two series of experiments were carried out. In calculation of Arrhenius parameters it is assumed that the percentage conversion of reactants is low and does not change significantly throughout the reaction. It is therefore required that reactions are restricted to less than about 5% conversion.

In the first series of experiments the quantity of termination products obtained was very small and bicyclopentyl and 1,1,1-trichloromethylcyclopentane, probably due to their long retention times, were not detectable. The only termination product present to a measurable extent was hexachloroethane.

Consequently, a further series of reactions was carried out to conversions in excess of 5%. Both additional termination products were observed and measured in this series and rates of formation calculated. As the peaks were small and very broad the accuracy of measurement was not good. However, since it is most unlikely that the mechanism had completely changed on increasing the conversion, this suggested that the peaks were present but undetectable in the low conversion runs.

The rates of formation of the different products observed are shown in Table 4.1.

TABLE 4.1

Rates of Product Formation in the CarbonTetrachloride-Cyclopentane System

(i) Low Conversion Runs

Temp (°C)	time (s)	R_{CHCl_3} (mol l ⁻¹ s ⁻¹)	R_{CpCl} (mol l ⁻¹ s ⁻¹)	$R_{\text{C}_2\text{Cl}_6}$ (mol l ⁻¹ s ⁻¹)
59	16,200	1.125x10 ⁻⁸	1.105x10 ⁻⁸	6.213x10 ⁻¹⁰
91.5	7,320	5.710x10 ⁻⁹	8.301x10 ⁻⁹	2.949x10 ⁻⁹
130	5,400	2.038x10 ⁻⁸	4.008x10 ⁻⁸	7.564x10 ⁻⁹
168.5	3,780	3.329x10 ⁻⁸	5.544x10 ⁻⁸	9.899x10 ⁻⁹
203	3,060	8.976x10 ⁻⁸	1.235x10 ⁻⁷	8.754x10 ⁻⁹
220	1,500	9.952x10 ⁻⁸	9.879x10 ⁻⁸	1.246x10 ⁻⁸
253	1,260	1.418x10 ⁻⁷	1.264x10 ⁻⁷	8.515x10 ⁻⁹

(ii) High Conversion Runs

Temp (°C)	time (s)	R_{CHCl_3} (mol l ⁻¹ s ⁻¹)	R_{CpCl} (mol l ⁻¹ s ⁻¹)	$R_{\text{C}_2\text{Cl}_6}$ (mol l ⁻¹ s ⁻¹)	R_{Cp^2} (mol l ⁻¹ s ⁻¹)	R_{CpCl_3} (mol l ⁻¹ s ⁻¹)
24.5	39,000	5.699x10 ⁻⁹	5.229x10 ⁻⁹	4.733x10 ⁻¹⁰	8.776x10 ⁻¹⁰	2.722x10 ⁻⁹
37	25,320	3.462x10 ⁻⁹	5.290x10 ⁻⁹	6.668x10 ⁻¹⁰	1.334x10 ⁻⁹	4.833x10 ⁻⁹
37.5	39,600	5.955x10 ⁻⁹	6.764x10 ⁻⁹	5.688x10 ⁻¹⁰	1.396x10 ⁻⁹	2.991x10 ⁻⁹
39	16,560	6.802x10 ⁻⁹	5.992x10 ⁻⁹	10.062x10 ⁻¹⁰	1.656x10 ⁻⁹	3.972x10 ⁻⁹
52	37,020	4.986x10 ⁻⁹	7.545x10 ⁻⁹	7.978x10 ⁻¹⁰	1.358x10 ⁻⁹	3.420x10 ⁻⁹
78	37,020	4.865x10 ⁻⁹	10.398x10 ⁻⁹	5.506x10 ⁻¹⁰	6.253x10 ⁻¹⁰	1.460x10 ⁻⁹
104	29,700	4.418x10 ⁻⁹	11.345x10 ⁻⁹	7.643x10 ⁻¹⁰	7.271x10 ⁻¹⁰	2.005x10 ⁻⁹
161	22,520	9.383x10 ⁻⁹	14.738x10 ⁻⁹	13.685x10 ⁻¹⁰	5.588x10 ⁻¹⁰	8.665x10 ⁻¹⁰
202	42,060	10.348x10 ⁻⁹	12.652x10 ⁻⁹	5.338x10 ⁻¹⁰	8.133x10 ⁻¹⁰	1.075x10 ⁻⁹

$$[\text{c-C}_5\text{H}_{10}]_i = 3.421 \times 10^{-3} \text{ mol l}^{-1}$$

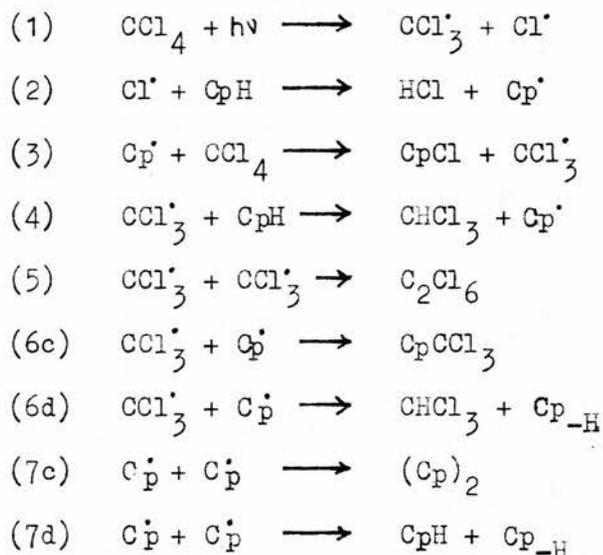
$$[\text{CCl}_4]_i = 1.140 \times 10^{-3} \text{ mol l}^{-1}$$

SECTION 4

The Photolysis of Carbon Tetrachloride With Cyclopentane

DISCUSSION

From product analysis it is apparent that the basic scheme of reactions is similar to that obtained in the carbon tetrachloride-propane system. We have (Cp=cyclopentyl, Cp-H = cyclopentene).



All the products expected from this reaction scheme were detected. The glc resolution was insufficient to obtain an accurate measurement of the concentration of cyclopentene present.

The ratio k_c/k_d of the combination and disproportionation rate constants for reactions (7c) and (7d) has been previously measured by Gunning and Stock¹⁶¹ as 1.0. This contrasts with an earlier result of Beck et al¹⁶² who produced cyclopentyl radicals by reaction between cyclopentane and Hg-6(³P₄) atoms. They reported $k_c/k_d = 5.3$. In Section 5 work is described in which azocyclopentane was photolysed and a value of $k_c/k_d = 0.7$ (i.e. $k_d/k_c = 1.40$) was obtained for cyclopentyl radicals.

No values have been published reporting the ratio of the combination and disproportionation rates for trichloromethyl and cyclopentyl radicals (reaction (6)). Some indication of

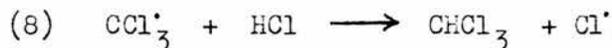
the order of magnitude of this ratio can be obtained by direct comparison with the results in Section 3 where a disproportionation to combination ratio of 0.45 was calculated for the reaction between trichloromethyl and isopropyl radicals. By examining the bond angles within the two radicals and the combination and disproportionation products it could be deduced that k_d/k_c would be lower for this system than in the trichloromethyl-isopropyl system. In the cyclopentyl radical the carbon atom at the radical site will have three electrons in sp^2 hybrid orbitals and an unpaired electron in a p orbital. In an unstrained system such as the isopropyl radical the bond angle at an sp^2 hybridised atom is 120° . The constraints of the 5 member ring will introduce some configurational strain. Although the internal angle of a planar pentagon is 120° the other four carbon atoms (sp^3 hybridised) will distort the planar molecule to attain as near a tetrahedral configuration as possible, thus introducing strain at the radical site (not present in isopropyl radicals). On reaction with a trichloromethyl radical the cyclopentyl radical can either combine to form trichloromethylcyclopentane or disproportionate to form cyclopentene and chloroform. In the former case the sp^2 hybridised carbon site will become an sp^3 hybridised site and, with five sp^3 hybridised carbon atoms in the cyclopentane ring, the ring can distort to minimise strain in the trichloromethylcyclopentane molecule such that all bond angles will be more or less equal to the tetrahedral bond angle (109°). In the disproportionation step a second carbon in the ring is sp^2 hybridised to form cyclopentene. Because of the inflexibility of the double bond, additional strain

will be placed on the system, causing the bond angle at the sp^2 sites to be less than the strain-free 120° , and the angle at the sp^3 sites to be greater than the strain free 109° .

These steric considerations therefore will favour formation of the combination product (relative to the strain-free conditions prevalent in the isopropyl system).

Assuming a k_d/k_c value of 0.075 (See table 3.3) one can calculate $k_d/k_c = 0.3$ for this system. The steric conditions outlined above will probably reduce this value still further. A graph of $\frac{R_{CHCl_3}}{R_{CpCl_3}}$ versus the reciprocal of temperature as in figure 3.2 does not show the low temperature levelling off sufficiently accurately to obtain a reliable value of k_d/k_c .

In addition to reactions (4) and (6d) chloroform may be produced from hydrogen chloride and trichloromethyl radicals.



In Sections 1 and 2 it was seen that the analogous system with hydrogen bromide and trichloromethyl radicals constituted an important source of chloroform. As the H - Cl bond is stronger than the H - Br bond, and as the Br^\cdot radical is more stable than the Cl^\cdot radical, reaction (8) above will be considerably less significant than the analogous HBr system and should not affect kinetic calculations so much.

Because of the difficulty in measuring the concentration of 1,1,1-trichloromethylcyclopentane and, as k_d/k_c has not been accurately determined for reaction (6), no quantitative estimate of the quantity of $CHCl_3$ arising from reaction (6d) can be made. In the previous section this quantity was calculated using the expression

$$[CHCl_3]_{6d} = \frac{k_d}{k_c} [RCCl_3]$$

and the value of $[\text{CHCl}_3]_{6d}$ was subtracted from the total final chloroform concentration to calculate the amount of chloroform produced from reaction (4). However, as the final concentration of 1,1,1-trichloromethylcyclopentane was too low to measure and as we have

$$[\text{CHCl}_3]_{6d} \leq 0.3[\text{C}_p\text{CCl}_3]$$

then the value of $[\text{CHCl}_3]_{6d}$ should be very small.

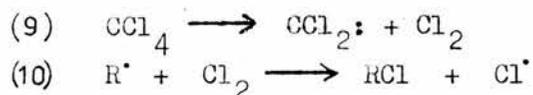
At the lower temperature runs (i.e. 24.5 to 39°C) the contribution to the final chloroform concentration from reaction (4) will be very small due to the activation energy required to abstract the hydrogen atom from cyclohexane. The maximum chloroform concentration arising from reaction (6d) can be calculated from the above equation as $0.3[\text{C}_p\text{CCl}_3]$. As can be seen from the following table, there is obviously an additional source of chloroform in the system.

TABLE 4.2

Chloroform Production in Low Temperature Runs

Temp (°C)	R_{CHCl_3} (mol l ⁻¹ s ⁻¹)	CHCl_3 final (mol l ⁻¹)	max $[\text{CHCl}_3]_{6d}$ (mol l ⁻¹)	Additional CHCl_3 (mol l ⁻¹)
24.5	5.70×10^{-9}	2.22×10^{-4}	3.18×10^{-5}	1.90×10^{-4}
37	3.46×10^{-9}	8.75×10^{-5}	3.67×10^{-5}	5.08×10^{-5}
37.5	5.96×10^{-9}	2.36×10^{-4}	3.55×10^{-5}	2.00×10^{-4}
39	6.80×10^{-9}	1.13×10^{-4}	1.97×10^{-5}	9.33×10^{-4}

In the previous section it was seen that the runs carried out at low temperatures yielded final alkyl chloride concentrations significantly in excess of the chloroform concentration (See Table 3.1.). This additional isopropyl chloride was believed to have been produced by the reactions

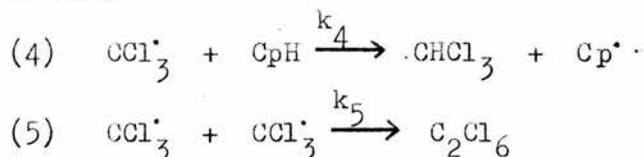


which would assume more significant proportions at lower temperatures.

However, an examination of the results in Table 4.1 shows that the rates of formation of chloroform and cyclopentyl chloride are of similar magnitude. Reaction (9) will be equally important in both the propane and the cyclopentane systems and it would therefore appear to confirm that the quantity of chloroform present in the products is greater than would be expected from this system. It seems likely that the chloroform had arisen as an impurity in one of the starting materials, most probably the carbon tetrachloride. Unfortunately, quality checks were not carried out each time the CCl_4 tube on the vacuum line was refilled and retrospective analysis is impossible. These results cannot therefore be used to calculate Arrhenius parameters for the system.

At higher temperatures (greater than 150°C) the errors will be less significant and some rate data can be estimated.

We have



Neglecting other sources of chloroform and assuming that there is no significant change in the cyclopentane concentration during reaction, we obtain

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

As $\log k_5 = 9.7$ (See Section 1) and $[\text{RH}]_{\text{initial}} = 3.421 \times 10^{-3} \text{ mol l}^{-1}$ we can calculate the value of k_4 at different temperatures.

Table 4.3 shows the values obtained which are plotted on a graph in Figure 4.3.

The graph has a gradient of -1.90 ± 0.74 and a y-axis intercept of 8.13 ± 0.35 (corresponding to $E_4 = 4.574 \times 1.9 = 8.63 \text{ kcal mol}^{-1}$ and $\log A_4 = 8.13 \text{ l mol}^{-1} \text{ s}^{-1}$).

At the highest temperature employed in the present series, 253°C , we have $\log k_4 = 4.5$. Substituting a value of $\log A_4 = 8.8 \text{ l mol}^{-1} \text{ s}^{-1}$ (as estimated for hydrogen abstraction from cyclohexane by White and Kuntz³⁹ and by Currie, Sidebottom and Tedder⁵³), this rate constant yields a value of $E_4 = 10.3 \text{ kcal mol}^{-1}$. This value is in excellent agreement with the results obtained in the aforementioned two papers where values of $E_4 = 10.0$ and $10.7 \text{ kcal mol}^{-1}$ are quoted for the analogous cyclohexane system. Wampler and Kuntz⁹⁹ have examined hydrogen abstraction reactions from several alkanes by trichloromethyl radicals. They obtained $\log A_4 = 9.0$ and $E_4 = 10.7 \text{ kcal mol}^{-1}$ for the cyclopentane system. A rate constant $\log k_4 = 4.5$ at 253°C , as obtained above yields $E_4 = 10.8 \text{ kcal mol}^{-1}$ when a value of $\log A_4 = 9.0$ is substituted.

As in previous sections, this high temperature rate constant confirms that at elevated temperatures the reaction mechanism is essentially similar to that encountered by other workers on

TABLE 4.3

Calculated Value of $\log k_4$ At Temperatures $> 150^\circ\text{C}$

Temperature	$1000/T$ ($^\circ\text{A}$)	$\log k_4$
161°C	2.303	3.72
168.5°C	2.264	3.84
202°C	2.104	3.97
203°C	2.100	4.30
220°C	2.028	4.27
253°C	1.900	4.50

$$\text{where } k_4 = \frac{R_{\text{CHCl}_3} k_5^{\frac{1}{2}}}{R_{\text{C}_2\text{Cl}_6}^{\frac{1}{2}} [\text{RH}]_{\text{init.}}}$$

$$\log k_5 = 9.7$$

$$[\text{RH}]_{\text{init.}} = 3.421 \times 10^{-3} \text{ mol l}^{-1}$$

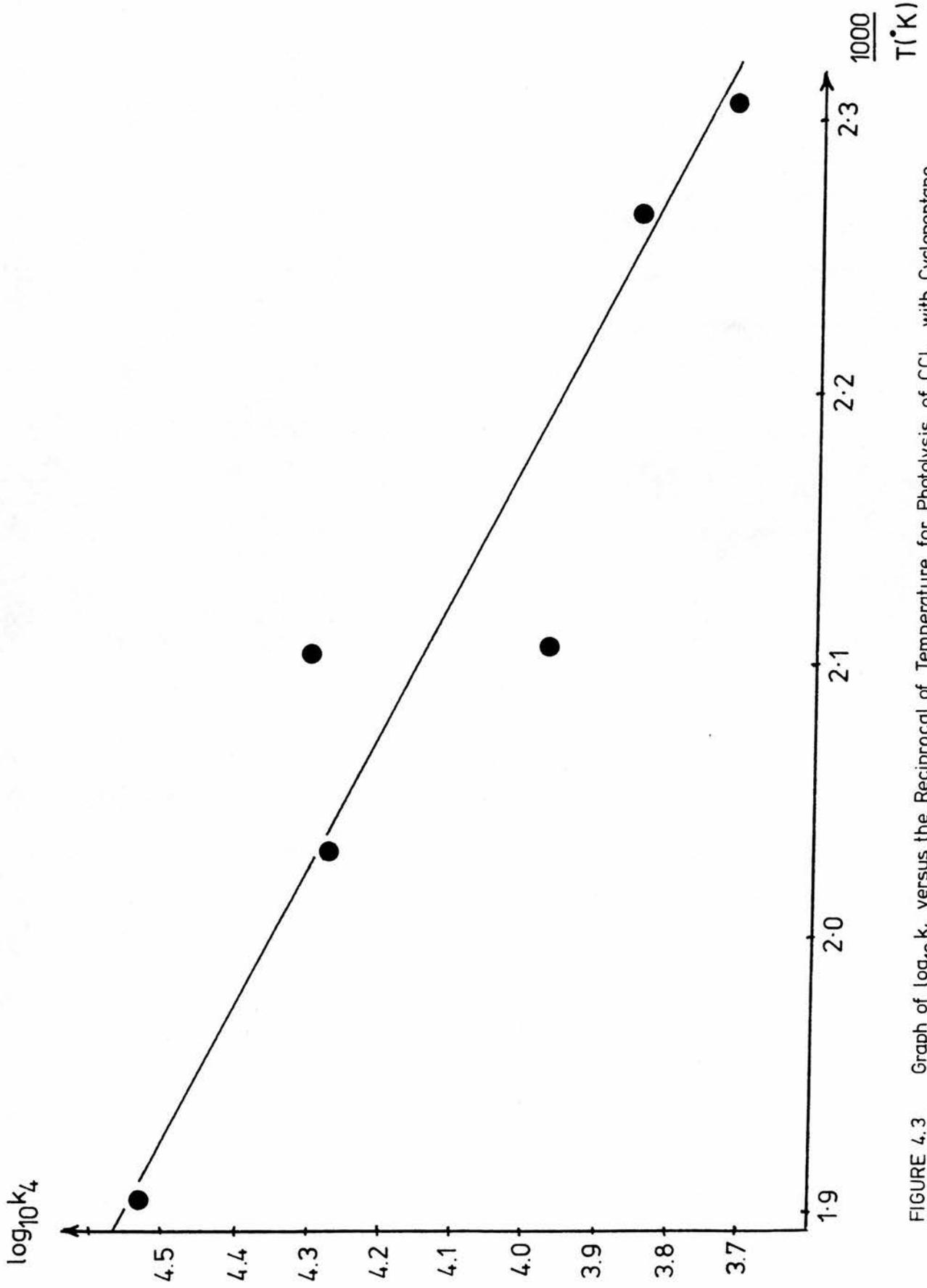


FIGURE 4.3 Graph of $\log_{10} k_4$ versus the Reciprocal of Temperature for Photolysis of CCl_4 with Cyclopentane.

similar systems. At lower temperatures, however, minor reactions such as photolysis of carbon tetrachloride to yield dichlorocarbene and disproportionation of trichloromethyl and cyclopentyl radicals assume sufficient importance to prevent calculation of absolute Arrhenius parameters.

As other sources of error are introduced at high temperature (e.g. decomposition of cyclopentyl chloride, overconversion of reactants) it is not feasible to carry out a full series of high temperature photolyses to obtain satisfactory kinetic data.

The following section describes further work carried out on the cyclopentane-carbon tetrachloride system but using azocyclopentane as the radical source; this eliminates the formation of CCl_2 species and makes calculation of Arrhenius parameters considerably simpler.

SECTION 5

The Photolysis of Azocyclopentane alone and
With Carbon Tetrachloride and Cyclopentane

INTRODUCTION

The results reported in the previous two sections have shown that, under the conditions employed in this work, the photolysis of carbon tetrachloride in the presence of alkanes is a complex process. The presence of two different initiation reactions (caused by the high energy radiation required to decompose carbon tetrachloride) makes calculation of Arrhenius parameters very difficult indeed. Similar problems have been encountered recently in this laboratory in a study of the cyclohexane-carbon tetrachloride system⁵³. The problem has been tackled by using an initiator to provide the radicals necessary to initiate the chain reaction; this system is analogous to the use of peroxides and azo compounds to initiate polymerisation of monomers such as styrene and vinyl chloride in industry. By using a species which yields radicals more readily than carbon tetrachloride the system can be initiated at too low an energy for the formation of dichlorocarbene, the offending species in the previous section. Azocyclopentane was used as initiator yielding cyclopentyl radicals and molecular nitrogen on photolysis at 365 nm.

Azoalkanes have been used as a source of alkyl radicals by many previous workers, the most commonly used being azomethane. In 1933 it was shown that decomposition products of azomethane would remove lead from cold mirrors¹⁶³ indicating that radicals were being formed in the decomposition. Eight years later Cannon and Rice¹⁶⁴ showed that the quantum yield of nitrogen formed on irradiation with uv light at 366 nm was equal to 1 at pressures up to 630 torr. Jones and Steacie¹⁶⁵ measured the effect of azomethane pressure on the formation rates of N_2 , CH_4 and C_2H_6 and proposed a mechanism for the photolysis.

They also proposed that a reaction took place between methyl radicals and azomethane; Sleppy and Calvert¹⁶⁶ showed that the active methyl radicals would abstract hydrogen atoms unless

collisionally deactivated by addition of inert gas.

Pilling and coworkers¹⁶⁷ studied the flash photolysis of azomethane and the higher energy irradiation yielded ethylene and acetylene among the products. The vapour phase γ -radiolysis of azomethane has been examined by Stief and Ausloos¹⁶⁸.

The quantity of work carried out to date to examine higher azoalkanes has not been very great. The kinetics of photolytic decomposition of azo-n-propane¹⁶⁹, azoisopropane¹⁷⁰, azo-n-butane¹⁷¹, azoisobutane^{172,173} and azocyclohexane⁵³ have been reported. Although in this section the azocyclopentane is used only as an initiator for the cyclopentane/carbon tetrachloride, several preliminary runs were carried out to examine the decomposition of azocyclopentane alone and with cyclopentane diluent.

The detailed mechanism of the primary processes in the photolysis of the azoalkanes has been studied by Collier, Slater and Calvert¹⁷⁴. They deduced that the excited state $R_2N_2^*$ formed when the azoalkane molecule R_2N_2 accepted a quantum of energy could decompose to yield $R + RN_2$ from either

- (a) The singlet ground state. S_0 at a very high level of vibrational excitation.
- (b) The excited singlet state S_1 at a low vibrational energy level.
- (c) The triplet state T_1 at a rather higher vibrational energy level.

Stabilisation of the triplet state T_1 produced by intersystem crossing ($S_1 \rightarrow T_1$) involves a 90° bond twist. This is not possible in complex cyclic azo compounds as studied by Turro and coworkers¹⁷⁵ so decomposition in such systems always takes place from the excited singlet state.

In this section the activation energy for decomposition of the excited state $R_2N_2^*$ ($R = \text{cyclopentyl}$) is calculated and shown to be

similar to the values calculated for other related azoalkanes. By analysis of the combination and disproportionation products of the reactions between two cyclopentyl radicals the value of k_d/k_c is calculated and shown to be temperature independent. The Arrhenius parameters for H-abstraction from cyclopentane by trichloromethyl radicals and for Cl-abstraction from carbon tetrachloride by cyclopentyl radicals are estimated and maximum values for the combination rates of cyclopentyl radicals with themselves and with trichloromethyl radicals are obtained. These results are shown to correlate well with results obtained by other workers from analogous systems.

SECTION 5

The Photolysis of Azocyclopentane alone and
With Carbon Tetrachloride and Cyclopentane

EXPERIMENTAL

5.1. REACTANTS

(a) Carbon Tetrachloride:- was Fisons Spectrograde reagent, as used in Sections 3 and 4. Before use it was shown to be chromatographically pure so no further purification was necessary.

(b) Cyclopentane:- was Fisons Laboratory Reagent and was used without further purification.

(c) Azocyclopentane:- was prepared in the laboratory by the method described in Appendix 3.

5.2 APPARATUS

Because of the involatility of the azocyclopentane it was found necessary to reduce the distance between the reaction flask and the product collection tube. Consequently, a side-arm was fitted to the capillary tube directly above the reaction flask with a connection on to which the product collection tube could be fitted (See Figure 5.1).

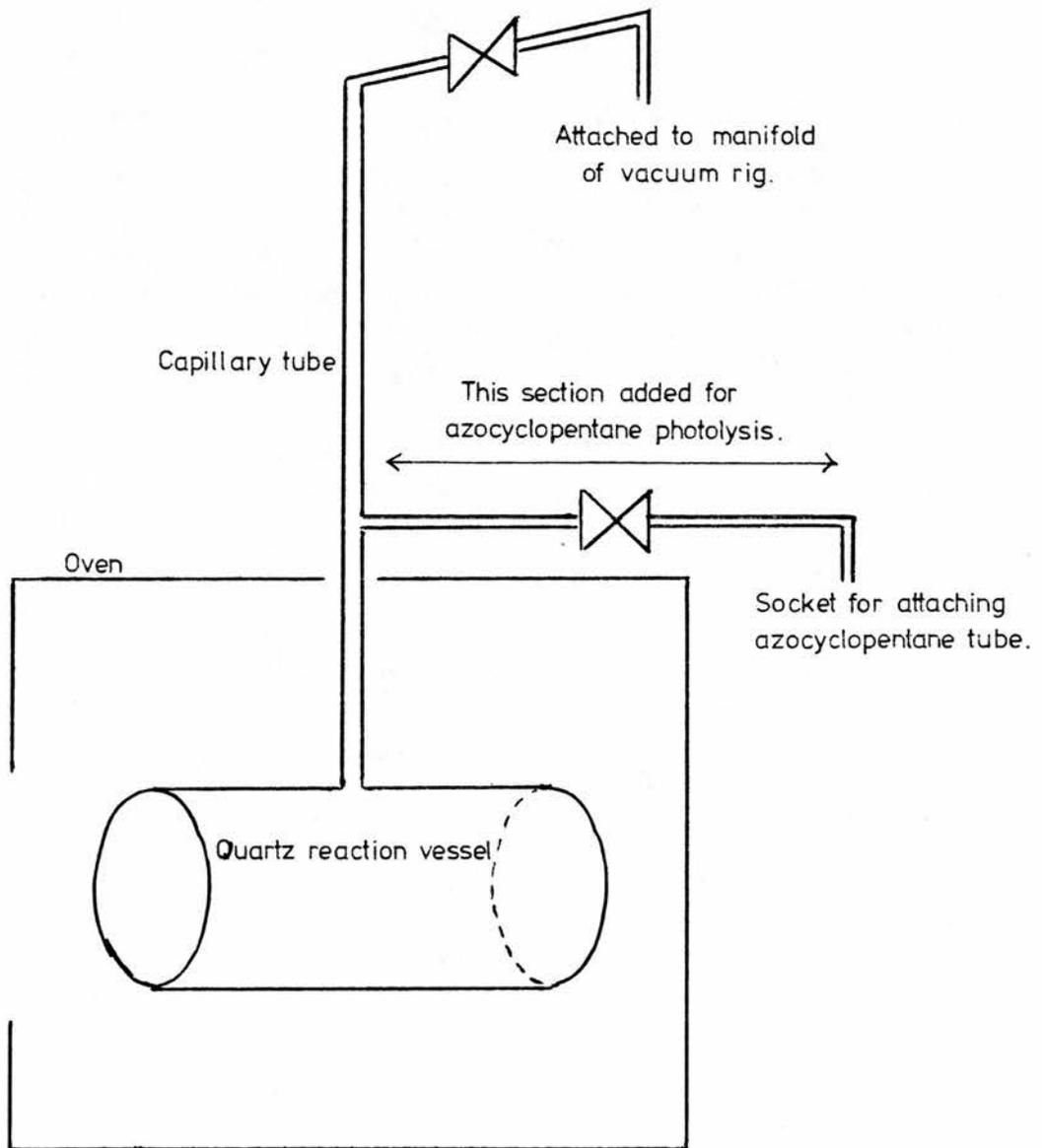
The vacuum system was similar to that used in the previous section. A cylindrical quartz reaction vessel of total volume 209ml (determined by completely filling with H_2O and weighing before and after) was used.

The light source was a 200W super high pressure mercury arc coupled to a Bausch and Lomb high intensity monochromator yielding a monochromatic source at 365 nm with a 10 nm bandwidth. A few runs (azocyclopentane + cyclopentane) were carried out with a medium pressure lamp as described in Section 1. A Pyrex light filter was employed in all but a few of these experiments where two Pyrex filters were used.

5.3. PROCEDURE

The procedure was varied several times in an attempt to overcome the many problems encountered in the series of experiments. In the first series of experiments the azocyclopentane was photolysed

FIGURE 5-1 Reaction Vessel Used for Photolysis of Azocyclopentane.



in the presence of cyclopentane with no added carbon tetrachloride. The azoalkane was added by Hamilton syringe to the tube on the side-arm of the reaction flask. The contents of the tube were cooled in liquid nitrogen then the air removed by opening the sidearm to the vacuum pumps. The sidearm was then sealed off and the azoalkane allowed to melt and heated with a hot air blower. The liquid nitrogen flask was replaced about the side-arm and the space evacuated again. This degassing procedure was repeated several times before the azocyclopentane was finally distilled into the reaction flask. The cyclopentane was added in a similar manner to the reactants used in Sections 1-4. A pressure of 60 torr was charged to bulb A prior to transfer to the reaction flask.

It proved very difficult to analyse the products from the run because of the very small volumes of reactants employed. To increase the volume of products available for analysis, a measured quantity of cyclohexane was added after photolysis had ceased. The quantity employed was initially 20 μ l but it was later found to be more convenient to add 60 torr of cyclohexane from bulb A when products were being distilled into the collection tube. To calculate absolute rates of formation it was hoped to measure product concentrations relative to the known quantity of cyclohexane. This proved a difficult operation as the cyclohexane/cyclopentane/azocyclopentane/ product mixture had a relatively high melting point, and when the mixture was melted to obtain a liquid sample for glc analysis small quantities of the volatile cyclopentane and cyclopentane were lost by evaporation. In later runs the absolute rates of formation were calculated by assuming that the cyclopentane concentration was unchanged throughout the reaction i.e. that conversions were small. The final product concentrations

(bicyclopentyl and cyclopentene) were then calculated relative to cyclopentane.

The second series of azocyclopentane photolyses were carried out in the presence of carbon tetrachloride. In Section 4 it was shown that the kinetic data obtained by photolysis of carbon tetrachloride and cyclopentane were complicated by many side reactions such as the production and subsequent reactions of dichlorocarbene species. By using azocyclopentane as the initiating species a less energetic radical initiation step was introduced and the use of a Pyrex glass filter should have ensured that photolysis of CCl_4 would not be a significant step.

The azocyclopentane was added as described above, 20 μl being added in some runs and 10 μl in the remainder. When 20 μl was employed it was noticed that small quantities of liquid condensed in the capillary tube of the reaction vessel outwith the oven. This would lead to errors in kinetic calculations so the volume used was reduced to 10 μl .

The cyclopentane and carbon tetrachloride were added from bulb A in the same way as in previous sections. The pressures used were 60 torr and 25 torr respectively.

In the final series of experiments 15 μl azocyclopentane were photolysed alone and 60 torr of cyclohexane from bulb A added after photolysis had ceased. As in the above series of experiments, all products were distilled into the collection tube on the side-arm on the reaction flask assembly and analysed by glc.

In all azocyclopentane photolyses there was considerable blackening of the face of the reaction vessel. This was cleaned as described in Section 2.3.

5.4 ANALYSIS OF PRODUCTS

The apparatus and column for the gas liquid chromatographic analyses were as described in Section 1. Because of the high retention times of bicyclopentyl, trichloromethylcyclopentane, hexachloroethane and azocyclopentane and the much lower retention times of cyclopentene, cyclopentane and cyclohexane, two series of analysis were carried out. The more volatile products were separated at room temperature with a carrier gas flow rate of 35 mlmin^{-1} and a chart speed of 48 inh^{-1} . The less volatile products were separated on the same column at 100°C with a carrier flow rate of 30 mlmin^{-1} and a chart speed of 24 inh^{-1} . The samples were injected using a $10 \mu\text{l}$ Hamilton syringe and $4 \mu\text{l}$ aliquots were used for each analysis.

5.5 IDENTIFICATION OF PRODUCTS

With the exception of azocyclopentane, all products had been detected in Section 4 and the peaks were similarly identified. The azocyclopentane retention time was approximately 2.3 times that of bicyclopentyl. It was therefore possible to inject a second sample for analysis at 100°C as soon as the termination products from the first injection had been detected. All the peaks required could then be obtained before the large azocyclopentane peak from the first injection was seen.

5.6 RESULTS

Mixtures of cyclopentane and azocyclopentane were photolysed over the temperature range $129\text{--}209^{\circ}\text{C}$. The results are shown in Table 5.1. The rates of formation of the run at 153°C were calculated by comparison of peak areas of products with the area of a peak obtained from added cyclohexane. In the other runs cyclohexane was still added to increase the product volume but rates of formation

TABLE 5.1

PHOTOLYSIS OF AZOCYCLOPENTANE IN THE PRESENCE OF CYCLOPENTANE

Temp. (°C)	Reaction Time (s)	Pyrex Filter	Added * Cyclohexane	$\frac{c-C_5H_8}{c-C_5H_{10}}$	$\frac{(c-C_5H_9)_2}{c-C_5H_{10}}$	kd/kc	Rc-C ₅ H ₈ (mol l ⁻¹ s ⁻¹)	R(c-C ₅ H ₉) ₂ (mol l ⁻¹ s ⁻¹)
129.5	18000	Double	60 torr	2.29x10 ⁻²	1.56x10 ⁻²	1.47	4.13x10 ⁻⁹	2.81x10 ⁻⁹
153	7500	Single	20μl	1.28x10 ⁻² +	9.29x10 ⁻³ +	1.38	3.16x10 ⁻¹⁰	2.80x10 ⁻¹⁰
185	13200	Double	30μl	1.23x10 ⁻²	8.67x10 ⁻³	1.42	3.02x10 ⁻⁹	2.13x10 ⁻⁹
209	23400	Double	60 torr	1.08x10 ⁻²	8.17x10 ⁻³	1.32	1.50x10 ⁻⁹	1.13x10 ⁻⁹

* 1μl = 9.27 x 10⁻⁶ mol l⁻¹

1 torr = pressure of 1 torr in Bulb A = 1.13 x 10⁻⁵ mol l⁻¹

+ concentrations measured relative to cyclohexane, not cyclopentane

$$[c-C_5H_{10}]_i = 3.244 \times 10^{-3} \text{ mol l}^{-1}$$

$$[(c-C_5H_9)_2 N_2]_i = 5.851 \times 10^{-4} \text{ mol l}^{-1}$$

were calculated by comparison of peak areas with the area of the cyclopentane peak. As conversion was very low the increase in cyclopentane concentration from disproportionation of cyclopentyl radicals will be small relative to the total initial cyclopentane concentration. The total initial value was used to calculate rates of formation.

Azocyclopentane was photolysed alone over the temperature range 57-150°C. The results are shown in Table 5.2. Rates of formation were calculated by comparison of concentrations of products with the concentration of cyclohexane added to increase product volume. The problems listed earlier in this section (i.e. condensation of azocyclopentane outside the reaction flask during photolysis and evaporation of cyclopentene and cyclopentane when products were warmed to melt cyclohexane) cause the experimental errors to be very high indeed; the formation rates of cyclopentene, the most volatile and least plentiful product, are shown to be insufficiently accurate for Arrhenius calculations.

In the third series of experiments, azocyclopentane was photolysed in the presence of carbon tetrachloride and cyclopentane in the temperature range 97-186°C. The early runs in the series were carried out with 20 μ l azocyclopentane but the later runs were carried out with 10 μ l azocyclopentane. The rates of formation of products are shown in Table 5.3.

TABLE 5.2 : PHOTOLYSIS OF AZOCYCLOPENTANE

Temp (°C)	$10^3/T$ (°K)	Reaction Time (s)	R_{RH} (mol l ⁻¹ s ⁻¹)	R_{R-H} (mol l ⁻¹ s ⁻¹)	R_{R_2} (mol l ⁻¹ s ⁻¹)	$\log R_{N_2}$ (mol l ⁻¹ s ⁻¹)	$\frac{R_{RH} - (R_{RH})_{7d}}{R_{R_2}^{1/2} [R_2^{N_2}]}$	$\log_{10} \frac{R_{RH} - (R_{RH})_{7d}}{R_{R_2}^{1/2} [R_2^{N_2}]}$
57	3.028	216000	7.321×10^{-11}	3.674×10^{-12}	2.624×10^{-12}	- 10.39	0.098	- 1.010
126	2.505	64800	1.704×10^{-10}	2.224×10^{-11}	1.589×10^{-11}	- 9.95	0.085	- 1.072
150	2.363	129600	3.552×10^{-10}	1.984×10^{-11}	1.417×10^{-11}	- 9.70	0.203	- 0.692

R-H = cyclopentene

RH = cyclopentane

(RH)_{7d} = cyclopentane ex reaction 7dR₂ = bicyclopentylR₂^{N₂} = azocyclopentane $[R_2^{N_2}]_i = 4.388 \times 10^{-4}$ mol l⁻¹

TABLE 5.3 : PHOTOLYSIS OF AZOCYCLOPENTANE IN THE PRESENCE
OF CARBON TETRACHLORIDE AND CYCLOPENTANE

Temp (°C)	$\frac{1000}{T(^{\circ}A)}$	Time (s)	R_{CHCl_3} (mol l ⁻¹ s ⁻¹)	R_{CpCl} (mol l ⁻¹ s ⁻¹)	$R_{C_2Cl_6}$ (mol l ⁻¹ s ⁻¹)	R_{CpCCl_3} (mol l ⁻¹ s ⁻¹)	R_{Cp_2} (mol l ⁻¹ s ⁻¹)
101	2.674	65100	1.90×10^{-10}	2.97×10^{-10}	6.06×10^{-11}	3.38×10^{-11}	n.a.
105	2.644	89100	4.09×10^{-10}	2.40×10^{-10}	6.30×10^{-11}	5.77×10^{-11}	n.a.
122	2.532	50400	6.50×10^{-10}	4.75×10^{-10}	8.45×10^{-11}	1.18×10^{-10}	n.a.
134	2.457	50400	5.99×10^{-10}	1.20×10^{-9}	6.64×10^{-11}	3.51×10^{-10}	n.a.
140	2.420	50400	5.57×10^{-10}	7.01×10^{-10}	6.36×10^{-11}	6.03×10^{-10}	n.a.
160	2.309	50760	2.26×10^{-9}	8.65×10^{-10}	8.65×10^{-11}	1.20×10^{-9}	n.a.
178	2.217	50400	1.95×10^{-9}	1.33×10^{-9}	9.86×10^{-11}	6.59×10^{-10}	n.a.
97	2.701	129600	1.54×10^{-10}	2.55×10^{-10}	3.33×10^{-11}	2.177×10^{-10}	2.10×10^{-10}
116	2.569	93600	1.53×10^{-10}	4.91×10^{-10}	1.75×10^{-11}	n.a.	2.72×10^{-10}
136	2.444	86400	2.11×10^{-10}	6.47×10^{-10}	2.29×10^{-11}	8.943×10^{-11}	1.30×10^{-10}
142	2.408	100800	n.a.	7.28×10^{-10}	3.66×10^{-11}	n.a.	6.04×10^{-11}
159	2.314	66600	7.94×10^{-10}	1.05×10^{-9}	4.77×10^{-11}	1.433×10^{-10}	2.08×10^{-10}
164	2.287	86400	n.a.	9.01×10^{-10}	3.39×10^{-11}	5.575×10^{-11}	8.08×10^{-11}
186	2.178	86400	1.08×10^{-9}	2.33×10^{-9}	2.01×10^{-11}	4.326×10^{-11}	7.88×10^{-11}

Series A

$$[R_2N_2]_i = 5.851 \times 10^{-4} \text{ mol l}^{-1}$$

Series B

$$[R_2N_2]_i = 2.926 \times 10^{-4} \text{ mol l}^{-1}$$

SECTION 5

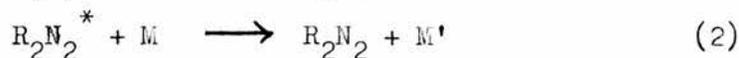
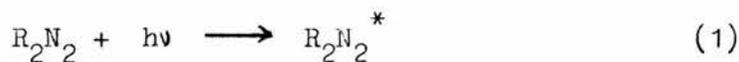
The Photolysis of Azocyclopentane alone and
With Carbon Tetrachloride and Cyclopentane

DISCUSSION

5.7.1 Photolysis of Azocyclopentane + Cyclopentane

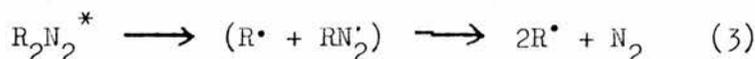
The ultraviolet spectrum of azocyclopentane, illustrated in Figure A3.1, shows an absorption band at 353 ± 3 nm. The shape of the spectrum in the range of wavelengths 200 - 440 nm is very similar to those reported by Collier, Slater and Calvert¹⁷⁴ (azomethane, azoethane) and, in this laboratory, by Currie¹⁷⁶ (azocyclohexane). It is therefore reasonable to assume that the electronic and/or vibrational excitations of azocyclopentane in this energy range are similar to those of the related azoalkanes and that the process of photolytic decomposition is likely to be very similar.

As long ago as 1933 Leermakers¹⁶³ predicted that radicals were formed when he decomposed azomethane. Twenty five years later Cerfontaine and Kutschke¹⁷⁷ showed that the quantum yield of nitrogen in the photolysis of azoethane was dependent on both temperature and concentration of the azo compound. They deduced that an important factor in the decomposition was collisional deactivation of light-excited molecules.



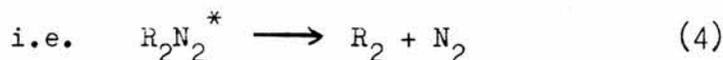
The lifetime of azoethane excited states has been studied by Worsham and Rice¹⁷⁸.

Almost all the azoalkane which escapes collisional deactivation will decompose to yield molecular nitrogen and two alkyl radicals.



There is no evidence to suggest that the RN_2 radical is formed as a transient intermediate or whether both C - N bonds break simultaneously. Several workers have shown that autoejection of a

nitrogen molecule is an insignificant process (< 1%)

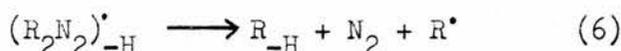


This has been confirmed for azomethane^{179,180,181}, azo-n-butane¹⁷¹, azoisobutane¹⁷², and azocyclohexane¹⁸².

The alkyl radicals formed by reaction (3) can undergo propagation reactions by abstraction of a hydrogen atom from R_2N_2 to yield the $(R_2N_2)_{-H}^{\bullet}$ radical.

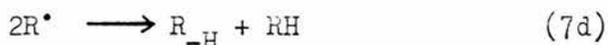


Morganroth and Calvert¹⁷¹ proposed that this radical will react further to yield nitrogen, an alkene and an alkyl radical.



However, Riem and Kutschke¹⁸³ prepared the large radical

$i-C_3H_7-N=N-iC_3H_6^{\bullet}$ in the dark through thermal decomposition of di-t-butylperoxide in the presence of azoisopropane. This large radical is the species $(R_2N_2)_{-H}^{\bullet}$ above with $R=i$ isopropyl. On decomposition of this radical, no nitrogen was obtained so Riem and Kutschke deduced that reaction (6) did not occur. Slater, Collier and Calvert measured the value of $\frac{k_d}{k_c}$ for isobutyl radicals in photolysis of azoisobutane and found that the ratio was constant till about 168°C, but increased at higher temperatures.¹⁷² They attributed this to the increasing importance of reactions (5) and (6).



In table 5.2 it can be seen that in the photolysis of azocyclopentane alone the rate of formation of cyclopentane is considerably greater than the rate of formation of cyclopentene. As reaction (7d) will yield equimolar quantities of both products the additional cyclopentane must have been produced by hydrogen abstraction from azocyclopentane,

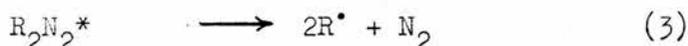
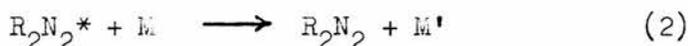
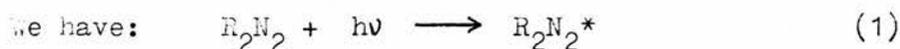
the only compound present in a sufficiently high quantity. This confirms the importance of reaction (5) and the relative unimportance of reaction (6) since, if both occurred to a similar extent, i.e. all $(R_2N_2)_{-H}^{\cdot}$ radicals decomposed to yield R_{-H} , the ratio of formation of RH and R_{-H} would be equal. It must be assumed therefore that the fate of the azocyclopentyl radicals will be in radical-radical reactions yielding involatile products not detected in the product analysis. In his study of the photolysis of azoisopentane, Currie¹⁷⁶ detected a product which he tentatively identified as the combination product of two azoisopentyl radicals.

In the first series of runs, the results of which are shown in Table 5.1, azocyclopentane was photolysed in the presence of cyclopentane to increase the product volume and permit analysis of products at both low and high glc oven temperatures so that concentrations of cyclopentene and bicyclopentyl could be determined. The relative rates of disproportionation reaction (7d) to combination reaction (7c) can be determined by measuring the ratio of cyclopentene to bicyclopentyl. A value of $\frac{kd}{kc} = 1.40 \pm 0.06$ is obtained and no temperature dependence was detectable over the temperature range studied viz. 129.5 to 209°C. Previous values quoted for $\frac{kd}{kc}$ for cyclopentyl radicals are 0.2 by Gunning, Beck and Kniebes¹⁶² and a later value of 1.0 by Gunning and Stock¹⁶¹. In the present work the most probable source of experimental error would be evaporation of cyclopentene; this would result in a still higher value of $\frac{kd}{kc}$. However, in view of the consistency of the results, it is felt that the error will be small.

The second series of results proved considerably more difficult to obtain. Azocyclopentane was photolysed alone and the products distilled into a collection tube containing a measured quantity of

cyclohexane which had been previously condensed from bulb A of the vacuum line. The rates of formation of cyclopentane and cyclopentene were measured by comparison of their respective peak sizes with cyclohexane in the glc trace. The relatively large cyclopentane peak could be determined much more accurately than that of the smaller peak of the more volatile cyclopentene. The rates of formation of bicyclopentyl quoted in Table 5.2 were calculated by dividing the rate of cyclopentene formation by 1.4.

These results can be used to calculate the activation energy for the decomposition of the excited azocyclopentane molecule $R_2N_2^*$



If the rate of formation of $R_2N_2^*$ is I_a (the absorbed light intensity, independent of temperature), we have, by steady state approximation, the equation:-

$$\frac{d}{dt} [R_2N_2^*] = 0 = I_a - k_2[M][R_2N_2^*] - k_3[R_2N_2^*]$$

$$\therefore [R_2N_2^*] = \frac{I_a}{k_3 + k_2[M]}$$

$$\text{We have } R_{N_2} = k_3 [R_2N_2^*]$$

$$\text{Hence } R_{N_2} = \frac{k_3 I_a}{k_3 + k_2[M]} \quad (A)$$

The value of R_{N_2} will be equal to the sum of the rates of reaction of pairs of cyclopentyl radicals in reactions (5), (7c) and (7d).

We have therefore

$$R_{N_2} = R_{R-H} + R_{R_2} + \frac{1}{2} (k_{RH})_5 \quad (B)$$

As cyclopentane is formed in reactions (5) and (7d) we have

$$(R_{RH})_5 = (R_{RH})_{total} - (R_{RH})_{7d}$$

and as

$$(R_{RH})_{7d} = R_{R-H}$$

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

Equations (B) and (C) have been used to calculate R_{N_2} and the values obtained are shown in Table 5.2.

To obtain a value of the activation energy E_3 we must make an approximation to the value of $k_2[M]$ in equation (A). If it is assumed that each collision with another molecule will result in deactivation the value of k_2 assumes a maximum of $3.2 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$, the collision number.

At low concentrations we have $[M] \cong [R_2N_2] = 4.388 \times 10^{-4} \text{ mol l}^{-1}$

$$k_2 [M] = 3.2 \times 10^{11} \times 4.388 \times 10^{-4} \text{ s}^{-1}$$

$$= 1.40 \times 10^8 \text{ s}^{-1}$$

Values of the Arrhenius parameters for reaction (3) have been determined by Morganroth and Calvert¹⁷¹ for $R = \text{Bu}^n$ ($A = 2.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, $E = 3.8 \text{ kcal mol}^{-1}$) and by Slater, Collier and Calvert¹⁷² for $R = \text{Bu}^i$ ($A = 4.85 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, $E = 4.8 \text{ kcal mol}^{-1}$).

These yield an average value of $k_3 = 3.675 \times 10^9 \exp^{-4300/RT} \text{ s}^{-1}$

At the highest temperature used in Table 5.2 (150°C) we can obtain $k_3 = 2.2 \times 10^7 \text{ s}^{-1}$. The value calculated for k_3 at 57°C and 126°C will be still lower. As these values are low compared with the estimated value of $k_2 [M] = 1.40 \times 10^8 \text{ s}^{-1}$ calculated earlier, we can write equation (A) as

$$R_{N_2} = \frac{k_3 I_a}{k_3 + k_2 [M]} \cong \frac{k_3 I_a}{k_2 [M]}$$

$$\log_{10} R_{N_2} = \log_{10} \left(\frac{I_a}{k_2 [M]} \right) + \log k_3$$

$$= \log_{10} \left(\frac{I_a}{k_2 [M]} \right) + \log A_3 - \frac{E_3}{2.303RT}$$

Hence, assuming $\frac{I_a}{k_2 [M]}$ to be temperature independent, a plot of $\log_{10} R_{N_2}$ against the reciprocal of temperature should have a gradient of $\frac{-E_3}{2.303R}$. This Arrhenius plot is shown in Figure 5.2 and has a gradient of -0.98 ± 0.14 yielding a value of $E_3 = 4.5 \text{ kcal mol}^{-1}$. This is in very good agreement with the other quoted literature values as shown in Table 5.4.

Table 5.4

Activation Energies for Decomposition
of Excited Species $R_2N_2^*$

R	E_3 (in kcal mol ⁻¹)	Reference
n-butyl	3.8	171
isobutyl	4.8	172
isopentyl	4.5	176
cyclopentyl	4.5	this work
cyclohexyl	3.1	182

Because the value of R_{RH} is much greater than the value of R_{R-H} in Table 5.2 it can be established that the value of $\log_{10} R_{N_2}$ will not be very dependent on the accuracy of the difficult-to-measure R_{R-H} .

In studies of analogous systems previous workers have obtained estimates of the Arrhenius parameters for reaction (5) by considering the equation

$$\frac{k_5}{k_{7c}^{\frac{1}{2}}} = \frac{(R_{RH})_5}{R_2^{\frac{1}{2}} [R_2N_2]}$$

where $(R_{RH})_5 = (R_{RH})_{\text{total}} - (R_{RH})_{7d}$

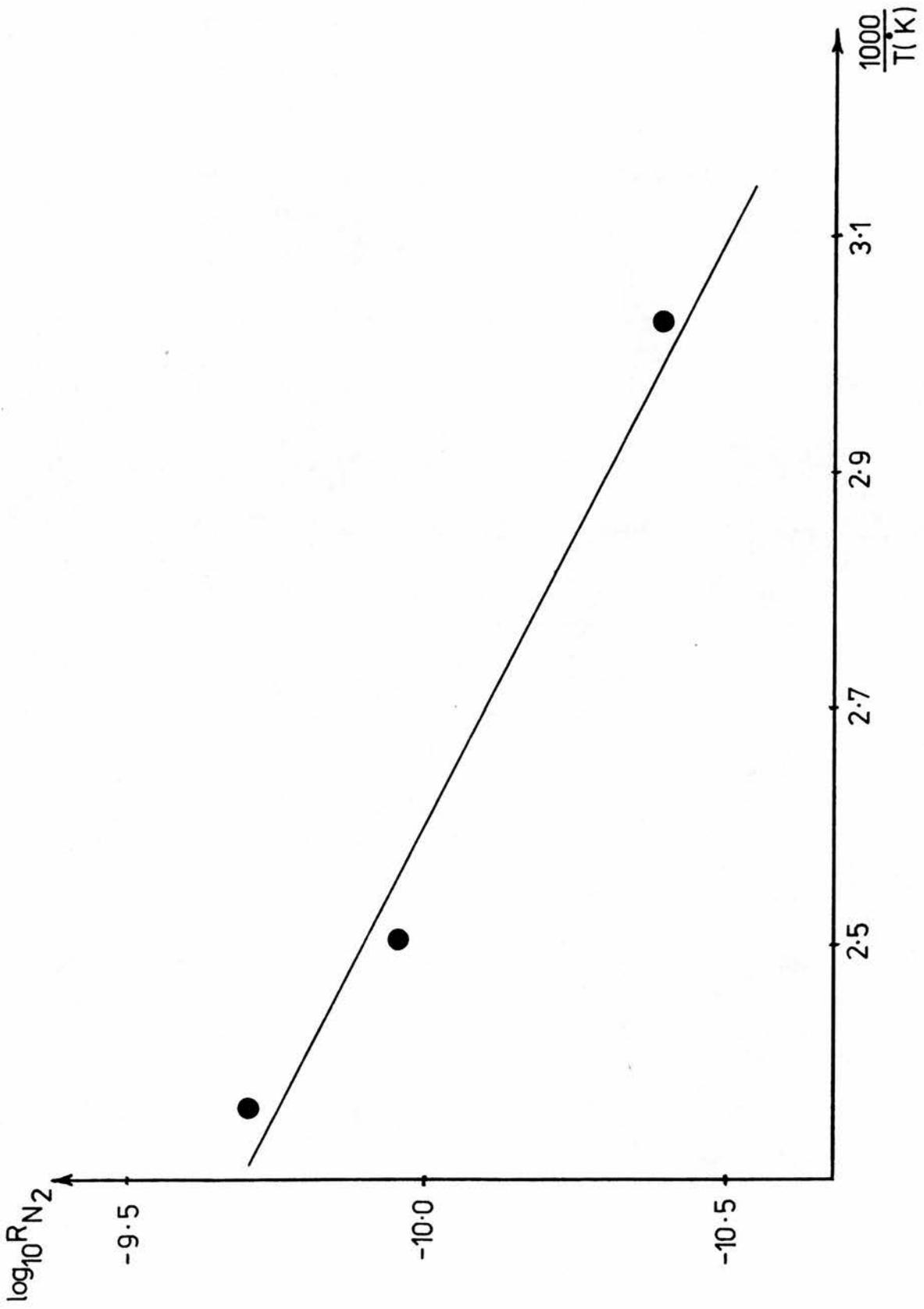


FIGURE 5.2 Graph of $\log_{10} R_{N_2}$ versus the Reciprocal of Temperature for the Photolysis of Azocyclopentane.

An Arrhenius plot of the right hand side versus the reciprocal of temperature should yield a line with gradient $-\frac{E_5 - E_7c}{2.303R}$ and

intercept $\log_{10} A_5 - \frac{1}{2} \log_{10} A_7c$. However, as can be seen from the final two columns of Table 5.2 the experimental error in measurement of R_{A-H} was too great to obtain a meaningful Arrhenius plot.

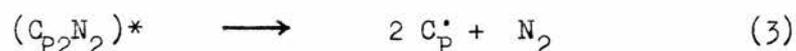
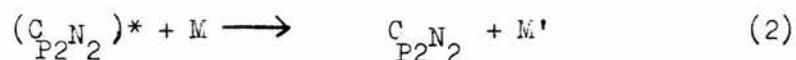
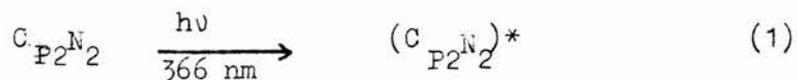
In the final set of experiments azocyclopentane was photolysed in the presence of cyclopentane and carbon tetrachloride. This system was introduced to study the reactions between alkane(cyclopentane) and carbon tetrachloride in the absence of the complicating side reactions identified in the previous sections of this thesis.

Bromotrichloromethane had yielded interesting results when photolysed at 250 nm in the presence of cyclohexane (Section 1) and propane (Section 2). These systems were complicated by the formation of HBr from which a hydrogen atom was readily abstracted by trichloromethyl radicals. This secondary source of chloroform caused problems in the study of hydrogen abstraction from the alkane by trichloromethyl radicals, a reaction which also produces chloroform.

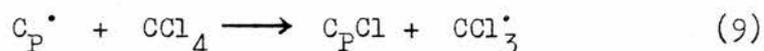
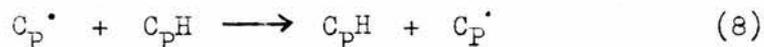
To overcome this complication carbon tetrachloride was used as a source of trichloromethyl radicals. Although HCl was formed in an analogous reaction to the HBr formation from bromotrichloromethane photolysis, the hydrogen atom was considerably less readily abstracted from HCl. Alkanes photolysed with CCl_4 were propane (Section 3) and cyclopentane (Section 4). Complications arose in these systems due to the secondary photolytic initiation reaction of CCl_4 which yielded dichlorocarbene and chlorine molecules.

In the present system the initiating reaction did not produce trichloromethyl radicals at all. The photolysis of azocyclopentane has been discussed in some detail earlier in this section. The

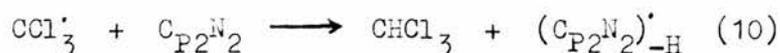
wavelength of ultraviolet light required to carry out this photolysis (366 nm) is at too low an energy to cause any significant photolysis of the carbon tetrachloride present. We have



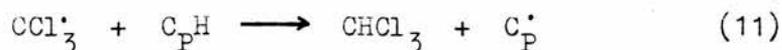
In the earlier part of this discussion the abstraction of a hydrogen atom from azocyclopentane to yield cyclopentane and an azocyclopentyl radical (reaction (5)) was a very significant step. In the presence of cyclopentane and carbon tetrachloride at concentrations considerably in excess of that of azocyclopentane, reaction (5) will cease to assume significant proportions. The reaction (8) with cyclopentane will yield products indistinguishable from the reactants unless labelled species are employed but the reaction (9) with carbon tetrachloride will abstract chlorine as in the carbon tetrachloride-cyclopentane photolysis to yield cyclopentyl chloride and trichloromethyl radicals.



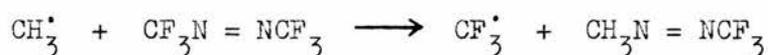
Currie¹⁷⁶ has studied the reaction between trichloromethyl radicals and azocyclohexane by photolysing bromotrichloromethane in the presence of azocyclohexane. The main product was hexachloromethane but a small amount of chloroform was produced by abstraction of a hydrogen atom from azocyclohexane. The analogous reaction must take place to a small extent in the present system.



However, as the concentration of cyclopentane is an order of magnitude greater than the concentration of azocyclopentane the main source of the chloroform observed in the present system will be from hydrogen abstraction from cyclopentane.

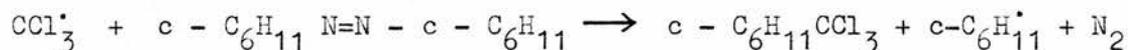


No evidence was found for replacement of a cyclopentyl group in azocyclopentane by trichloromethyl radicals analogous to the replacement of a trifluoromethyl group by a methyl group described by Batt and Pearson¹⁸⁴

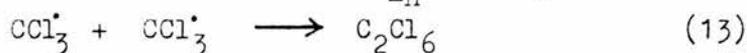
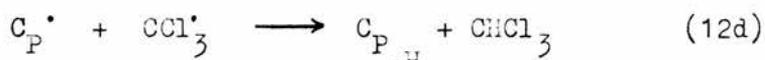
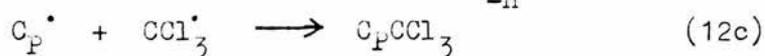
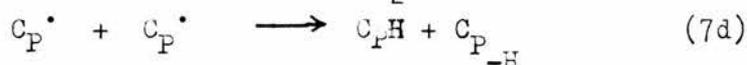
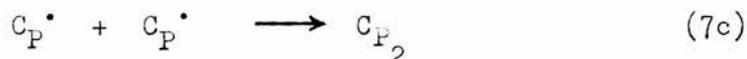


The retention time of $\text{CCl}_3\text{N}=\text{NC}_5$ would be expected to lie between that of bicyclopentyl and azocyclopentane. At such a long retention time trace products would not be detectable.

In the study of the bromotrichloromethane-azocyclohexane system by Currie¹⁷⁶, referred to earlier, it was shown that the elimination of nitrogen by reaction between trichloromethyl radicals and azocyclohexane does not take place.



Although trichloromethylcyclopentane was observed among the products in the present study it is assumed that the source of this compound was the combination reaction of cyclopentyl and trichloromethyl radicals. The termination reactions in this system will be the same as those in the carbon tetrachloride-cyclopentane photolysis described in the previous section, viz:-



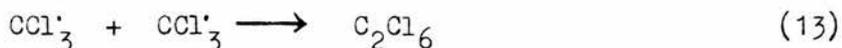
Two different initial concentrations of azocyclopentane were employed in the photolysis, 5.851×10^{-4} and 2.926×10^{-4} mol l⁻¹. The higher concentration was too great because on each occasion liquid was condensed inside the glass capillary tube at the entrance to the oven. Because of this observation, caused by the very low vapour pressure of azocyclopentane, the initial concentration was halved and reaction times extended for the second series of results. As the glc retention times increase in the order $C_2Cl_6 < C_P CCl_3 < C_{P_2}$ the chromatogram peaks become increasingly broad and difficult to measure quantitatively. In the first series of experiments hexachloroethane was the only termination product for which reliable data was obtained. In the second series of experiments all these termination products were measured. Table 5.3 shows the rates of formation of all products obtained in the glc analysis. (The rate of formation of cyclopentene was not measured). The results marked "n.a." were not available either due to instrument malfunction or due to the sample size being too small for consistent data to be obtained by successive chromatograms.

Evaluation of $R_{C_P CCl_3} / R_{C_2Cl_6}^{1/2} R_{C_{P_2}}^{1/2}$ yields values of 1.1 to 2.6. Rocquitte and Wijnen^{134, 135} have studied this ratio for many radical termination systems and, in association with many other workers, it is agreed that the value of this ratio is 2 for almost all systems ($CH_3 + CH_3COCH_2$; ratio = 1.0^{155}). The results of the present study are therefore in good agreement with those of other workers but the presence of significant experimental error is confirmed by the scatter of results.

The rates of formation of the products can be used to calculate Arrhenius parameters for the propagation steps (9) and (11).

As in previous sections we can calculate the rate of reaction

(11) relative to that of reaction (13).



$$R_{\text{CHCl}_3} = k_{11} [\text{CCl}_3\cdot] [\text{C}_5\text{H}]$$

$$R_{\text{C}_2\text{Cl}_6} = k_{13} [\text{CCl}_3\cdot]^2$$

$$\frac{R_{\text{CHCl}_3}}{R_{\text{C}_2\text{Cl}_6}^{1/2} [\text{C}_5\text{H}]} = \frac{k_{11}}{k_{13}^{1/2}} = \frac{A_{11} \exp\left(\frac{-E_{11}}{RT}\right)}{\left(A_{13} \exp\left(\frac{-E_{13}}{RT}\right)\right)^{1/2}} = \frac{A_{11}}{A_{13}^{1/2}} \exp\left(\frac{\frac{1}{2}E_{13} - E_{11}}{RT}\right)$$

Hence a plot of the logarithm of the left hand side versus the reciprocal of temperature yields a straight line of gradient $\frac{1}{2.303R}$

$(\frac{1}{2}E_{13} - E_{11})$ and intercept $\log A_{11} - \frac{1}{2} \log A_{13}$. The points are shown in Table 5.4 and the results are plotted on Figures 5.3 ($[\text{C}_5\text{H}]_i = 5.851 \times 10^{-4} \text{ mol l}^{-1}$) and 5.4 ($[\text{C}_5\text{H}]_i = 2.926 \times 10^{-4} \text{ mol l}^{-1}$).

The assumptions must be made in this argument that all chloroform has come from reaction (11) and the concentration of cyclopentane has not altered to a significant extent throughout the reaction.

The gradients of the slopes in Figures 5.3 and 5.4 are -1.87 ± 0.33 and -1.86 ± 0.26 respectively yielding values of $E_{11} - \frac{1}{2}E_{13} = 8.54$ and $8.52 \text{ kcal mol}^{-1}$. As $E_{13} = 0^{\text{96}}$ we have values for $E_{11} = 8.54 \pm 1.50 \text{ kcal mol}^{-1}$ and $8.52 \pm 1.19 \text{ kcal mol}^{-1}$. The y-axis intercepts of the graph, as calculated by the least squares method are 2.97 ± 0.81 (Figure 5.3) and 2.83 ± 0.63 (Figure 5.4). As $\frac{1}{2} \log A_{13} = 4.85^{\text{41}}$ we obtain values of $\log A_{11} = 7.82$ and $7.68 \text{ l mol}^{-1} \text{ s}^{-1}$. These values confirm the self-consistency of the two series of runs. However, as stated earlier, this calculation is based on the assumptions that (i) the concentration of cyclopentane does not significantly alter during the course of the reaction and (ii) all chloroform was produced via reaction (11).

TABLE 5.4

Arrhenius Parameter Calculation in Azocyclopentane/
Cyclopentane/Carbon Tetrachloride System

Temp (°C)	$\frac{1000}{T(^{\circ}\text{K})}$	$\log \frac{R_{\text{CHCl}_3}}{R_{\text{C}_2\text{Cl}_6}^{\frac{1}{2}} [\text{C}_5\text{H}]}$	$\log \frac{R_{\text{C}_5\text{H}_2\text{Cl}}}{R_{\text{C}_2\text{Cl}_6}^{\frac{1}{2}} [\text{CCl}_4]}$
101	2.674	-2.15	n.a.
105	2.644	-1.82	n.a.
122	2.532	-1.68	n.a.
134	2.457	-1.67	n.a.
140	2.420	-1.69	n.a.
160	2.309	-1.15	n.a.
178	2.217	-1.24	n.a.
97	2.701	-2.11	-1.91
116	2.569	-1.97	-1.68
136	2.444	-1.89	-1.40
142	2.408	n.a.	-1.18
159	2.314	-1.47	-1.29
164	2.287	n.a.	-1.15
186	2.178	-1.15	-0.73

$$[\text{C}_5\text{H}] = 3.420 \times 10^{-3} \text{ mol l}^{-1}$$

$$[\text{CCl}_4] = 1.425 \times 10^{-3} \text{ mol l}^{-1}$$

n.a. = not available

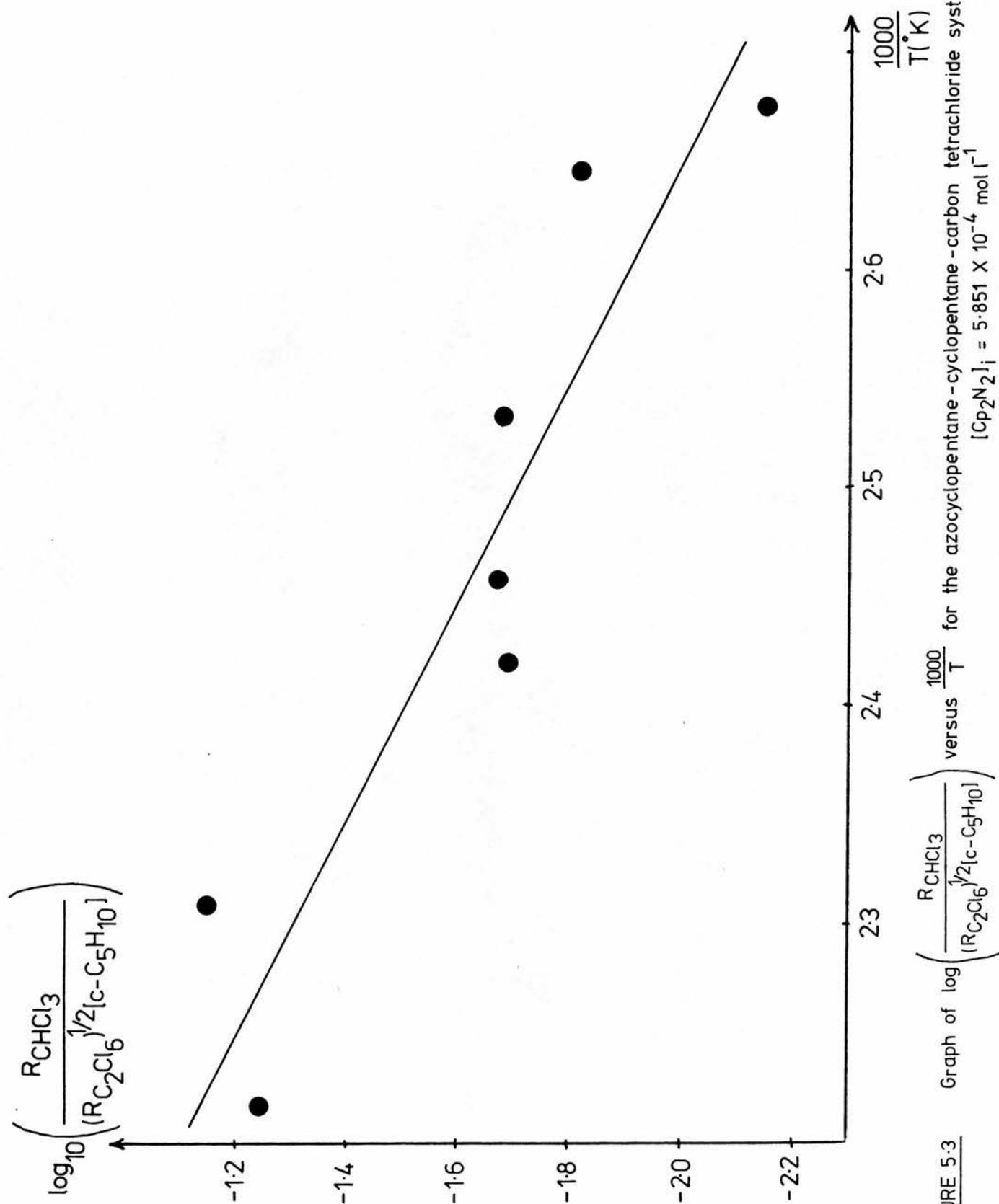


FIGURE 5.3 Graph of $\log \left(\frac{R_{CHCl_3}}{(R_{C_2Cl_6})^{1/2} [c-C_5H_{10}]} \right)$ versus $\frac{1000}{T}$ for the azocyclopentane-cyclopentane-carbon tetrachloride system. $[Cp_2N_2]_i = 5.851 \times 10^{-4} \text{ mol l}^{-1}$

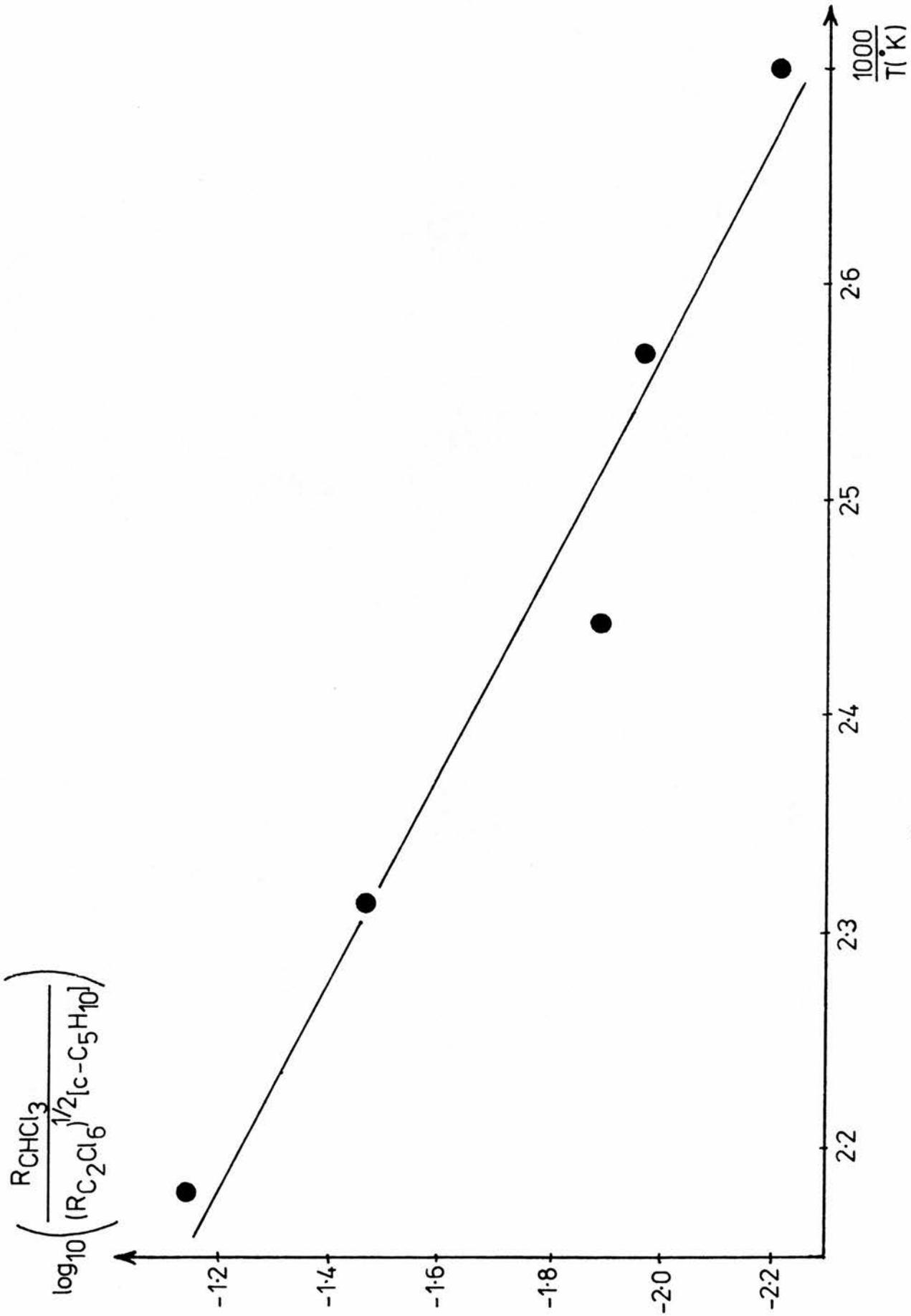


FIGURE 5.4 Graph of $\log \left(\frac{R_{CHCl_3}}{(R_{C_2Cl_6})^{1/2} [c-C_5H_{10}]} \right)$ versus $\frac{1000}{T}$ for the azocyclopentane-cyclopentane-carbon tetrachloride system. $[Cp_2N_2] = 2.926 \times 10^{-4} \text{ mol l}^{-1}$.

In Section 4 of this thesis the value of k_d/k_c for combination of trichloromethyl and cyclopentyl radicals is estimated as 0.3. As the quantity of chloroform produced by the disproportionation of trichloromethyl and cyclopentyl radicals will thus be equal to 0.3 times the quantity of trichloromethylcyclopentane formed we have

$$(R_{\text{CHCl}_3})_{11} = (R_{\text{CHCl}_3})_{\text{total}} - 0.3 R_{\text{C}_5\text{H}_9\text{CCl}_3} \quad (\text{D})$$

where $(R_{\text{CHCl}_3})_{11}$ = rate of formation of CHCl_3 from reaction (11)

In the series of runs carried out with an initial azocyclopentane concentration of $2.926 \times 10^{-4} \text{ mol l}^{-1}$, the calculated formation rates of the termination products were reasonably accurate (as $R_{\text{C}_5\text{H}_9\text{CCl}_3} / R_{\text{C}_2\text{Cl}_6}^{1/2} R_{\text{C}_2\text{Cl}_6}^{1/2} \cong 2$). The value of $(R_{\text{CHCl}_3})_{11}$ can therefore be estimated from equation (D). This value can be used to recalculate the value of $\log_{10} \left(R_{\text{CHCl}_3} / R_{\text{C}_2\text{Cl}_6}^{1/2} [\text{C}_5\text{H}_9] \right)$. The results are shown in Table 5.5.

TABLE 5.5

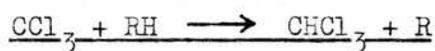
Arrhenius Data Using Corrected CHCl_3 Formation Rate

$\frac{1000}{T(^{\circ}\text{K})}$	$(R_{\text{CHCl}_3})_{11}$	$\log_{10} \frac{(R_{\text{CHCl}_3})_{11}}{R_{\text{C}_2\text{Cl}_6}^{1/2} [\text{C}_5\text{H}_9]}$
2.701	8.90×10^{-11}	-2.35
2.444	1.84×10^{-10}	-1.95
2.314	7.51×10^{-10}	-1.50
2.178	1.07×10^{-9}	-1.16

Using this corrected value of R_{CHCl_3} , the graph shown in Figure 5.4. can be redrawn to yield more accurate values of A_{11} and E_{11} . The figures in Table 5.5 are plotted on Figure 5.5 and yield a straight line of gradient -2.29 ± 0.29 and intercept 3.78 ± 0.64 . These results yield Arrhenius parameters $E_{11} = 10.47 \pm 1.33 \text{ kcal mol}^{-1}$ and $\log A_{11} = 8.63 \pm 0.64 \text{ l mol}^{-1} \text{ s}^{-1}$. These figures are in excellent agreement with rates of hydrogen abstraction calculated by other workers as shown in Table 5.6.

TABLE 5.6

Arrhenius Parameters for the Reaction



RH	$\log_{10} A (\text{l mol}^{-1} \text{s}^{-1})$	$E (\text{kcal mol}^{-1})$	Reference
Cyclopentane	8.63	10.47	This work
Cyclopentane	9.00	10.70	99
Cyclohexane	8.79	10.70	40
Cyclohexane	8.86	10.00	53
Cyclopentane	9.07	9.90	99
Cyclooctane	9.11	9.60	99

By a similar calculation to that employed to determine E_{11} we can write

$$\frac{R_{\text{C}_2\text{P}_2\text{Cl}}}{R_{\text{C}_2\text{P}_2}^{\frac{1}{2}} [\text{OCl}_4]} = \frac{k_9}{k_{7c}^{\frac{1}{2}}} = \frac{A_9}{A_{7c}^{\frac{1}{2}}} \exp \left(\frac{\frac{1}{2}E_{7c} - E_9}{RT} \right)$$

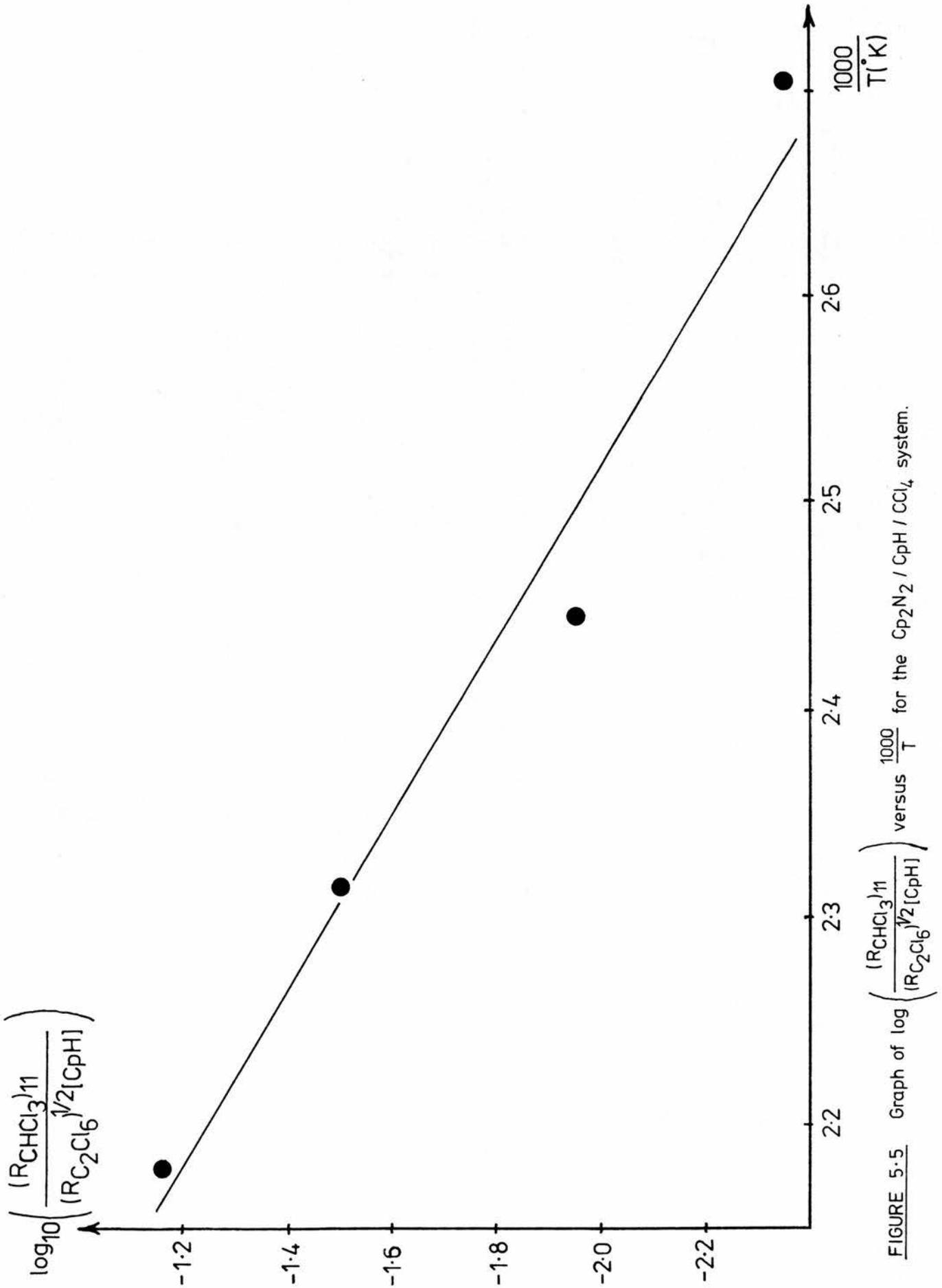
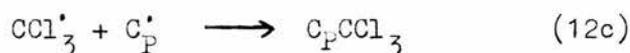
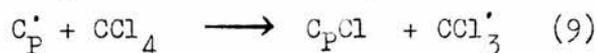
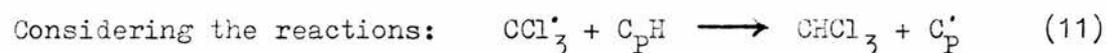


FIGURE 5.5 Graph of $\log \left(\frac{(R_{CHCl_3})^{11}}{(R_{C_2Cl_6})^{1/2} [CpH]} \right)$ versus $\frac{1000}{T}$ for the $Cp_2N_2 / CpH / CCl_4$ system.

Hence a plot of the logarithm of the left hand side versus the reciprocal of temperature yields a straight line of gradient $\frac{1}{2.303R}$ ($\frac{1}{2}E_{7c} - E_9$) and intercept $\log A_9 - \frac{1}{2} \log A_{7c}$. The values of $\log_{10}(R_{C_P Cl} / R_{C_P}^{1/2} [CCl_4])$ are calculated in Table 5.4 and are plotted against $10^3/T(^{\circ}K)$ on Figure 5.6. This graph has a gradient of 2.07 ± 0.24 and intercept 3.67 ± 0.59 .

As E_{7d} will be equal to or almost equal to zero we obtain $E_9 = 9.47 \pm 1.10 \text{ kcal mol}^{-1}$ and $\log A_9 - \frac{1}{2} \log A_{7d} = 3.67 \pm 0.59$. In the absence of the reaction producing bicyclopentyl by autoejection of N_2 from azocyclopentane (as discussed earlier), there should be no other source of significant quantities of either bicyclopentyl or cyclopentyl chloride to introduce errors into this calculation. The bicyclopentyl peak was however the least accurately measured in the gas chromatograph because of its increased breadth resulting from its longer retention time. The value of E_9 can be calculated by an alternative route involving the rate of formation of trichloromethyl cyclopentane, the cross combination product.



we can obtain the relationship

$$\frac{(R_{CHCl_3})_{11} R_{C_P Cl}}{R_{C_P CCl_3} [CCl_4] [C_P H]} = \frac{k_{11} k_9}{k_{12c}} = \frac{A_9 A_{11}}{A_{12c}} \exp \left(\frac{E_{12c} - E_9 - E_{11}}{RT} \right)$$

Hence a plot of the logarithm of the left hand side versus the reciprocal of temperature yields a straight line of gradient $\frac{1}{2.303R}$ ($E_{12c} - E_9 - E_{11}$) and intercept $\log A_9 + \log A_{11} - \log A_{12c}$. The values of

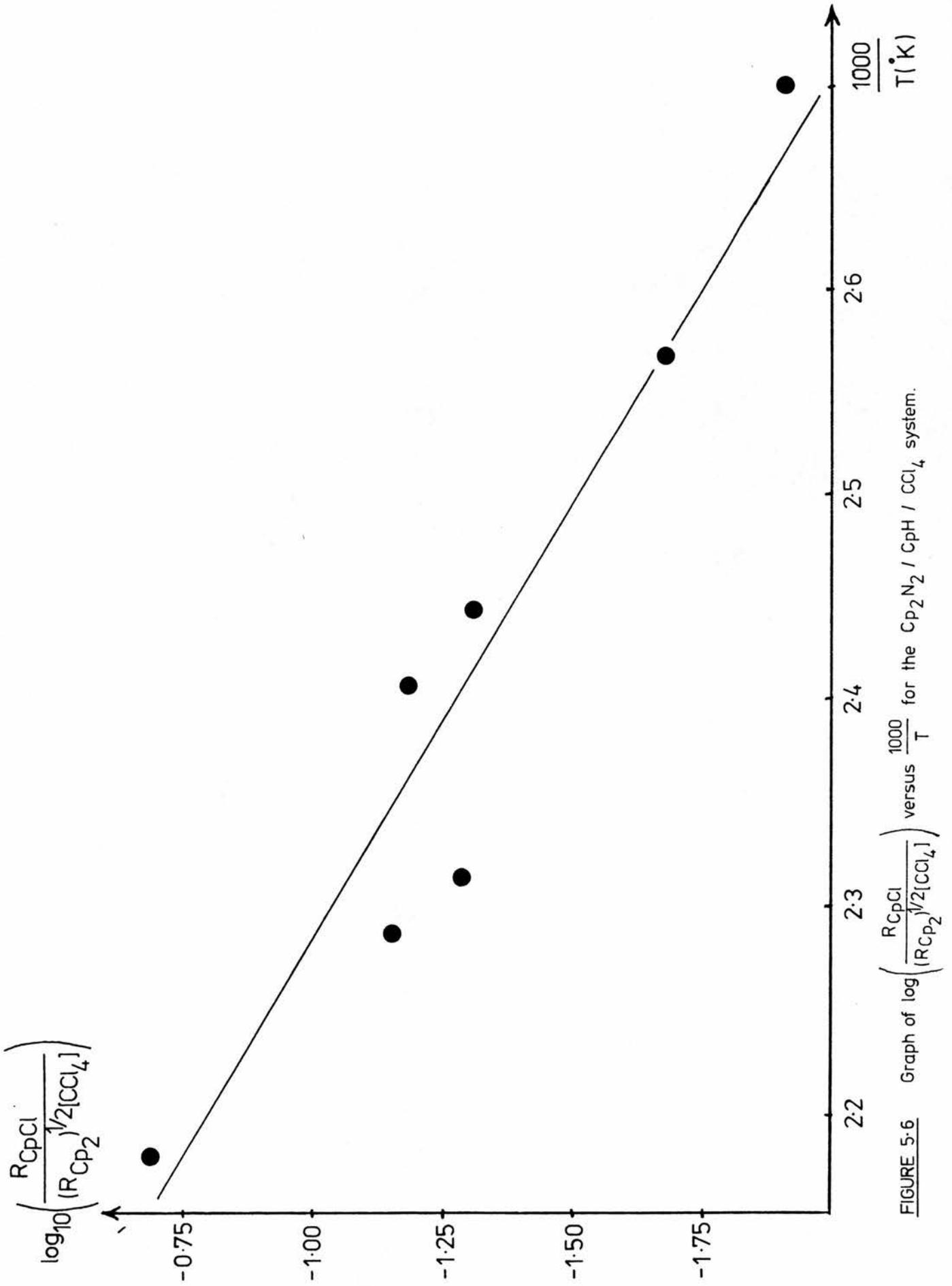


FIGURE 5.6 Graph of $\log \left(\frac{R_{\text{CpCl}}}{(R_{\text{Cp}_2})^{1/2} [\text{CCl}_4]} \right)$ versus $\frac{1000}{T}$ for the $\text{Cp}_2\text{N}_2 / \text{CpH} / \text{CCl}_4$ system.

$\log_{10} \left(\frac{(R_{\text{CHCl}_3})_{11} R_{\text{C}_2\text{H}_5\text{Cl}}}{R_{\text{C}_2\text{H}_5\text{CCl}_3} [\text{CCl}_4] [\text{C}_2\text{H}_5]} \right)$ are calculated in Table 5.7 and are plotted against $10^3/T(^{\circ}\text{A})$ on Figure 5.7. The graph has a gradient of -5.09 ± 0.49 and intercept of 8.99 ± 0.68 .

TABLE 5.7

Arrhenius Data Calculations

$\frac{1000}{T(^{\circ}\text{K})}$	$\log \frac{(R_{\text{CHCl}_3})_{11} R_{\text{C}_2\text{H}_5\text{Cl}}}{R_{\text{C}_2\text{H}_5\text{CCl}_3} [\text{CCl}_4] [\text{C}_2\text{H}_5]}$
2.701	-4.67
2.444	-3.56
2.314	-2.95
2.178	-1.93

Hence we obtain $E_{12c} - E_9 - E_{11} = -23.28$ kcal. As reaction (12c) is a radical combination reaction, the activation energy E_{12c} will be approximately zero, and as E_{11} has been calculated earlier in this discussion as 10.47 kcal mol⁻¹ we obtain

$$\begin{aligned} E_9 &= (23.28 \pm 2.24) - (10.47 \pm 1.33) \\ &= 12.81 \pm 3.57 \text{ kcal mol}^{-1} \end{aligned}$$

This value is significantly greater than the value 9.47 ± 1.10 kcal mol⁻¹ calculated earlier in this discussion.

From the y-axis intercepts on Figures 5.5, 5.6 and 5.7 we have

$$\begin{aligned} \log A_{11} &= 8.63 \pm 0.64 \text{ l mol}^{-1} \text{ s}^{-1} \\ \log A_9 - \frac{1}{2} \log A_{7c} &= 3.67 \pm 0.59 \text{ l mol}^{-1} \text{ s}^{-1} \\ \log A_9 + \log A_{11} - \log A_{12c} &= 8.99 \pm 0.68 \text{ l mol}^{-1} \text{ s}^{-1} \\ \text{i.e. } \log A_9 - \log A_{12c} &\cong 0.36 \text{ l mol}^{-1} \text{ s}^{-1} \end{aligned}$$

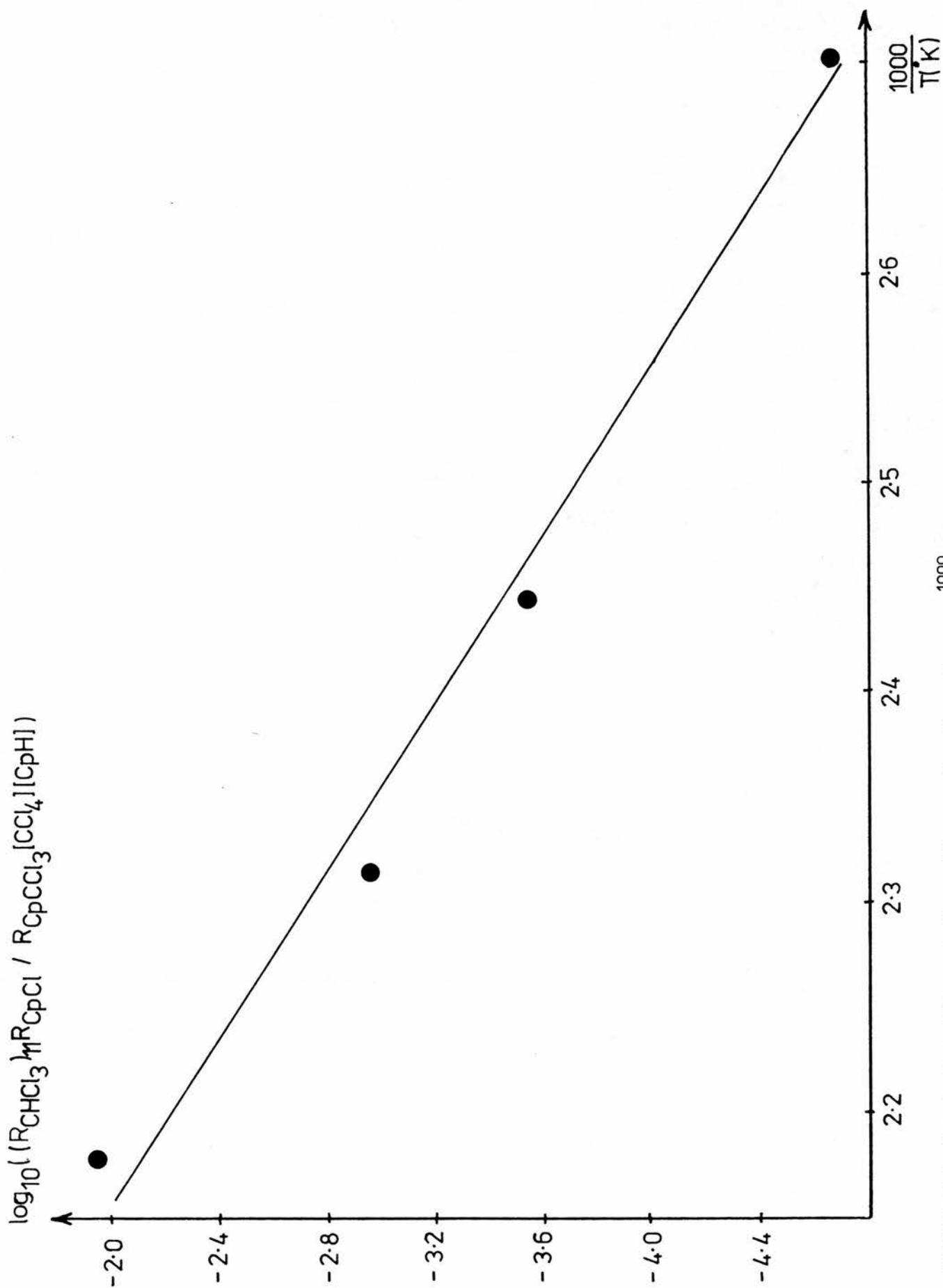
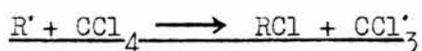


FIGURE 5.7 Graph of $\log \left(\frac{(R_{\text{CHCl}_3})_{11} R_{\text{CpCl}}}{R_{\text{CpCCl}_3} [\text{CCl}_4][\text{CpH}]} \right)$ versus $\frac{1000}{T}$ for the $\text{Cp}_2\text{N}_2 / \text{CpH} / \text{CCl}_4$ system.

Values of E_9 and $\log A_9$ have been estimated by other workers in this laboratory and the results obtained are shown in Table 5.8.

TABLE 5.8

Arrhenius Parameters for the Reaction



R	$\log_{10} A$ ($l \text{ mol}^{-1} \text{ s}^{-1}$)	E (kcal mol^{-1})	Reference
Methyl	8.6	9.1	53
Methyl	10.2	13.4	137
Ethyl	8.4	8.9	53
Cyclopentyl	See Text	9.5-12.8	This work
Cyclohexyl	8.6 estimate	11.8	53

It can be seen that the range calculated for E_9 ($R = C_P$) is in good agreement with previous work. The value of $\log A_9 = 8.6$ $l \text{ mol}^{-1} \text{ s}^{-1}$ was estimated by considering that cyclohexyl radicals will have probably more stringent steric requirements than methyl and ethyl groups and the value of 8.6 was inserted as an upper limit. A similar argument can be raised for cyclopentyl radicals.

If $\log A_9 \leq 8.6$ we have from the intercept of Figure 5.6, $\log A_{7c} \leq 9.86$, and from the intercept of Figure 5.7, $\log A_{12c} \leq 8.24$. As $\log A_{13} = 9.7$ we can calculate values of $\log A_{12c}$ from Figure 5.6 and $\log A_{7d}$ from Figure 5.7 by using the relationship

$$\frac{k_{12c}}{k_{7c}^{1/2} k_{13}^{1/2}} = 1.6. \quad (\text{This value should equal 2.0 but the value 1.6}$$

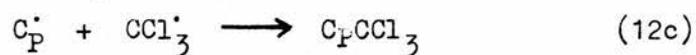
is obtained by averaging all formation rates in Table 5.3). We

obtain values of $\log A_{12c}$ and $\log A_{7d}$ of 10.0 and 6.4 respectively.

The above calculations yield estimates for the maximum value of the rate constants for the two combination rates involving cyclopentyl radicals. We have:



$$\max k_{7c} = 10^{8.13 \pm 1.73} \text{ l mol}^{-1} \text{ s}^{-1}$$



$$\max k_{12c} = 10^{9.12 \pm 0.88} \text{ l mol}^{-1} \text{ s}^{-1}$$

Calculations by Currie⁵³ yielded a value of the combination rate of cyclohexyl radicals as $k \leq 10^{7.0} \text{ l mol}^{-1} \text{ s}^{-1}$ which because of the greater steric requirements for cyclohexyl radical combination relative to cyclopentyl is in very good agreement with the result of the present study.

APPENDIX 1Stiff Systems

Let $\underline{y}'(x) = \underline{f}(x, \underline{y})$ be a system of n first order differential equations. The Jacobian of $\underline{f}(x, \underline{y})$, evaluated at (x_0, \underline{y}_0) is the $n \times n$ matrix

$$J(x_0, y_0) = \left[\left(\frac{\delta f_i}{\delta y_j} \right)_{(x_0, \underline{y}_0)} \right]_{i,j}$$

If the matrix has eigenvalues with large negative real parts then the equations are stiff and are characterised by the fact that the solution y usually changes quite rapidly with x over a "small" range before settling down to some "smoother" behaviour. In attempting to follow this behaviour, conventional numerical methods which involve a step length h are usually forced to take very small values for h .

e.g. $y'(t) = \lambda(y - F(t)) + F'(t)$ with $\lambda \ll 0$

has solution $y(t) = F(t) + ce^{\lambda t}$

Using the numerical scheme,

$$\begin{aligned} \tilde{y}(t+h) &\approx \tilde{y}(t) + h \tilde{y}'(t) \\ &\approx \tilde{y}(t) + h\lambda(\tilde{y} - F(t)) + hF'(t) \end{aligned}$$

We see that the error e_n defined by $y(t) - \tilde{y}(t)$ behaves as

$$e_{n+1} = (1 + \lambda h)e_n + \text{local truncation error}$$

Consequently, if $\lambda h < -2$ the error grows in magnitude at each step.

The reactions simulated in Section 2.7.3 constitute a stiff system as the rates of change of species' concentrations will change very rapidly in a short period of time before settling down to smoother behaviour.

Multi-Step Methods

The idea behind multi-step methods is to express the value of the solution y_n linearly in terms of past values of y and its derivatives.

Formally, we write:-

$$(1) \quad \alpha_k y_n + \alpha_{k-1} y_{n-1} + \dots + \alpha_0 y_{n-k} + h (\beta_k y'_n + \beta_{k-1} y'_{n-1} + \dots + \beta_0 y'_{n-k}) = 0$$

where the values k, α_i, β_i define the method.

If $\beta_k = 0$ formula (1) is "explicit", i.e. we may obtain y_n directly from (1) without any trouble. If $\beta_k \neq 0$ then (1) is "implicit" since $y'_n = f(x, y_n)$ and we have to derive some iterative scheme to obtain y_n from (1). Implicit formulae have better numerical properties than their explicit counterparts and so we invariably have to solve the non-linear equation (1). A method commonly employed uses two formulae of type (1). The first is explicit and is called the "predictor", the second is implicit and called the "corrector". The predictor is used to give a value $y_n^{(1)}$ which is then used to evaluate $f(x, y_n^{(1)})$ and so start an iterative procedure for $y_n^{(i+1)}$ in the corrector. This defines the standard predictor-corrector methods.

Gear's Method

Gear's method is an implementation of a set of multi-step methods of order 1 up to 6. It uses implicit corrector formulae which make it suitable for stiff systems since these allow a larger step size h . The order and step size are controlled by estimating the local error at each step. Since it is designed for stiff systems the predictor, corrector, corrector, ... system is not used as the convergence would only be guaranteed for $h |\lambda| < 1$. Instead a Newton iteration is used to solve the corrector, starting from a value obtained from the predictor. The Jacobian is estimated by differencing methods and is not usually reevaluated after every step

but only when the iteration "fails". Finally, easy change of step, a feature not found in conventional multi-step methods is facilitated by storing not the past values y_{n-i} but approximations to the "reduced derivatives" of y_n ,

$$h y'_n, \frac{h^2}{2!} y''_n, \frac{h^3}{3!} y'''_n \text{ etc.}$$

which are obtained by differencing. Using these, past values y_{n-1} can in effect be obtained from the Taylor expansions, although this process is masked within any implementation.

APPENDIX 2Preparation of Bicyclopentyl

10g of sodium were added to 50 ml of toluene and the mixture heated in an oil bath until the sodium melted. The mixture was stirred vigorously and allowed to cool while still being stirred. A fine sodium sand was obtained. This was washed with dry ether and the sodium added to a further 70 ml of dry ether. While the mixture was being gently stirred, 10 ml of cyclopentyl chloride was slowly added and the reaction left stirring for 24 hours.

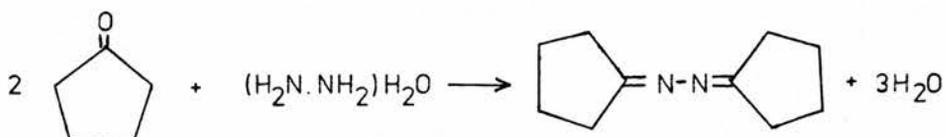
Distilled water was added to remove the unreacted sodium and the precipitated sodium chloride. The aqueous layer was discarded and the organic layer fractionally distilled. Bicyclopentyl boils at 190°C so the distillate obtained between 175 and 200°C was collected. A mass spectrograph of this product confirmed that it was almost pure bicyclopentyl. This sample was used to identify bicyclopentyl as a termination product in Sections 4 and 5.

APPENDIX 3Preparation of Azocyclopentane

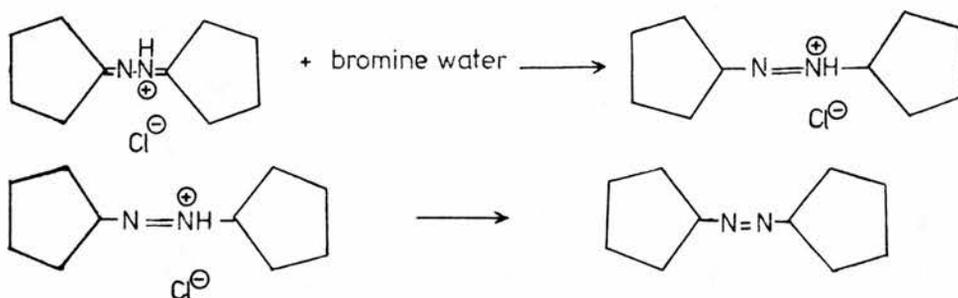
Two methods were employed in an attempt to produce azocyclopentane CpN:NCp. The first method used a cyclopentanone precursor and proved unsuccessful, whereas the latter method employing cyclopentylamine yielded sufficient azocyclopentane for all subsequent experimental studies.

a. Cyclopentanone Precursor

The cyclopentanone was reacted with hydrazine hydrate to yield cyclopentyl hydrazine.



Harkins and Lochte¹⁸⁵ used cyclohexyl hydrazine to produce azocyclohexane by reduction with bromine water and a parallel reaction was attempted with the cyclopentyl hydrazine. It was hoped to produce azocyclopentane via the reactions

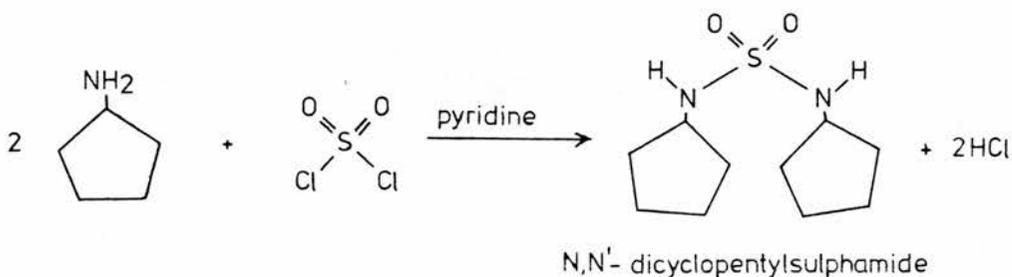


The process was repeated twice but no azocyclopentane was detected.

b. Cyclopentylamine Precursor

This method was described by R. Sowada¹⁸⁶ who prepared N,N'-dialkylsulphamides and by Ohme et al^{187,188} who subsequently prepared the azoalkanes, and previous experiments in this laboratory⁵³ have succeeded in producing azocyclohexane from cyclohexylamine. The first step of the preparation was the preparation of the N,N'-disubstituted sulphuric acid diamide. 25g of cyclopentylamine and 20 ml of pyridine were added to 90 ml 40-60°C petroleum spirit. 9.5 ml of SO₂Cl₂ dissolved in 30 ml of petroleum spirit (40-60°C) were added dropwise, the temperature being kept below -20°C throughout the reaction. White HCl fumes were evolved and a creamy precipitate was obtained. After addition (ca. 90 min.) the mixture was stirred at < -20°C for 20 min. The liquid was decanted. It was noticed that on attaining room temperature more precipitate was obtained, but this rapidly turned dark brown and was discarded.

The white precipitate was treated with conc. HCl(27 ml) in 150 ml H₂O, cooled and filtered. The precipitate was then heated under reflux for 2 hours with conc. HCl(45 ml), EtOH(45 ml) and H₂O(45 ml). It was cooled and filtered as a flaky white solid which was then recrystallised from EtOH/H₂O. The reaction was



The melting point of the product (probably present as hydrochloride) was 145.5-147°C. The total yield was 9.9g (57% based on SO_2Cl_2). 3.143g (77.6 mM) NaOH was added to 51.7 ml of 1.5 M NaOCl solution (77.6 mM) and to this mixture 9g (38.8 mM) N,N'-dicyclopentylsulphamide was added. The sulphamide was found to be only sparingly soluble in the aqueous solution. Despite literature reports of the sulphamide dissolving in several hours to form the required azo compound as an oil, none was observed after stirring for 60 hours. A further 10 ml of 1.5 M NaOCl was added and the mixture stirred for 48 hours. The unreacted sulphamide and about 1 ml of oil separated from the filtrate. This was identified as azocyclopentane by mass spectrometry and an ultraviolet spectrum showed a maximum absorption at 353 nm (See Fig. A3.1), similar to that observed for azoisopentane and azocyclohexane prepared in this laboratory.

The unreacted sulphamide was added to the aqueous layer and stirred overnight with 0.5 g NaOH and 10 ml of 1.5 M NaOCl added. All the sulphamide dissolved and a further 3.75 ml of yellowish sweet-smelling azocyclopentane oil obtained which was purified by distillation at reduced pressure.

The azocyclopentane was used without further purification as glc analysis did not reveal the presence of impurities.

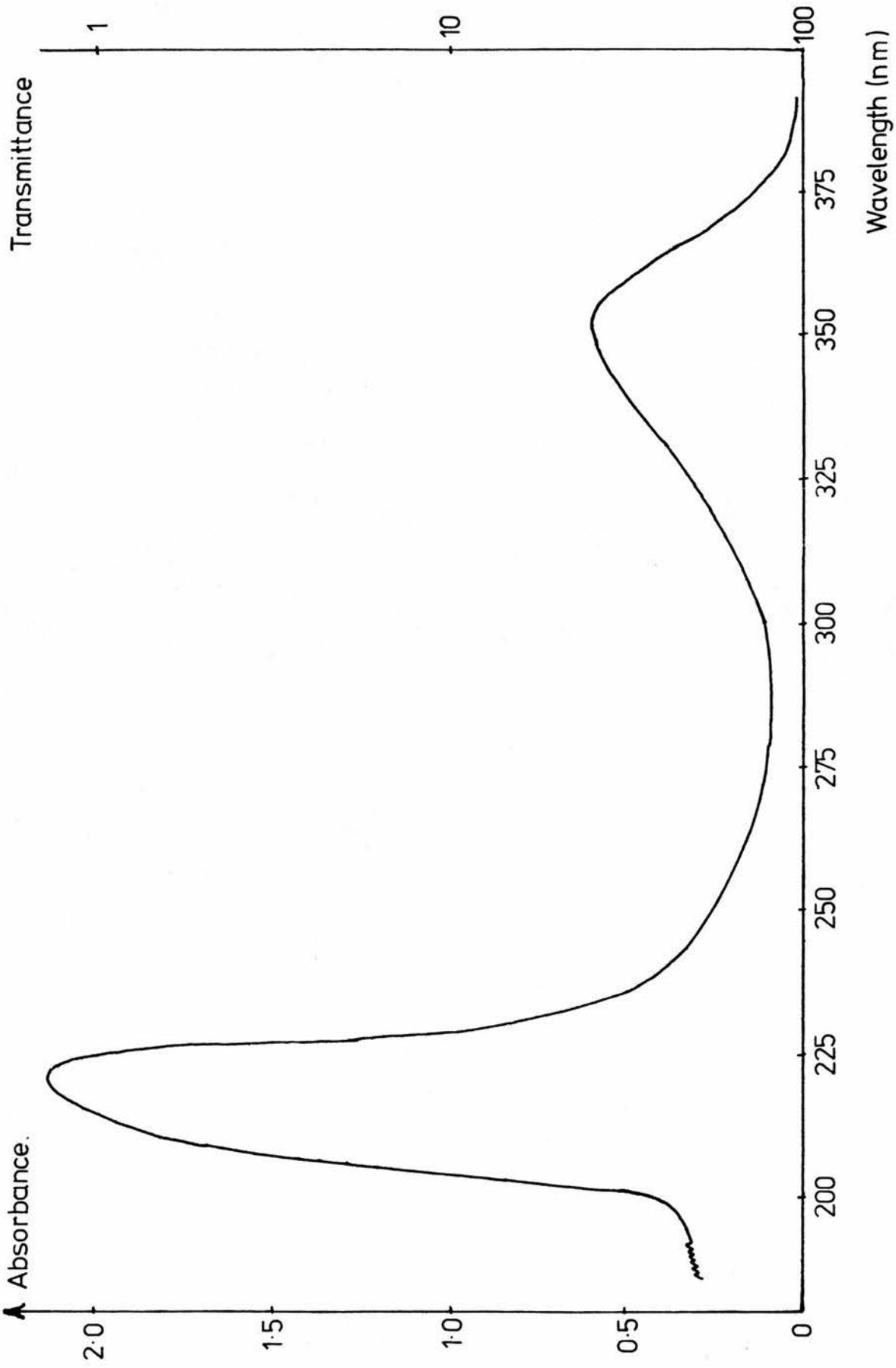


FIGURE A.1 Ultraviolet Spectrum of Azocyclopentane.

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