A STUDY OF THE VAPOUR PHASE PYROLYSIS AND ALKALINE HYDROLYSIS OF CHLOROFORM

Thesis presented for the degree of
Doctor of Philosophy
by
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February, 1979

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TO MY PARENTS,

AND TO THE MEMORY OF MY

GRANDFATHER, JOSEPH GRUMMETT

CONTENTS

PART THREE — DISCUSSION AND CONCLUSIONS

ABSTRACT

The decomposition of chloroform at 510°C was investigated in a continuous flow system, using nitrogen as the carrier gas. The main products of the reaction were hydrogen chloride, tetrachloroethylene, pentachloroethane and hexachloroethane; hydrogen and chlorine could not be detected. Neither the addition of a radical initiator (azobisisobutyronitrile) nor an inhibitor (phenol) affected the breakdown, and so we have rejected the idea that the main reaction mechanism is of a radical nature.

From the results obtained by varying the surface to volume ratio of the reactor, the reaction appeared to be catalysed by the surface of the reactor, but pretreating the tube by steaming, soaking in water or EDTA solution did not affect the pyrolysis. The reaction appeared to be virtually unaltered when a tube made from very pure silica was used.

Kinetic investigations showed that the reaction was first order with respect to chloroform, and exhibited an induction period. Carrying out the reaction in a carbonised tube resulted in a faster reaction, and an increase in the induction period.

To account for the results obtained, a mechanism is suggested which involves the formation of a carbon polymer on the silica reactor. Chloroform could then be adsorbed onto the polymer where reaction could occur. In a carbonised tube a graphite-like carbon structure may begin to take over as the catalyst.

The alkaline hydrolysis of chloroform was studied in aqueous

1,4-dioxane (32 % w/v), at 36°C. The rate of disappearance of chloroform was followed by gas-liquid chromatography, whilst the sodium hydroxide concentration was determined by titration with dilute hydrochloric acid. The reaction was second order overall, first order with respect to each of the reactants. Data obtained at 25°C, 31°C, 36°C and 41°C was used to determine the activation parameters.

Increasing the concentration of dioxane in the solvent decreased the reaction rate. The reaction showed a definite negative salt effect, sodium chloride exhibiting a greater effect than potassium nitrate.

The reaction between deuterochloroform and sodium deuteroxide in deuterium oxide/dioxane was faster than the reaction in the corresponding proton system.

Application of the Yagil approach suggested that the transition state is associated with seven water molecules. This led us to suggest an alternative mechanism for the reaction, involving nucleophilic attack by water on the trichloromethyl anion, formed by loss of a proton from chloroform.

In order to apply the Yagil criterion the hydration number of dioxane had to be determined; a value of 2.25 was obtained.

ACKNOWLEDGEMENTS

I should like to express my gratitude to my supervisor, Dr. R.E. Busby, for his guidance and encouragement throughout the course of this work.

I am grateful to Mr. R.J. Langston and Mr. D.C. Reed for their technical assistance.

My thanks are also extended to Mrs. Z. Curry for her care and patience in typing this thesis, and to Dr. R.J.J. Dorgan for his help in preparing the diagrams.

I would also like to thank the Science Research Council for the award of a Research Studentship.

PART ONE

INTRODUCTION

CHAPTER 1

PYROLYSIS OF CHLORINATED HYDROCARBONS

1.I.i. PYROLYSIS OF CHLOROFORM

The vapour phase decomposition of chloroform was first studied by Herndon and Reid[1] in 1928, who identified chlorine, hydrogen chloride, and hexachloroethane amongst the reaction products. In 1932 Lessig[2] reported the formation of a 'yellow crystalline material, together with a tar', and found that kinetic data for the reaction was very irregular. Subsequent work by Verhoek[3] (1935), identified the solid formed as hexachloroethane, and showed that all the hydrogen of the chloroform was converted to hydrogen chloride.

The first comprehensive study of this reaction was undertaken by Semeluk and Bernstein[4,5] in 1954. Chloroform was introduced into a carrier stream of helium and passed through a reaction chamber (450-525°C) packed with Vycor rings. The products in the exit gases were collected in a series of cold traps and analysed, after removal of hydrogen chloride, by infrared spectrophotometry. Hydrogen chloride, tetrachloroethylene, hexachloroethane, pentachloroethane, trichloroethylene, dichloromethane and symetrical tetrachloroethane were formed in decreasing amounts, together with possible trace amounts of carbon tetrachloride, 1,1-dichloroethylene, *cis*- and *trans*-dichloroethylene and dichloroacetylene. Hydrogen, chlorine and phosgene were definitely not present. Various suspected intermediates were pyrolyzed to ascertain whether the above compounds were formed directly, or from a secondary breakdown.

It was found that, with increasing extent of decomposition, hydrogen chloride and tetrachloroethylene became the major products, leading the authors to suggest that the stoichiometry of the reaction when allowed to go to completion might be

$$2CHCl_3 \longrightarrow 2HCl + C_2Cl_4$$

This would predict a pressure rise $\Delta P/\Delta P_0$ of 0.5, compared with the values of 0.460 ± 0.005^4 and 0.55^3 obtained when the reaction was studied in a static system. However, if appreciable amounts of other products are still present because the reaction has not gone to completion, lower than predicted values would be expected.

The following radical mechanism was proposed by Semeluk and Bernstein to account for the observed results.

primary dissociation

$$CHCl_3 \longrightarrow \cdot CHCl_2 + \cdot Cl$$

abstractions

$$\cdot Cl + CHCl_3 \rightleftharpoons HCl + \cdot CCl_3$$

$$\cdot CHCl_2 + CHCl_3 \longrightarrow CH_2Cl_2 + \cdot CCl_3$$

recombination

$$\cdot CCl_3 + \cdot Cl \longrightarrow CCl_4$$

disproportionation

$$\cdot CCl_3 \longrightarrow :CCl_2 + \cdot Cl$$

dehydrochlorination

$$:CCl_2 + CHCl_3 \longrightarrow C_2Cl_4 + HCl$$

Once the initial radical formation has taken place, a large variety of reactions may follow, and thus explain the formation of the products obtained.

Rupture of a carbon-chlorine bond rather than the carbon-hydrogen bond in the rate determining step, was substantiated by a small secondary isotope effect (20 % decrease), when the rate of chloroform breakdown was compared with that of deuterochloroform under the same conditions. The isotope effect was measured by direct comparison of rates, and by a competitive method which gave comparable results.

Kinetic experiments[5] using the flow system, in which the reaction rate was determined from the rate of hydrogen chloride formation, showed that the reaction was first order in chloroform. Rate constants were determined graphically, from plots of x/a; the fraction of hydrogen chloride produced, against the contact time.

TABLE 1

Initial rate constants and isotope effect for the pyrolysis of $CHCl_3$ and $CDCl_3$ [5]

T(K)	k_H (sec^{-1})	k_D (sec^{-1})	k_H/k_D
725	$3.66 \times 10^{-3} \pm 10\%$	$2.90 \times 10^{-3} \pm 10\%$	1.26
750	1.01×10^{-2}	8.30×10^{-3}	1.22
775	1.84×10^{-2}	1.54×10^{-2}	1.19
785	2.52×10^{-2}	2.00×10^{-2}	1.26
800	4.56×10^{-2}	3.80×10^{-2}	1.20

Activation energies were calculated as 37.2 ± 2.0 and 37.5 ± 2.0 Kcal. mol.$^{-1}$,. for chloroform and deuterochloroform respectively, somewhat lower than the value of 49 Kcal.mol.$^{-1}$ obtained by Verhoek[3]. The frequency factor was calculated to be 6.3×10^{8} sec.$^{-1}$ for both compounds.

Changing the surface to volume ratio from 19 cm.$^{-1}$ in the flow system, to 1.3 cm.$^{-1}$ in the static system, appeared to have little effect on the reaction, which was therefore thought to proceed homogeneously under the given experimental conditions. Similarly, the reproducibility of rate measurements once the reactors had been carbonised suggested that the reaction occurred in the bulk of the gas.

The addition of hydrogen chloride had an inhibiting effect on the decomposition of both chloroform and deuterochloroform, whilst addition of tetrachloroethylene accelerated the reaction. Product inhibition gives rise to a rate law of the form

$$\frac{-d\,[CHCl_3]}{dt} = \frac{k\,[CHCl_3]}{f(c)} \qquad (1)$$

where f(c) is a function of the concentration of hydrogen chloride. The inhibition function $f(c) = (1 + bC)^{\frac{1}{2}}$, gave the best representation of Semeluk and Bernstein's data, hence, at low extent of reaction

$$\frac{-d\,[CHCl_3]}{dt} = \frac{k\,[CHCl_3]}{(1 + b[HCl])^{\frac{1}{2}}} \qquad (2)$$

Howlett[5] suggested that a bimolecular mechanism is more probable, thus

$$\frac{-d\ [CHCl_3]}{dt} = \frac{k[M]\ [CHCl_3]}{([M] + b[HCl])^{\frac{1}{2}}} \tag{3}$$

where M is the carrier gas in the flow runs, giving a rate law which is indistinguishable from that observed. In the static system however, M is a second molecule of chloroform, resulting in an order of 3/2, which does not agree with the observed results.

The catalytic effect of tetrachloroethylene has been explained[4] as being due to the removal of trichloromethyl radicals, with subsequent breakdown to give two molecules of tetrachloroethylene for every one which reacts.

$$\cdot CCl_3 + C_2Cl_4 \longrightarrow CCl_3CCl_2CCl_2\cdot$$

$$CCl_3CCl_2CCl_2\cdot + CCl_3\cdot \longrightarrow 2Cl_2Cl_5\cdot \longrightarrow 2C_2Cl_4 + 2Cl\cdot$$

The alternative, removal of hydrogen chloride, was thought unlikely since this does not occur readily in the gas phase.

Further support for the radical mechanism came from Errede and Cassidy[6], who studied the pyrolysis of chloroform both on its own, and also, by coaxial pyrolysis with p-xylene which will be discussed later.

An alternative mechanism for chloroform breakdown was suggested by Shilov and Sabirova[7-9] in 1957. They studied the reaction in a vacuum flow system using either excess toluene vapour as a carrier gas, or none at all, and determined the extent of reaction from hydrogen chloride formation. First order rate constants were found to be independent of the presence of carrier gas, and, packing the reaction vessel with glass wool or quartz glass, did not cause any noticeable change in the reaction rate. A mechanism based on the existence of dichlorocarbene was suggested, since the decomposition rate constant was thought too great, and the activation energy too low, to substantiate homogeneous radical decomposition. Also, in carrying out the reaction in the presence of toluene, any radicals formed (e.g. $\cdot Cl$ and $\cdot CHCl_2$), would be expected to abstract a proton from the toluene to give a benzyl radical, which would result in the formation of a considerable amount of bibenzyl, as has been found in the decomposition of bromoethanes[10,11].

The possibility of a chain mechanism was discarded, since the presence of toluene does not have an inhibiting effect on the reaction. Similarly, carbon tetrachloride did not accelerate the reaction[9], as might be expected if a radical mechanism was involved, since initial removal of a chlorine atom should take place more readily from carbon tetrachloride than from chloroform.

More recently[12,13] however, it has been shown that carbon tetrachloride does in fact accelerate the decomposition of chloroform, although this may result from an additional reaction by which chlorine atoms originating from carbon tetrachoride abstract a proton from the chloroform molecule, rather than an increase in reaction by the usual mechanism.

$$CCl_4 \longrightarrow \cdot Cl + \cdot CCl_3$$

$$\cdot Cl + CHCl_3 \longrightarrow HCl + \cdot CCl_3$$

A study of the decomposition of deuterochloroform[9] gave a larger isotope effect, ($k_H/k_D = 1.65$), than that reported previously[5]. However, this may have resulted from the fact that the former authors were using shorter contact times. This, together with the fact that the reaction was first order in chloroform, has led the authors to suggest that the initial, rate determining step, is the removal of hydrogen chloride from chloroform.

$$CHCl_3 \longrightarrow :CCl_2 + HCl$$

This was thought to be energetically more favourable than rupture of the carbon-chlorine bond, because of the stability of the dichlorocarbene produced. Since deuterium is known to exchange between $CDCl_3$ and HCl, during decomposition[4], and hydrogen chloride has an inhibiting effect on the reaction[5], it was assumed that the reaction must be reversible.

Once dichlorocarbene had been formed, it was thought to react either with another chloroform molecule, or, with a molecule of toluene, when the latter is used as a carrier gas. This explained the formation of hydrogen chloride during the decomposition of deuterochloroform in the presence of toluene, since it has been shown that under the same experimental conditions this does not occur by simple exchange.

The following reactions have therefore been postulated

$$:CCl_2 + CHCl_3 \longrightarrow CHCl_2CCl_3 \longrightarrow Cl_2C{=}CCl_2 + HCl$$

or, in the presence of toluene

$$:CCl_2 + C_6H_5CH_3 \longrightarrow HCl + C_6H_5CH{=}CHCl$$

The eventual formation of trichloromethyl radicals must be included to account for the formation of hexachloroethane.

$$:CCl_2 + CHCl_3 \longrightarrow \cdot CCl_3 + \cdot CHCl_2$$

$$2:CCl_2 \longrightarrow \cdot CCl_3 + \cdot CCl$$

$$2\cdot CCl_3 \longrightarrow C_2Cl_6$$

Further criticism of the radical mechanism has been based on a comparison of the decomposition of chloroform, with that of methyl chloride and carbon tetrachloride. In the presence of toluene both of the latter reactions involve cleavage of the carbon-chlorine bond to form radicals, as the rate determining step.

$$CCl_4 \longrightarrow \cdot CCl_3 + \cdot Cl$$

$$CH_3Cl \longrightarrow \cdot CH_3 + \cdot Cl$$

Since free radicals are stabilized by chlorine atoms, the decomposition of carbon tetrachloride (600°C) is about 64,000 times faster than that of methyl chloride. If it is assumed that each additional α-chlorine atom increases the reactivity by about twenty-five times, radical cleavage of the carbon-chlorine bond in chloroform should be approximately $1/25$ times as fast as that in carbon tetrachloride. It has been found, however, that chloroform breaks down twenty times as fast as carbon tetrachloride, more than five hundred times faster than predicted by a free radical mechanism.

Decomposition products have been studied[14] as soon as they leave the reaction zone, in an attempt to detect any intermediates present. The gaseous product mixture was rapidly deep frozen (-190°C) to prevent dimerization of any trichloromethyl radicals to hexachloroethane, and then analysed by infrared spectroscopy. In the pyrolysis of chloroform (700-900°C), HCl, C_2Cl_4, C, $\cdot CCl_3$, C_2Cl_6, C_2Cl_2 and C_3Cl_4 were detected, whilst C_2HCl_3 and Cl_2 were also reported as being present when a glow discharge tube was used.

In an attempt to distinguish between postulated mechanisms, the pyrolysis was carried out in the presence of silver wool[14], so that any chlorine atoms formed would be removed as silver chloride. Since the production of hydrogen chloride was not affected by the presence of silver, it was thought unlikely that chlorine atoms are involved in its formation, by a mechanism such as the following.

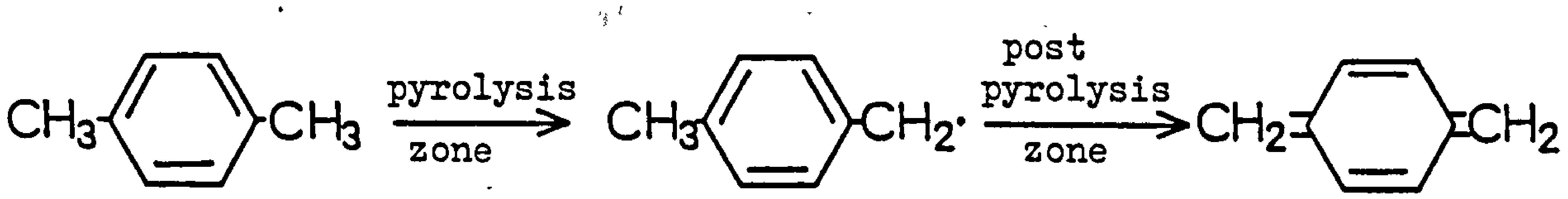
$$CHCl_3 \longrightarrow \cdot CHCl_2 + \cdot Cl$$

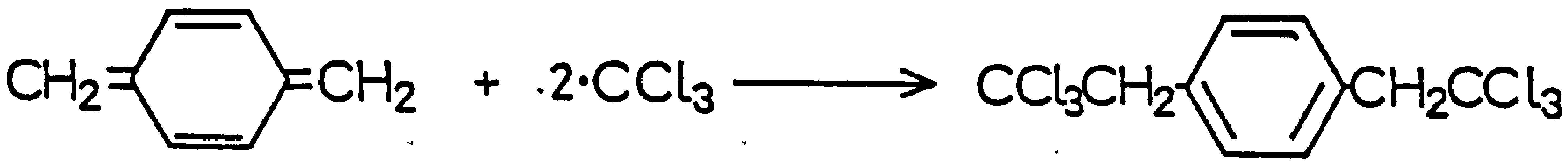
$$\cdot Cl + CHCl_3 \longrightarrow \cdot CCl_3 + HCl$$

1.I.ii. PYROLYSIS OF CHLOROFORM IN THE PRESENCE OF A SUBSTRATE

The pyrolysis of chloroform in the presence of other compounds has been studied by many people, in an attempt to gain more insight into the decomposition of chloroform on its own. In the simplest cases chloroform vapour was mixed with an organic carrier gas, such as p-xylene[6] and the reaction products studied at various distances beyond the point of mixing.

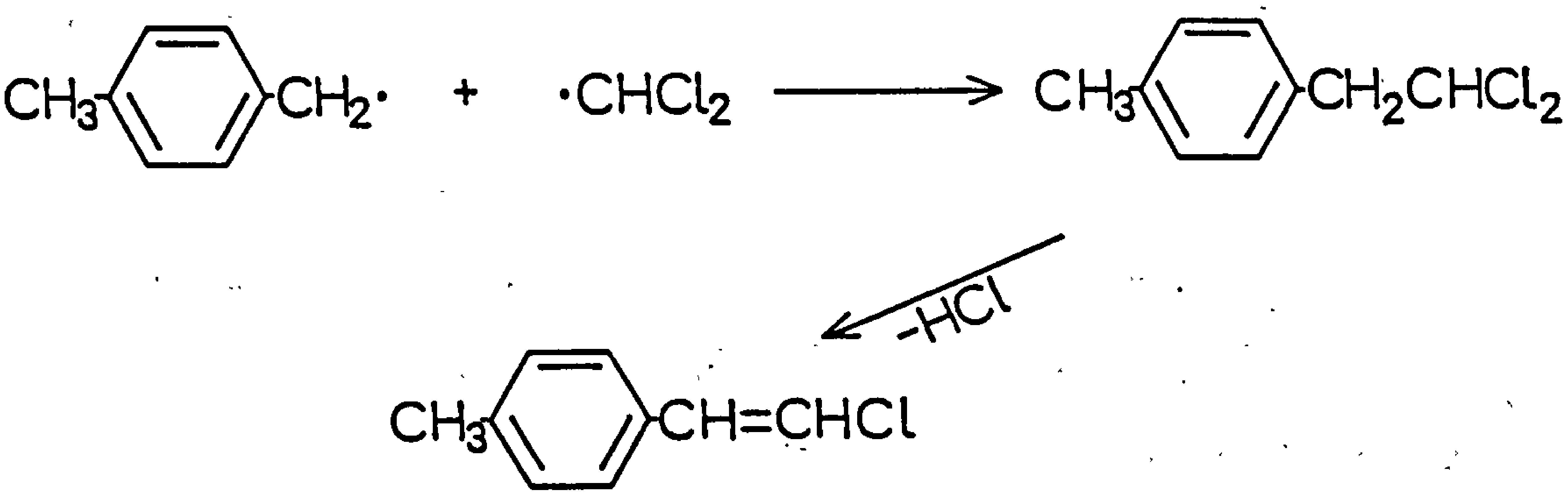
The reaction products and their distribution have been explained by a radical mechanism.



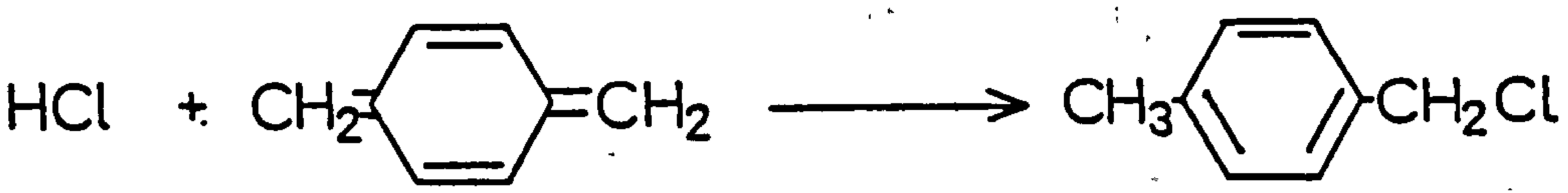


(1)

Formation of α,α'-bistrichloromethyl-p-xylene (1) by the above mechanism reached a maximum when the two pyrolysis streams were allowed to blend just beyond the furnace. When mixing occurred within the pyrolysis zone, coupling of p-methylbenzyl radicals with the mixture of radicals which might have resulted from chloroform breakdown ($\cdot Cl$, $\cdot CHCl_2$ and $\cdot CCl_3$), with subsequent loss of hydrogen chloride was thought to have taken place.



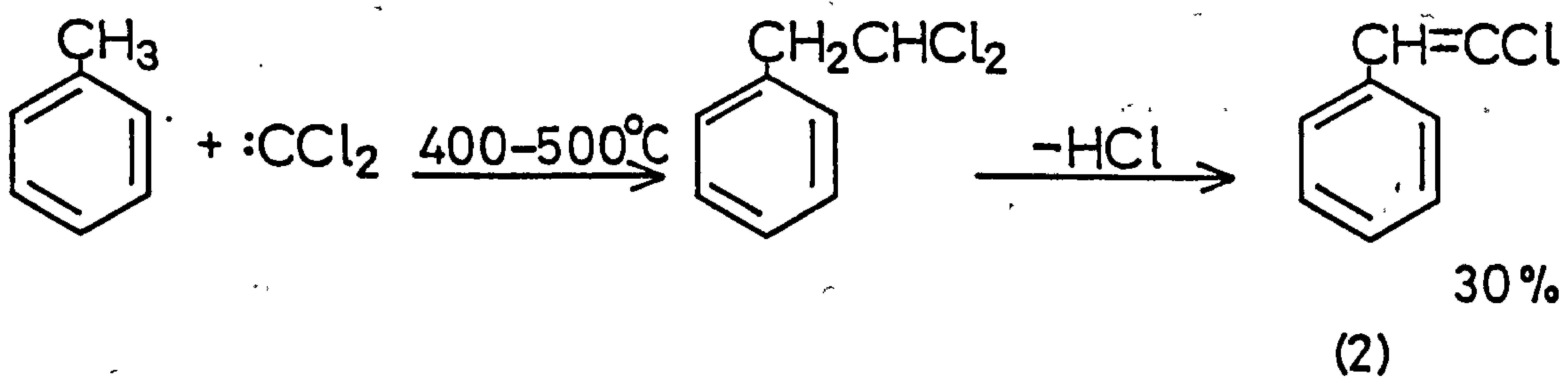
p-Methylbenzylchloride formation reached a maximum when the two streams were allowed to mix at a considerable distance from the pyrolysis zone, and was thought to involve addition of hydrogen chloride to p-xylylene. This has been shown to occur readily when the gas stream is condensed at low temperatures[15].



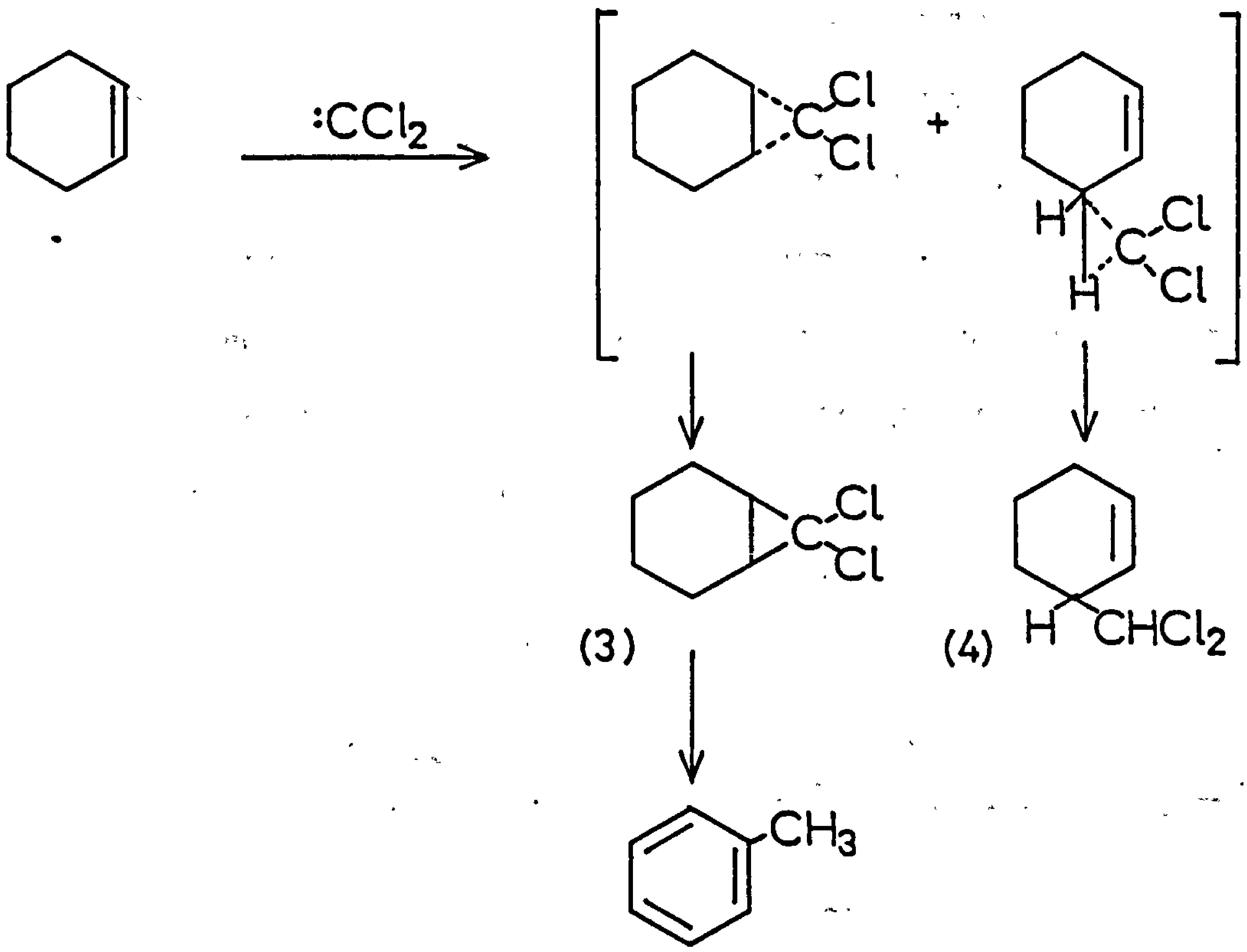
Abstraction of a hydrogen atom from chloroform by p-methylbenzyl radicals was shown to be unimportant. Addition of chloroform to a stream of pyrolysed p-xylene immediately beyond the pyrolysis zone gave poly(p-xylene) (60 %) together with expected low molecular weight products (40 %).

A radical mechanism has also been postulated[12,16,17] to explain the sensitization of n-alkane decomposition by chloroform and carbon tetrachloride. Propane and n-heptane were found to decompose under conditions where they were normally stable in the presence of chloroalkanes, the decomposition of which was also accelerated. Radicals formed from the chloroform are thought to initiate alkane radicals by abstraction of a proton, and these, once formed, can then accelerate the formation of radicals from chloroform. The products contained the expected mixture of alkenes together with considerable amounts of dichloromethane, in the case of chloroform, and chloroform, when carbon tetrachloride was used.

Formation of β-chlorostyrene (2) from the pyrolysis of chloroform in the presence of excess toluene[18] has been explained by attack of dichlorocarbene on toluene, followed by dehydrochlorination of the intermediate.



The pyrolysis of chloroform in the presence of alkenes has been studied extensively[19-26]. Kung and Bissinger[19], in 1964, proposed the formation of dichlorocarbene from chloroform, its addition to the double bond and insertion into a carbon-hydrogen bond, to give dichloronorcarane (3) and 3-dichloromethylcyclohexene (4) respectively.

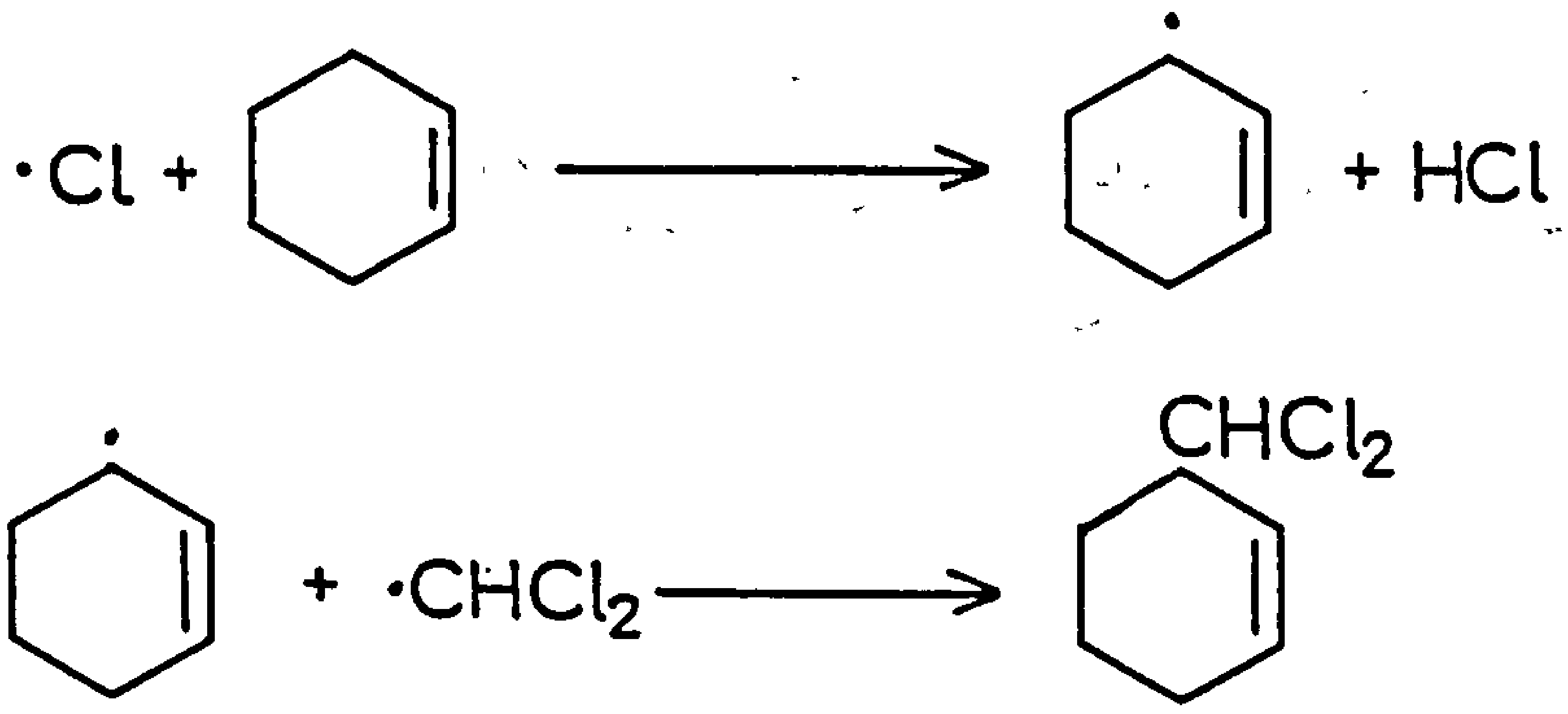


(3)

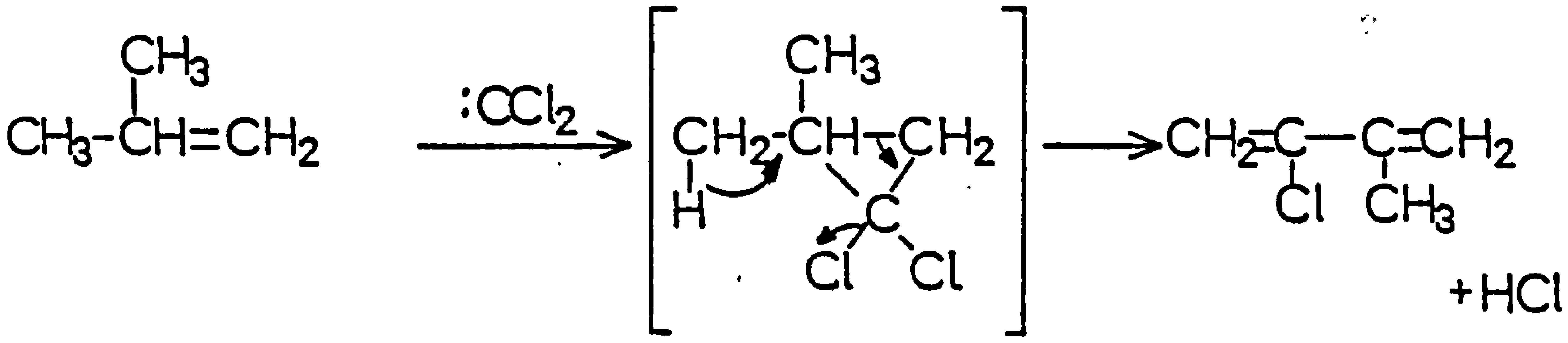
(4)

Formation of appreciable amounts of toluene[19,20] as a reaction product, appeared to support the dichlorocarbene mechanism, since it had been shown[21] that the adduct, dichloronorcarane, formed toluene when pyrolysed. A radical mechanism has also been suggested.

$$CHCl_3 \longrightarrow \cdot CHCl_2 + \cdot Cl$$

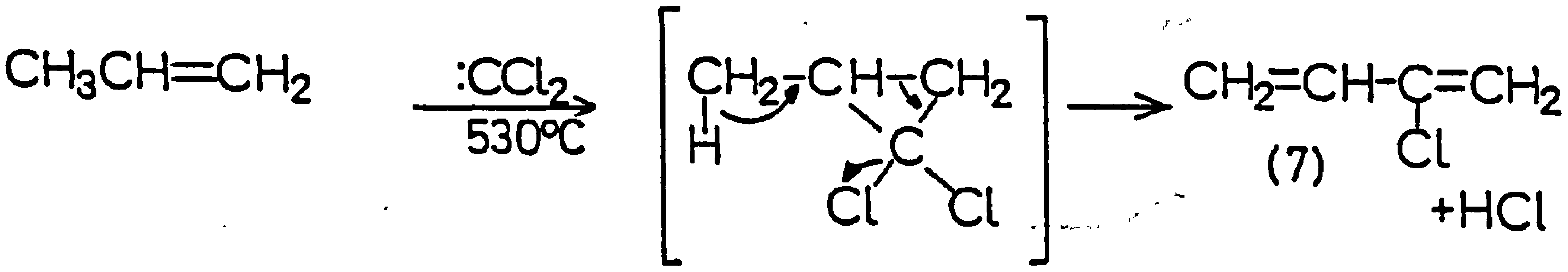


Engelsma[22,23] has studied the gas phase decomposition of chloroform (400-500°C) with various alkenes, to give chlorodienes and hydrogen chloride. Formation of dichlorocarbene, and its addition to the double bond, giving a dichlorocyclopropane adduct (5) which then rearranged to the chlorodiene (6), has been suggested as the possible mechanism. Isolation of the dichlorocylopropane intermediate[24] gave further support for the mechanism.



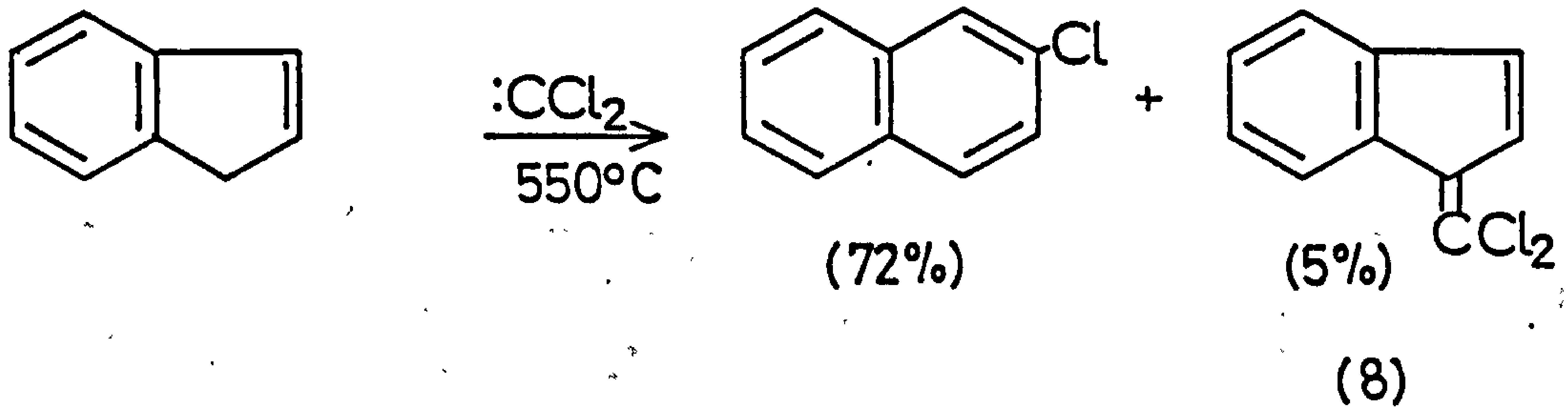
(5) (6)

Chloroprene (7) has similarly been obtained[20,22] from chloroform and propylene.

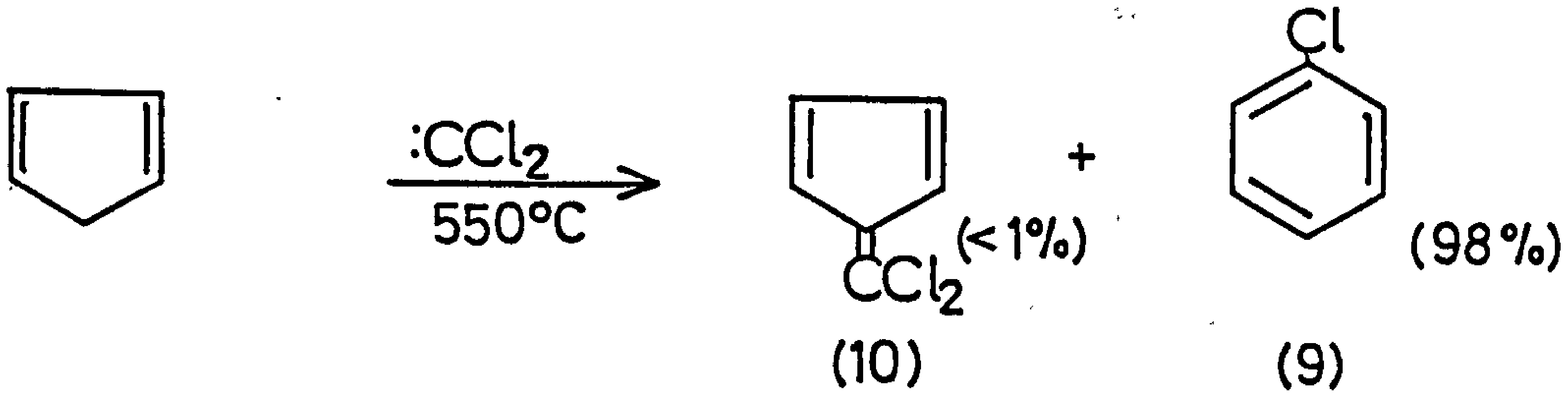


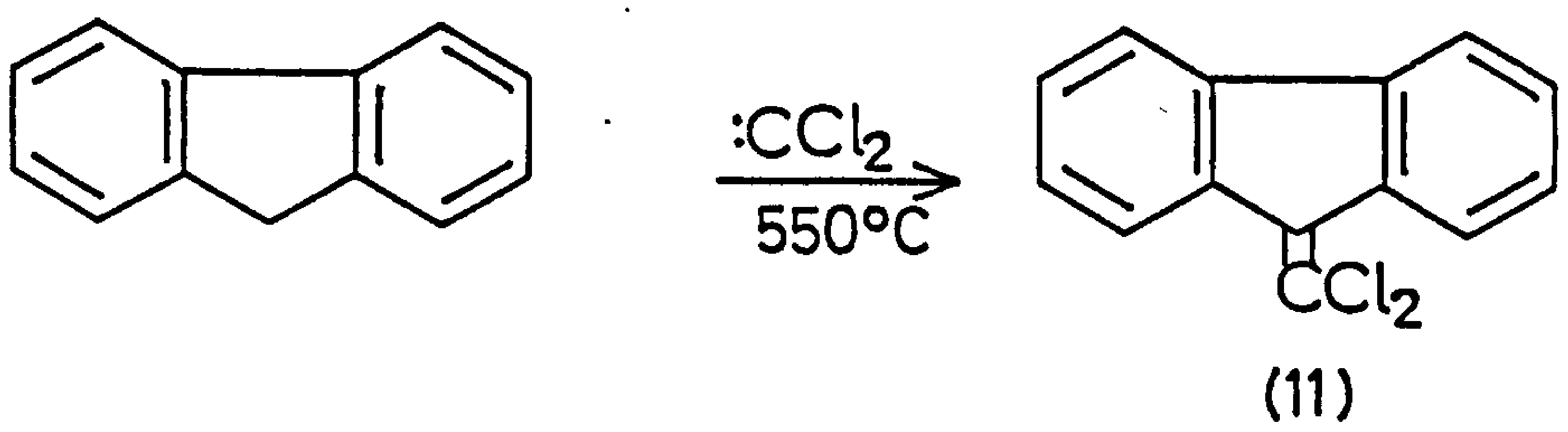
(7)

The formation of 2-chloronaphthalene from chloroform and indene[25,26] has been explained on the same basis. However, a small amount (5 %) of 1-dichloromethyleneindene (8) was also isolated, suggesting that direct insertion of dichlorocarbene into the cyclic olefin had also occurred.

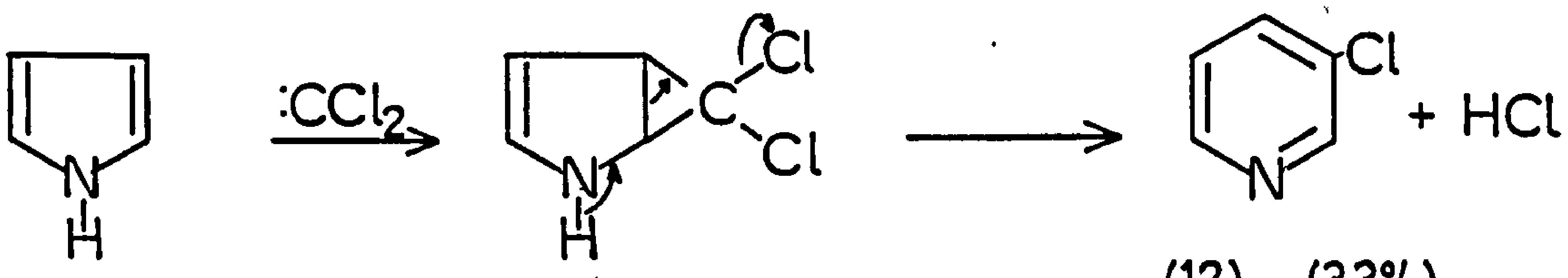


Cyclopentadiene also gave both the ring expanded (9) and direct insertion (10) products, whereas with fluorene, ring expansion cannot take place and only the direct insertion product (11) was obtained.



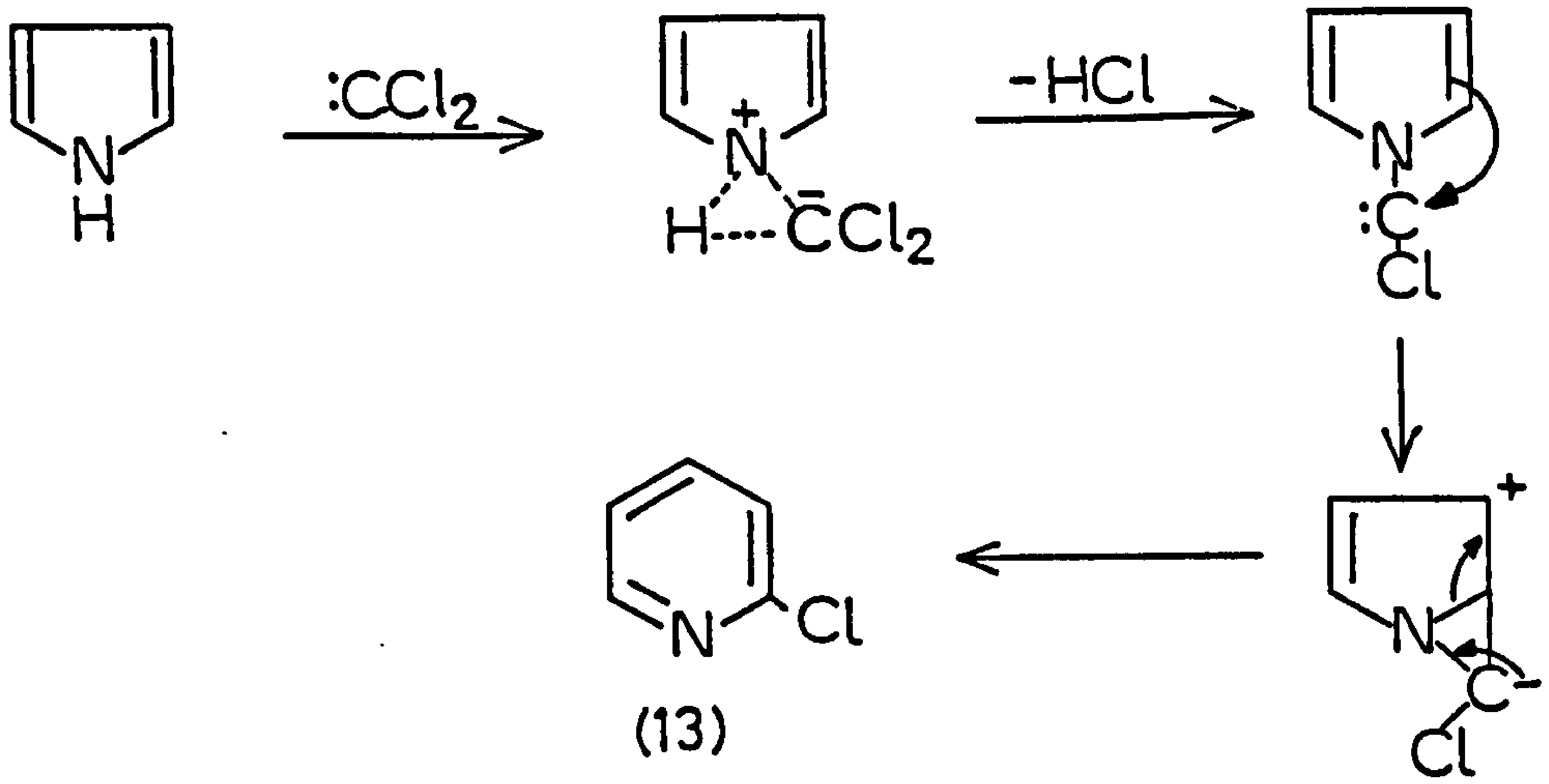


Co-pyrolysis of chloroform with heterocyclic substrates has been studied with a view to finding new synthetic routes. An improved synthesis of 3-chloropyridine (12) was achieved[27,28] by pyrolysing chloroform with pyrrole at 500-600°C. As for the reactions with cyclic alkenes, ring expansion, by addition of dichlorocarbene to the double bond, seemed a feasible mechanism.



(12) (33%)

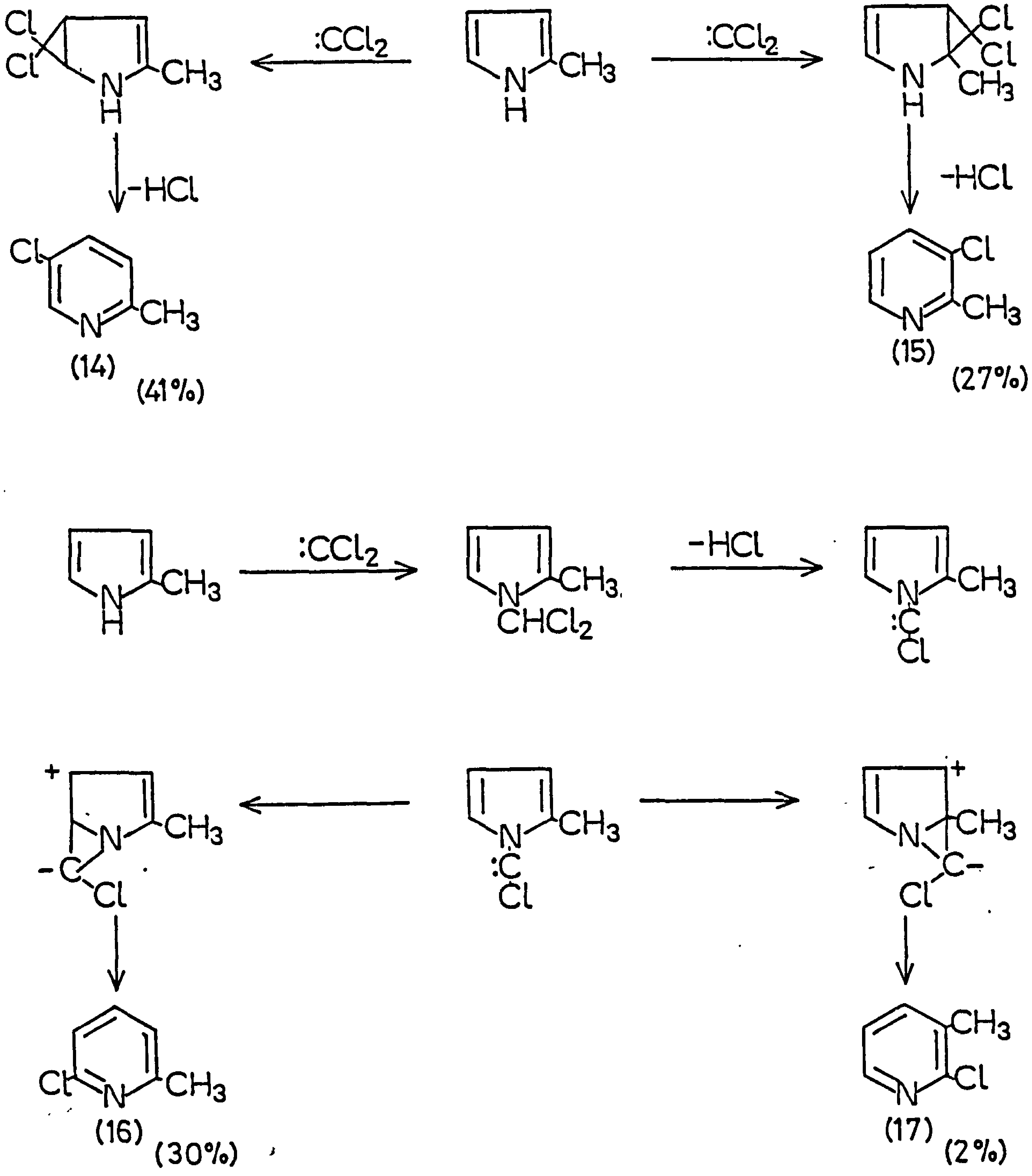
A small amount (5 %) of the 2-chloro- isomer (13) was also formed. Since this cannot be explained by the same mechanism, nor is it formed by thermal rearrangement of 3-chloropyridine, an alternative mechanism involving dichlorocarbene insertion into the N-H bond to give a three-centred transition state has been suggested[29].



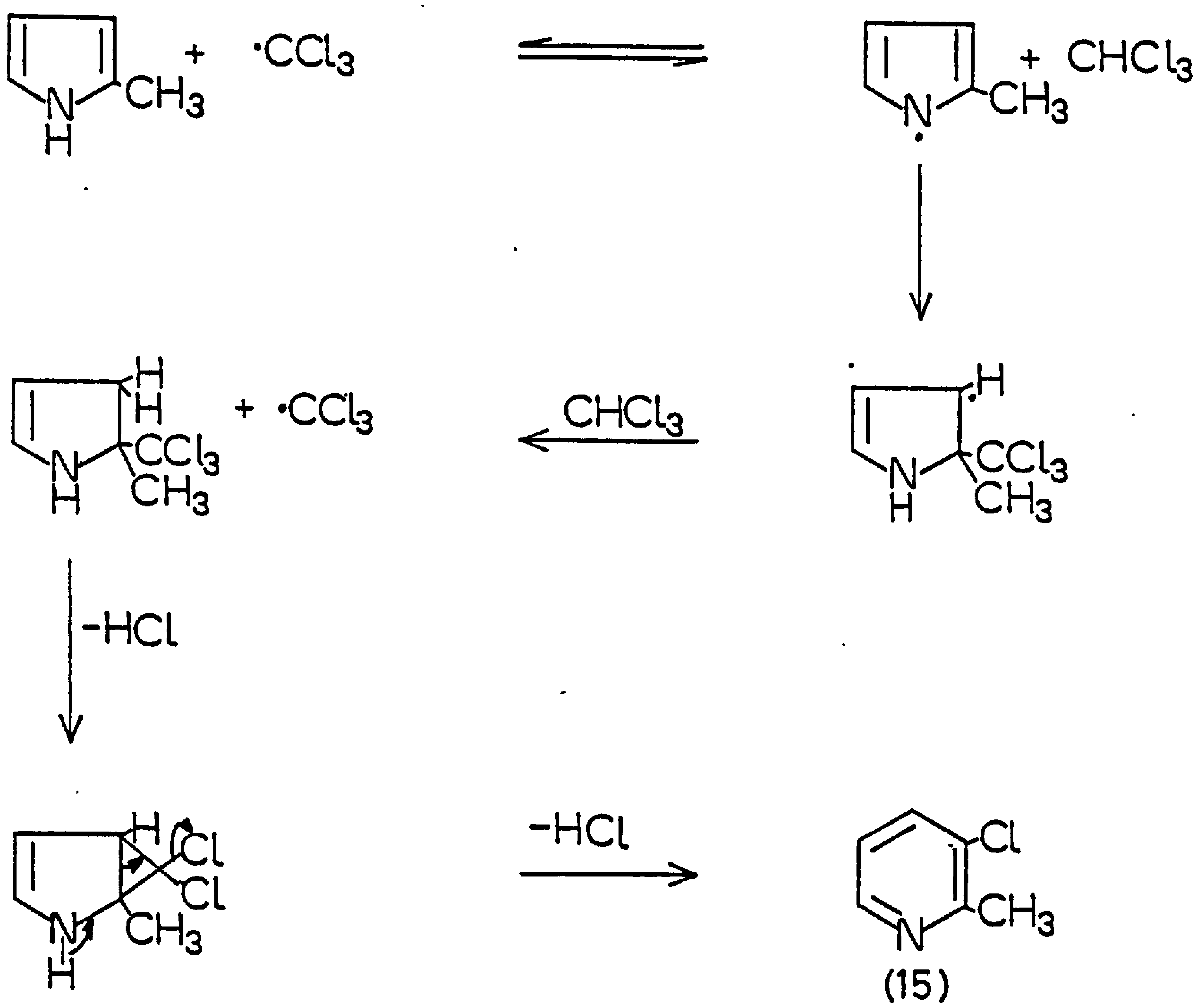
The vapour phase decomposition of methyl substituted pyrroles has been studied in great detail, both synthetically[29,30] and from a kinetic point of view[30,31], with an aim to determining the reaction mechanism.

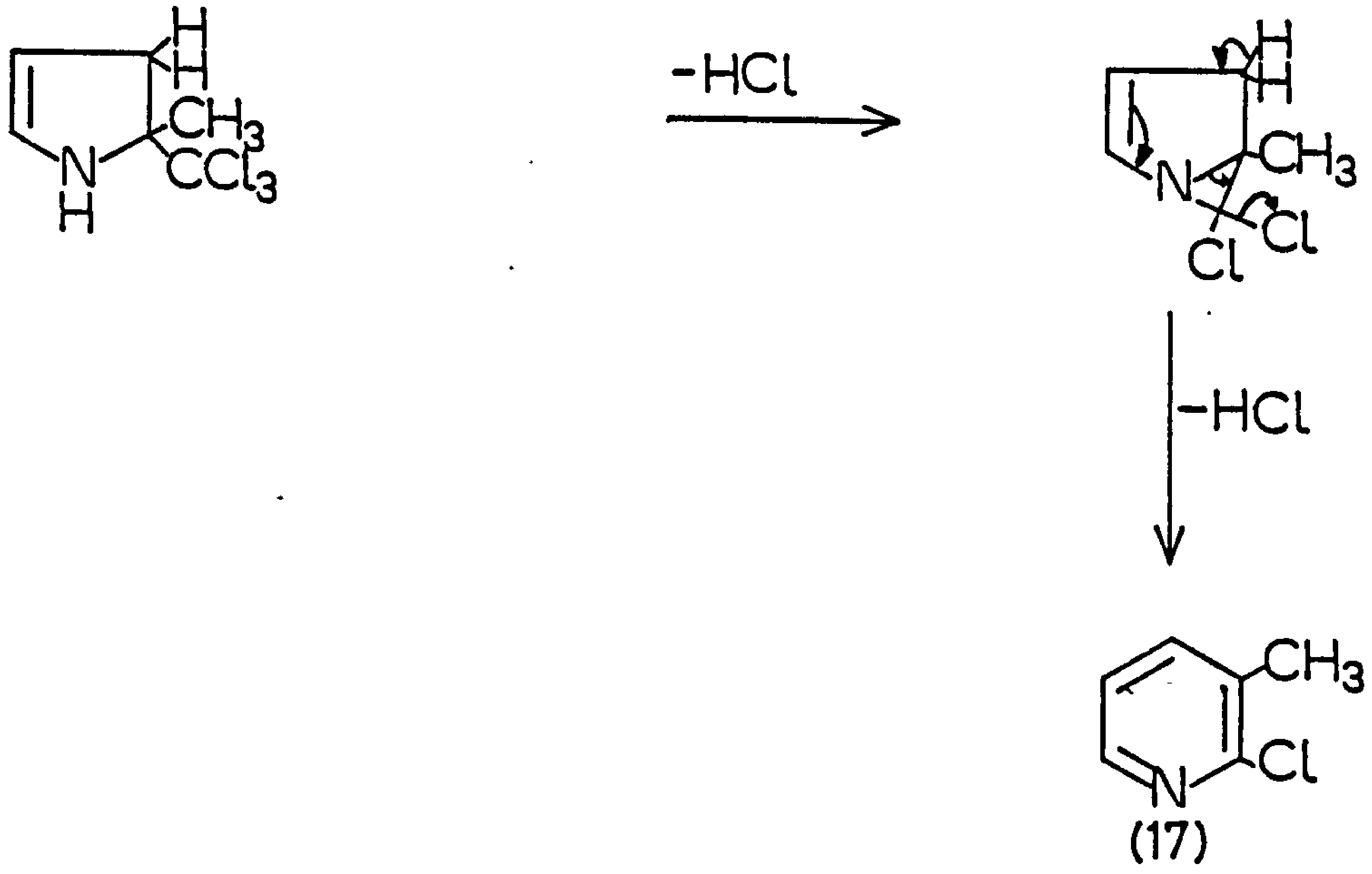
1-Methylpyrrole appeared[29] to undergo demethylation to give pyrrole, which then reacted to give 3- and 2-chloropyridines.

Methyl substituents in any other positions gave mixtures of chloropicolines (14-17), the formation of which could be explained by insertion of dichlorocarbene both into the double bonds, and into the N-H bond.



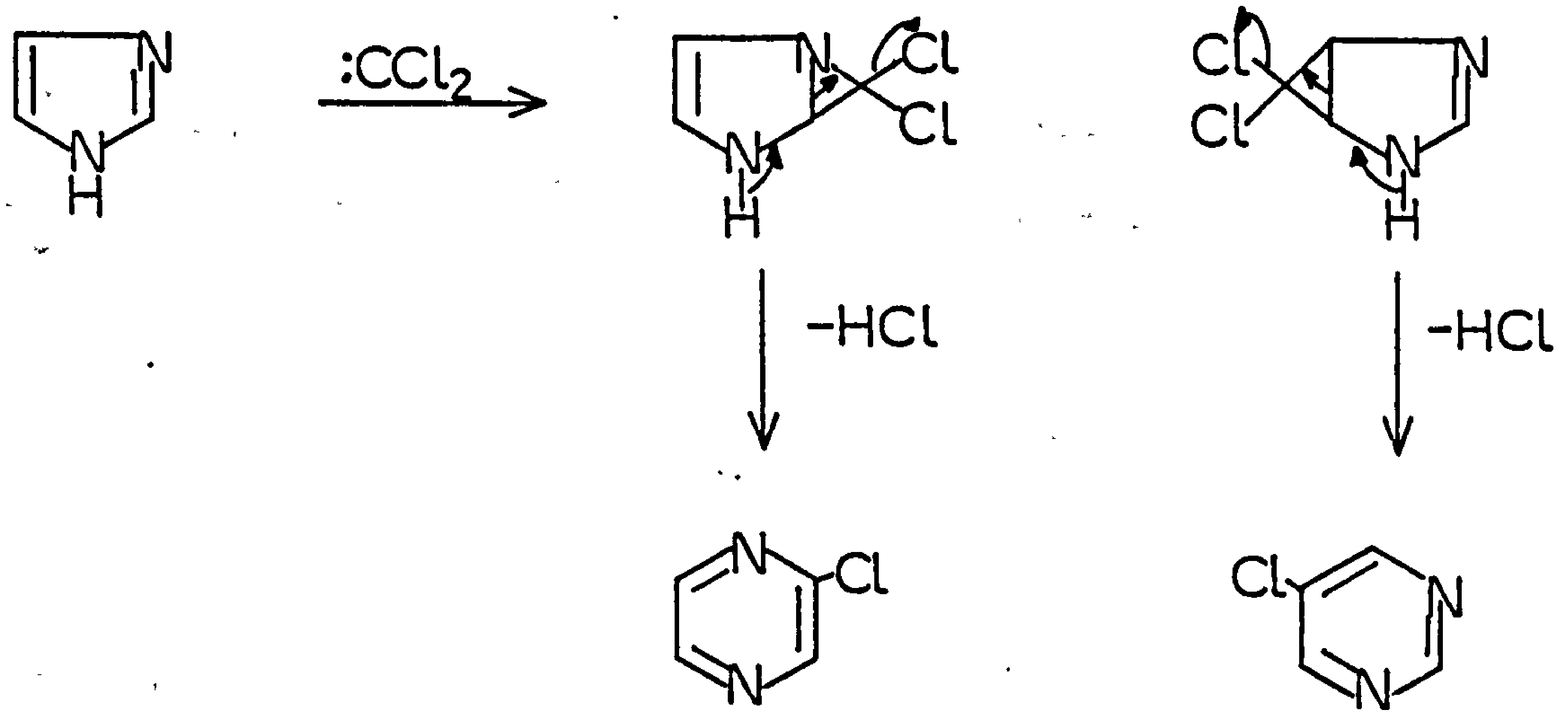
An alternative, free radical mechanism has been suggested[30].


·CCl3
CHCl3
CHCl3
·CCl3
-HCl
-HCl
(15)


-HCl
-HCl
(17)

A study[30] of the kinetics of the reaction of 2,5-dimethylpyrrole, showed the reaction to be first order with respect to the substrate. The proposed radical scheme above appeared to explain this first order dependence more satisfactorily than the hitherto accepted dichlorocarbene mechanism.

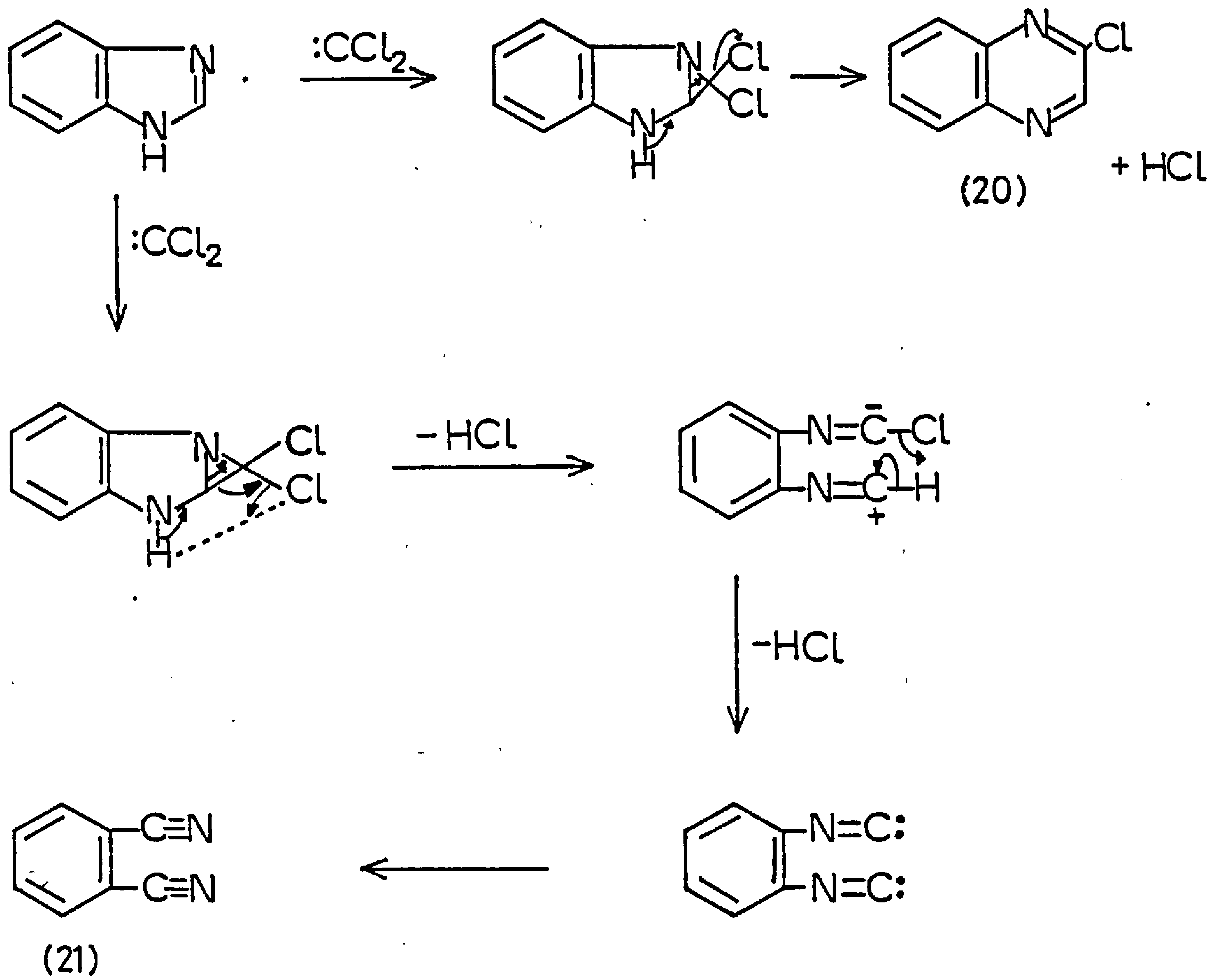
Imidazole and its derivatives were found to react in a similar manner[32], to give the ring expanded products expected. Addition of dichlorocarbene to the C=C, or C=N double bonds can be imagined to give 5-chloropyrimidine (18) and chloropyrazine (19) respectively.



(19) (10%) (18) (90%)

Results show that the C=C double bond is more susceptible to attack than the C=N double bond.

In the case of benzimidazole[33], as well as the ring expanded product: 2-chloroquinoxaline (20), a rearrangement product: phthalonitrile (21), was obtained as the major product (78 %). The formation of this compound by pyrolytic breakdown of benzimidazole alone was ruled out, and the following mechanism proposed.



Numerous other heterocyclic compounds have been reacted with chloroform in the vapour phase, and these reactions are summarized in Table 2.

TABLE 2

The pyrolysis of chloroform with heterocyclic substrates

Compound	% Yield	Products	Relative percentage	Ref.
Pyrrole	86	3-Chloropyridine	76	33
		2-Chloropyridine	24	
Indole	42	3-Chloroquinoline	95	33
		2-Chloroquinoline	3	
		Quinoline	2	
Imidazole	43	5-Chloropyrimidine	90	33
		Chloropyrazine	10	
Benzimidazole	89	Phthalonitrile	88	33
		2-Chloroquinoxaline	12	
1,7-Azaindole	10-11	3-Chloronaphthyridine	91	33
		Naphthyridine	9	
Pyrazole	80	2-Chloropyrimidine	100	34
Indazole	71	2-Chloroquinazoline	100	34
Furan		None		34
1,2,4-Triazole		None		34
Thiophene		None		34
Benzoxazole		None		34

1.II. PYROLYSIS OF OTHER CHLORINATED METHANES

1.II.i. METHYL CHLORIDE

Decomposition of methyl chloride begins at about 700°C[35], giving mainly hydrogen chloride, methane and acetylene, in the mole ratio 3 : 1 : 0.5[36]. Small amounts of hydrogen, benzene, toluene, xylene, mono- and dichlorobenzene, naphthalene, methyl-, chloro- and chloromethylnaphthalene, diphenyl, monochlorodiphenyl, anthracene and monochloroanthracene have been identified by gas liquid chromatography[35], infrared spectroscopy[35] and mass spectrometry[35,37].

The mechanism, however, appeared to be fairly simple; the formation of radicals in the initial rate determining step gave rise to large numbers of possible abstractions and recombinations which explained the variety of products obtained. The following reaction scheme has been proposed[36].

$$CH_3Cl \longrightarrow CH_3\cdot + Cl\cdot$$

$$CH_3\cdot + CH_3Cl \longrightarrow CH_4 + CH_2Cl\cdot$$

$$Cl\cdot + CH_3Cl \longrightarrow HCl + CH_2Cl\cdot$$

$$CH_2Cl\cdot + CH_3Cl \longrightarrow CH_2Cl_2 + CH_3\cdot$$

$$2CH_2Cl\cdot \longrightarrow CH_2ClCH_2Cl \xrightarrow{-HCl} CH_2CHCl \xrightarrow{-HCl} CH{\equiv}CH$$

Cyclisation of acetylene to benzene explained the formation of aromatic products[35].

Shilov and Sabirova[36] showed that the reaction was unimolecular, and by analysis of their data[38] concluded that the rate of formation of hydrogen chloride afforded a measure of the reaction rate. Unimolecular reaction rate theory was applied[38,39] in a study of the first step in the decomposition.

1.II.ii. DICHLOROMETHANE

Dichloromethane pyrolysis has been studied by many people[13,37,40-45], in an attempt to elucidate the somewhat complex kinetics. Norrish and coworkers[40] showed in 1942, that the reaction took place by a degenerate chain process, rather than by simple molecular rupture. Subsequent work showed that the reaction was preceded by a considerable induction or incubation period; that is, the time required for the reaction to attain its maximum velocity. In all cases 100 % reaction was eventually obtained, corresponding to the overall reaction

$$CH_2Cl_2 \longrightarrow C + 2HCl$$

The reaction could be followed by estimation of the hydrogen chloride formed. Both trans-dichloroethylene and nitric oxide were found to reduce the incubation period, and, in both the static and flow-through systems the reaction appeared to be catalysed by the clean quartz surface of the vessels, reverting to a slower, more reproducible rate, as the surface became covered with carbon.

Analysis by gas chromatography enabled the identification of minor products, which were found to be; methylchloride, trichloroethylene, sym-tetrachloroethane, chloroform, carbon tetrachloride, cis- and trans-dichloroethylene, and tetrachloroethylene. More recently, chlorinated derivatives of benzene, naphthalene, decalin and biphenyl have also been identified[37,41].

The presence of sym-tetrachloroethane suggested the involvement of the radical $CHCl_2\cdot$, rather than $CH_2Cl\cdot$, since products which might be formed by recombination of the latter, such as 1,2-dichloroethane or 1,1,2-trichloroethane, could not be detected in the products. Assuming this to be true, the following mechanism was proposed[40].

Primary chain

$$CH_2Cl_2 + Cl\cdot \longrightarrow HCl + CHCl_2\cdot$$

$$CH_2Cl_2 + CHCl_2\cdot \longrightarrow CHCl{=}CHCl + HCl + Cl\cdot$$

Secondary chain

$$CHCl{=}CHCl + Cl\cdot \longrightarrow C_2HCl_2\cdot + HCl$$

$$C_2HCl_2\cdot \longrightarrow (C_2HCl) + Cl\cdot$$

$$\downarrow$$

$$C_2 + HCl$$

Chain branching

$$CHCl{=}CHCl \longrightarrow C_2H_2Cl\cdot + Cl\cdot$$

$$C_2H_2Cl\cdot + CH_2Cl_2 \longrightarrow CH_3Cl + C_2HCl_2\cdot$$

Termination

$$2CHCl_2\cdot \xrightarrow{walls} CHCl_2CHCl_2 \xrightarrow{-HCl} CHCl{=}CCl_2$$

$$CHCl_2\cdot + Cl\cdot \xrightarrow{walls} CHCl_3$$

$$2Cl\cdot \xrightarrow{walls} Cl_2$$

The most important evidence for the proposed mechanism is the effect of added dichloroethylene in removing the incubation period without changing the maximum rate of reaction.

Shilov[40] has suggested that it is unlikely that 1,2-dichloroethylene could act as a chain branching agent, and that it may have been chloroacetylene, formed from the breakdown of dichloroethylene, which was responsible.

Sensitization of the reaction by nitric oxide was explained by a direct reaction with dichloromethane.

$$NO + CH_2Cl_2 \longrightarrow NOCl + CH_2Cl\cdot$$

An investigation of the reaction by Vacherot, Niclause and Dzierzynski[42,43] confirmed the overall reaction to give carbon and hydrogen chloride, but disputed the mechanism proposed by Norrish and coworkers to explain it. In particular, the involvement of 1,2-dichloroethylene as the chain branching intermediate was questioned, since they found neither this compound, nor the precursor, sym-tetrachloroethane amongst the products. The solid deposit obtained was shown to be carbon containing neighbouring hydrogen and chlorine atoms, which tended to be lost as hydrogen chloride, as the reaction proceeded.

The reaction products were described, in general, as polymers, which progressively lost hydrogen chloride until only carbon was left, in the form C_n, rather than C_2, as previously suggested[40].

Initiation

$$CH_2Cl_2 \longrightarrow CH_2Cl\cdot + Cl\cdot$$

or, alternatively

$$CH_2Cl_2 \longrightarrow HCl + :CClH$$

$$:CHCl + CH_2Cl_2 \longrightarrow \cdot CH_2Cl + \cdot C(HCl)Cl$$

Propagation

$$\cdot CH_2Cl + CH_2Cl_2 \longrightarrow CH_3Cl + \cdot C(HCl)Cl$$

Chain reaction

$$\cdot Cl + CH_2Cl_2 \longrightarrow HCl + \cdot C(HCl)Cl$$

$$\cdot C(HCl)Cl + CH_2Cl_2 \longrightarrow HCl + \cdot C_2(HCl)_2Cl$$

Overall

$$\cdot C_{i-1}(HCl)_{i-1}Cl + CH_2Cl_2 \longrightarrow HCl + C_i(HCl)_iCl$$

Termination

$$\cdot C_p(HCl)_pCl + \cdot C_q(HCl)_qCl \longrightarrow C_n(HCl)_nCl_2$$

$$\text{or } C_n(HCl)_{n-1}Cl_2 + HCl$$

for $p = 1$, $q = 0$ or $q = 1$, this gave the reaction products observed.

also

$$\cdot C_n(HCl)_nCl \longrightarrow C_n(HCl)_n + \cdot Cl$$

although this is not strictly a termination step, since $\cdot Cl$ may restart the chain.

Chloroform and hexachloroethane were found to inhibit the reaction, possibly due to blocking of the reaction sites, or, reaction with radicals formed during the reaction, to give less reactive radicals.

Early work had shown[40,42,43] that the surface of the reaction vessel was catalytically involved in the reaction, notably in the initiation and termination steps, but its exact role has only recently been fully investigated[44,45]. It has now been shown[44], that increasing the surface to volume ratio (s/v) resulted in a linear increase in the maximum reaction rate, and that a high s/v resulted in the disappearance (or reduction to an undetectable level), of the induction period.

The activation energy (31 Kcal.mol.$^{-1}$) was found to be practically independent of s/v at very high values of this parameter ($s/v > 100$-$120\ cm^{-1}$). At s/v greater than 150 cm^{-1}, the reaction was first order, whilst decreasing the ratio resulted in an increase in the order to a maximum value of 2 ($s/v = 0.6$-$0.7\ cm^{-1}$). Decomposition did not go to completion, and termination was found to occur earlier at high surface to volume ratios as would be expected if termination involves the walls of the reactor.

Initiation by formation of a biradical, :CHCl, rather than a monoradical: $\cdot CH_2Cl$, was supported, since the energy of activation (62.5 Kcal.mol.$^{-1}$) was in closer agreement with that required for biradical formation (66.5 Kcal.mol.$^{-1}$), than with the energy required to cleave the C-Cl bond (78.5 Kcal.mol.$^{-1}$). Catalysis by the wall of the vessel lowered the observed value from that which was predicted.

Hence:

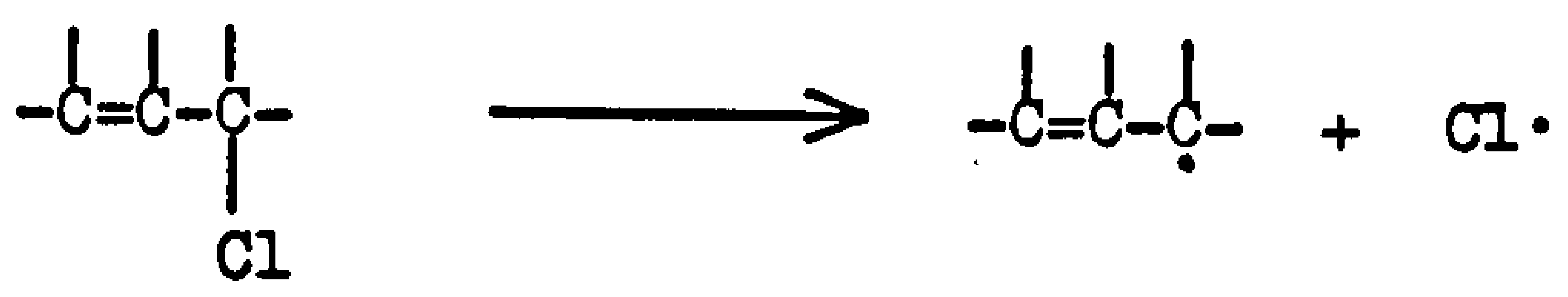
$$CH_2Cl_2 \longrightarrow :CHCl + HCl$$

$$:CHCl + CH_2Cl_2 \longrightarrow \cdot CH_2Cl + \cdot CHCl_2$$

Propagation continues in a similar manner to that previously suggested[40], the $\cdot CH_2Cl$ radical giving rise to analogous reactions.

The growth of polymeric chains was also suggested. This could be interrupted by deactivating impact with the surface, by collision with another growing chain, or by chain transfer to give a nonradical, which was strongly absorbed on the walls. Subsequent heterogeneous loss of hydrogen chloride has been shown[46] to occur rapidly.

Chain branching was thought[44] to take place more readily after dehydrohalogenation, because of lower stability of hydrogen atoms β to the unsaturated bond. Homolytic cleavage of the carbon-chlorine bond resulted in the formation of two new radicals, and it was suggested that this process was mainly responsible for chain branching.



$$-\overset{|}{C}=\overset{|}{C}-\underset{Cl}{\overset{|}{C}}- \longrightarrow -\overset{|}{C}=\overset{|}{C}-\underset{\bullet}{\overset{|}{C}}- + Cl\cdot$$

Termination occurred when a fairly stable, graphitic type structure was obtained on the surface. Such a structure could not supply new radicals for chain branching, strongly absorbed radicals already formed, and also decreased the catalytic action of the surface, with regard to the formation of new radicals. To test the inhibiting effect of this type of structure, the reaction vessel was soaked in a solution of

2-butene-1,4-diol, dried at 500°C, and the pyrolysis of dichloromethane carried out in the usual manner. The decomposition was strongly inhibited.

A continuation of this work[45], showed that the reaction was enhanced by metal surfaces. However, rapid corrosion of the surface resulted from attack by hydrogen chloride, and this inhibited the reaction.

1.II.iii. CARBON TETRACHLORIDE

The thermal decomposition of carbon tetrachloride commences at about 580°C, and is thought to involve a radical mechanism[13,14,16,47-53]. Tetrachloroethylene, hexachloroethane, chlorine and carbon were shown to be the main products, although, hexachlorobenzene[47-50], dichloroacetylene[51] and hexachlorobutadiene[47] have also been identified in small amounts. The relative amounts of products formed, has been shown to depend on the temperature of the reaction[49,50,54,55]. At temperatures below 600°C hexachloroethane was obtained as the major product, whilst at 700°C tetrachloroethylene was obtained in highest yield, and above this hexachlorobenzene[49,50,54]. From an industrial point of view the temperature is very important if maximum yields of tetrachloroethylene are required[47,52], and it has been shown[53] that this varies from 43 % at 900-1,000°C, to 80 % at 1,300-1,400°C.

Again, dichlorocarbene has been suggested as an intermediate[54,56,57]. Schmeiser and Schröter[56] claimed to have isolated this species, which they identified by analysis and molecular weight. In a subsequent paper[57], however, they reported that the existence of dichlorocarbene could not be shown. Blanchard and LeGoff[58] also claimed to have identified the diradical by the large increase in the intensity of the CCl_2^+ peak, observed when they studied the reaction by mass spectrometry. The concentration of trichloromethyl radicals on the other hand, was insignificantly small.

The following mechanism has been suggested[51], in which tetrachloroethylene is formed from the dechlorination of hexachloroethane, rather than the dimerization of dichlorocarbene.

$$CCl_4 \longrightarrow \cdot CCl_3 + \cdot Cl$$

$$2CCl_3\cdot \longrightarrow C_2Cl_6$$

$$C_2Cl_6 \xrightarrow{-Cl_2} Cl_2C{=}CCl_2 \xrightarrow{-Cl_2} ClC{\equiv}CCl$$

No direct evidence was found[59] for the presence of hexachloroethane as a precursor to tetrachloroethylene, and it was suggested that the compound was held on the surface where dechlorination occurred. Further dechlorination afforded dichloroacetylene, which could then trimerize to hexachlorobenzene[59].

1.III. PYROLYSIS OF CHLORINATED ETHANES AND ETHYLENES

Chlorinated ethanes and ethylenes are the major products in the pyrolytic decomposition of chloroform, and, since their rate of decomposition is fast relative to that of chloroform, the secondary pyrolysis of these compounds, which is summarised below, must be considered.

TABLE 3

Pyrolysis of various chlorinated ethanes/ethylenes at 500°C. [4]

Compound	Major products	Relative rate
Pentachloroethane	HCl, C_2Cl_4	fast
sym-Tetrachloroethane	HCl, C_2Cl_3H	very fast
Hexachloroethane	Cl_2, C_2Cl_4	fast
Dichloromethane	HCl, C_2ClH_3, C_2Cl_3H	very slow
Tetrachloroethylene	None	—
1,1,2-Trichloroethane	HCl, cis & trans-$C_2Cl_2H_2$, CH_2CCl_2	very fast
1,2-Dichloroethane	HCl, C_2ClH_3	very fast
Trichloroethylene	HCl, hexachlorobenzene	very fast

As a result of their very comprehensive study of the dehydrochlorination of chlorinated hydrocarbons, Barton and Onyon[60] were able to postulate a general mechanism. They had established three general mechanisms; 1) heterogeneous decomposition on glass surfaces, 2) homogeneous first order unimolecular decomposition, and 3) homogeneous first order decomposition by radical chains. They predicted that a chloro-compound would decompose by a radical chain mechanism only so long as neither the compound itself, nor the reaction products, are chain inhibitors.

The radical chain mechanism was characterized by four steps.

a) Initiating step(s) which are kinetically first order leading to the production of chlorine atoms.

b) First propagation step involving attack of a chlorine atom on the substrate with abstraction of a hydrogen atom and formation of a "large" chlorine-containing radical.

c) Decomposition of the "large" radical to give the olefin or chloro-olefin and a further chlorine atom which can participate again in step b).

d) Terminating step comprising the attack of a chlorine atom on the "large" radical to give non radical products. The stoichiometry of the reaction was explained by steps b) and c), the observed first order kinetics by step d). Inhibitors were thought to suppress the reaction by interference in steps b) and c).

Chlorinated ethanes have, in fact, been shown to decompose by the mechanisms predicted. All except chloroethane and 1,1-dichloroethane react by a radical chain mechanism, although in the case of

1,1,1-trichloroethane two mechanisms are thought to operate simultaneously.

Chloroethane has been shown to decompose to ethylene and hydrogen chloride, by a simple homogeneous, first order reaction[61-63], the predicted activation energy of which, agreed well with the experimentally determined value. Packing the vessel had no effect on the reaction, nor did the addition of propylene or cyclohexene[64], known for their ability to inhibit radical chain reactions. This, together with the absence of any induction period, made the possibility of a radical chain reaction unlikely. The following mechanism was therefore proposed[61].

$$C_2H_5Cl \longrightarrow C_2H_5\cdot + Cl\cdot$$

$$Cl\cdot + C_2H_5Cl \longrightarrow HCl + C_2H_4Cl\cdot$$

$$C_2H_5\cdot + C_2H_4Cl\cdot \longrightarrow C_2H_5Cl + C_2H_4$$

Attack by a chlorine atom on chloroethane gives the 1-chloroethyl radical as opposed to the 2-chloroethyl radical, as demonstrated by the formation of 1,1-dichloroethane by radical chlorination of chloroethane in the gas phase[65].

$$Cl\cdot + CH_3CH_2Cl \xrightarrow{-HCl} CH_3CHCl\cdot \xrightarrow{Cl_2} CH_3CHCl_2 + Cl\cdot$$

Since formation of a stable olefin, by removal of a chlorine atom, may only occur if it is accompanied by migration of a hydrogen atom, it can readily be understood why chloroethane may act as an inhibitor for its own radical chain. Decomposition, therefore, occurs by a unimolecular reaction, in accordance with Barton and Onyon's theory[60].

A study[66] of the transition state in the initiation step, showed that moderate lengthening of the C-Cl bond had occurred, but that there was little motion of the chlorine atom.

The dichloroethanes lost hydrogen chloride to give mainly vinyl chloride, together with traces of acetylene which was shown to have been formed by dehydrochlorination of the vinyl chloride[61]. In the case of 1,1-dichloroethane the first order reaction was nearly homogeneous[61,67], packing the reaction vessel increased the rate only slightly.

1,2-Dichloroethane differed from its isomer in that its decomposition exhibited an induction period, which was explained as the time required to build up a steady state concentration of the chain carrying species[68]. The reaction was powerfully inhibited by propylene; the inhibited reaction remaining first order and having the same activation energy (47 Kcal.mol.$^{-1}$),as the uninhibited reaction. It was therefore, suggested that the reaction involved a radical chain mechanism, which could be readily induced by traces of oxygen or chlorine[70].

Inhibition was shown to depend only on the concentration of propylene, not on the initial pressure of dichloroethane, suggesting that a chain carrying species, such as $C_2H_4Cl\cdot$,which was not involved in direct reaction with dichloroethane, was being destroyed.

$$C_2H_3Cl_2^{\cdot} + CH_3CH{=}CH_2 \longrightarrow CHCl{=}CH_2 + HCl + {\cdot}CH_2CH{=}CH_2$$

On this basis the following mechanism was postulated[69]

$$CH_2ClCH_2Cl \longrightarrow C_2H_4 + Cl_2$$

$$Cl_2 + C_2H_4Cl_2 \longrightarrow Cl\cdot + HCl + C_2H_3Cl_2\cdot$$

$$Cl\cdot + C_2H_4Cl\cdot \longrightarrow HCl + C_2H_3Cl_2\cdot \longrightarrow CHCl{=}CH_2 + Cl\cdot$$

$$Cl\cdot + C_2H_4Cl\cdot \longrightarrow HCl + C_2H_3Cl$$

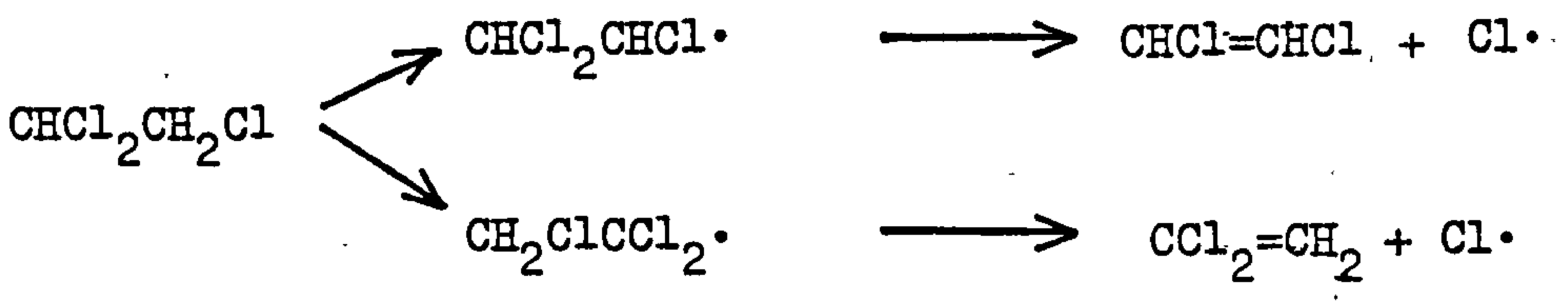
The effect of the vessel walls has been investigated[69-74], since it was shown that packing the vessel inhibited the reaction, as did decreasing the diameter of the reaction vessel[70]. Similarly, the reaction rate was greater on a clean surface, probably because chain initiation occurred more readily, and this variation was thought[73] to account for discrepancies between the results from various studies of this reaction[75].

A calorimetric investigation[71-72] showed that the reaction occurred mainly in the bulk of the gas, but that chain initiation and inhibition occurred on the vessel walls. This explained how it was possible for very low concentrations of propylene to have a strongly inhibiting effect, but that as the concentration was increased a limit was reached, beyond which the rate was barely effected.

The fact that the two dichloroethane isomers react by different mechanisms, may be explained by considering the radicals involved. Chlorine atom attack on 1,1- and 1,2-dichloroethane gives 1,1- and 1,2-dichloroethyl radicals respectively. The latter may lose a chlorine atom to form a stable olefin, whereas the former cannot, and hence, unlike 1,2-dichloroethane, 1,1-dichloroethane does not decompose by a radical chain mechanism.

In all of the following reactions, decomposition by a radical chain mechanism may be similarly explained.

1,1,2-Trichloroethane decomposed by a first order radical chain mechanism[76] which exhibited a temperature dependent induction period.



$$CHCl_2CH_2Cl \begin{cases} \nearrow CHCl_2CHCl\cdot \longrightarrow CHCl{=}CHCl + Cl\cdot \\ \searrow CH_2ClCCl_2\cdot \longrightarrow CCl_2{=}CH_2 + Cl\cdot \end{cases}$$

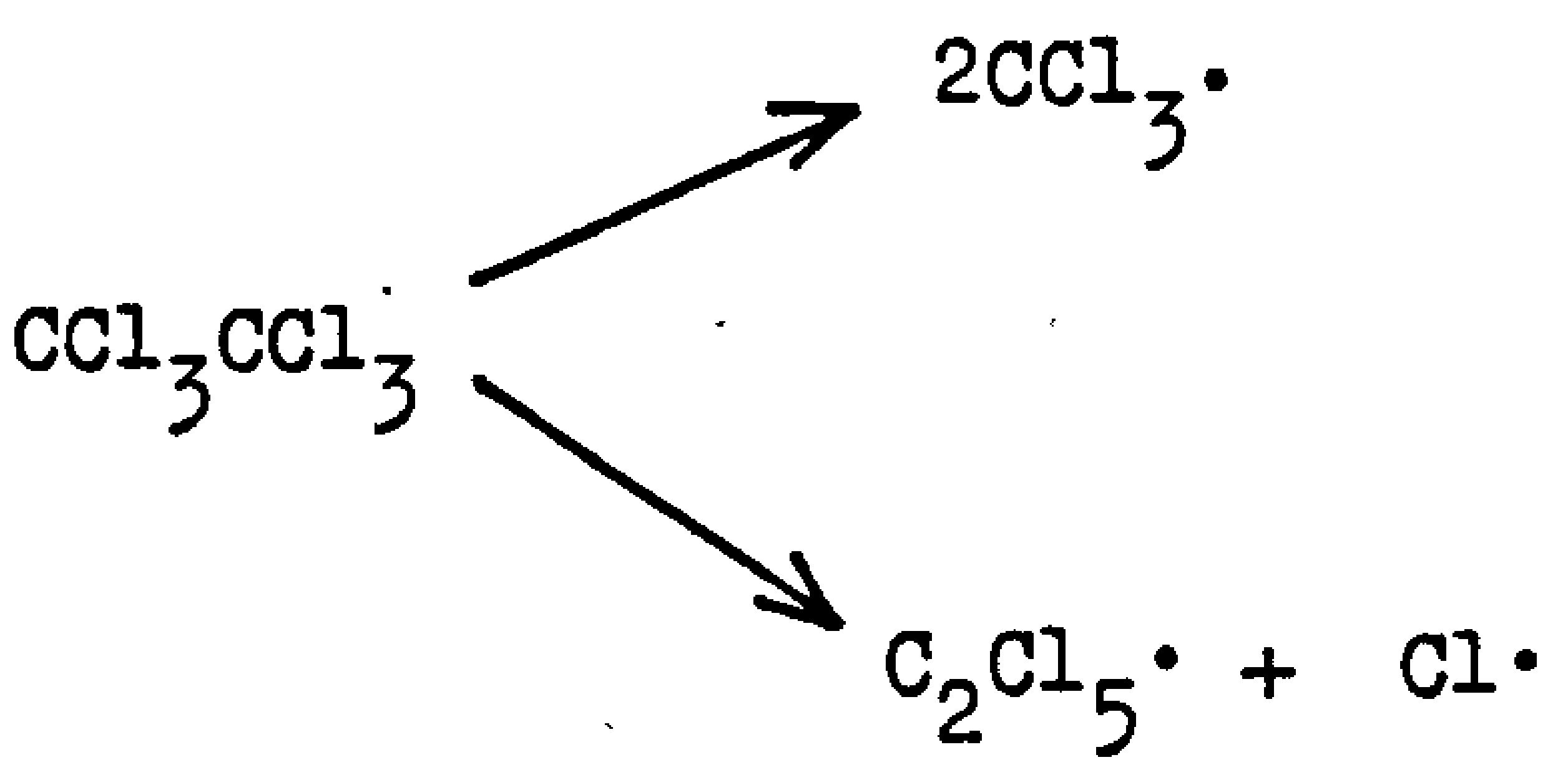
The breakdown of 1,1,1-trichloroethane on the other hand appeared to involve two simultaneous mechanism[77], one of which was suppressible by the addition of propylene, and thought to be a radical chain mechanism analogous to that given for 1,1,2-dichloroethane. The reaction obeyed first order kinetics only during the initial stages, possibly due to partial inhibition by vinylidene dichloride formed in the reaction. Packing the reactor decreased the reaction rate, suggesting heterogeneity. The second mechanism operating was first order, had no induction period, and appeared to be substantially homogeneous. Elimination of a second molecule of hydrogen chloride from the products, to give chloroacetylene, was not observed[78].

Thermal decomposition of both 1,1,2,2- and 1,1,1,2-tetrachloroethane took place by a homogeneous, first order reaction[68], to give trichloroethylene and hydrogen chloride. A temperature dependent induction period was observed which was proportionately prolonged by the addition of propylene, but unaffected by packing the reactor. Thus, it would appear that a radical chain mechanism was operating in the bulk of the gas, rather than on the surface of the vessel.

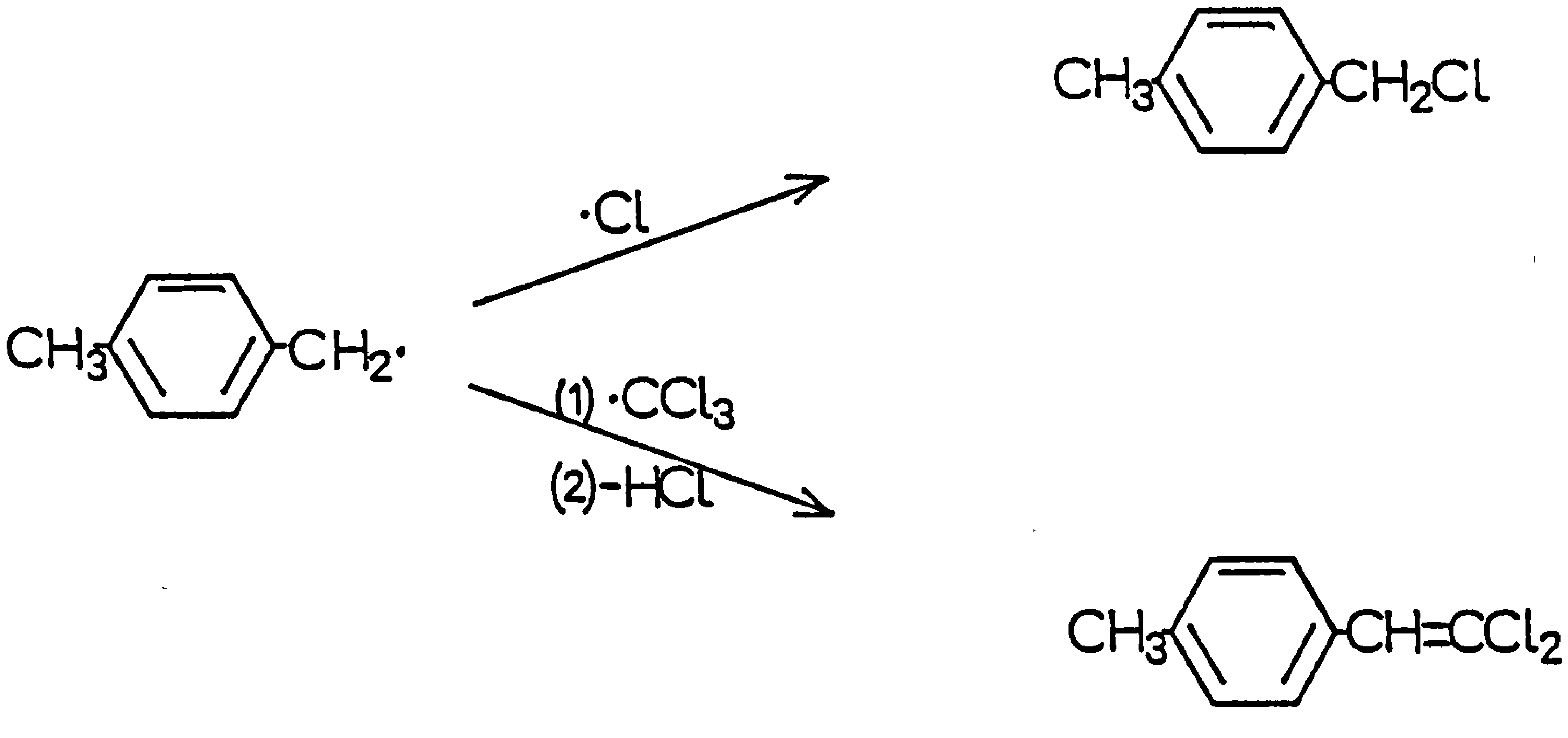
The pyrolysis of pentachloroethane was found[70,79] to involve a first order, radical chain mechanism, initiated by rupture of the carbon-chlorine bond. Tetrachloroethylene and hydrogen chloride were the major products, and, of the minor products, trichloroethylene inhibited the reaction, whilst chlorine acted as a catalyst.

The pyrolysis of hexachloroethane was studied by Faraday[80] in 1821. It was shown that tetrachloroethylene could be produced by passing hexachloroethane through a heated tube containing porcelain chips. Other reaction products are carbon tetrachloride and chlorine.

The reaction has since been shown[81,82] to proceed by a radical chain mechanism which was autocatalysed by chlorine, - the chlorine once formed acted as the main source of chain centres. Dainton[82] was unable to distinguish between cleavage of the carbon-carbon bond or a carbon-chlorine bond during initial radical formation, although calculated bond energies (63 and 68 Kcal. respectively)[83], suggested that the former was more feasible.



Co-pyrolysis of hexachloroethane and p-xylene[83] gave mainly β,β-dichloro-p-methylstyrene (22), the formation of which was explained by the addition of a $CCl_3\cdot$ radical to the p-xylene radical, whereas addition of chlorine atoms would have given rise to p-methylbenzyl chloride.



(22)

This corroborated cleavage of the hexachloroethane carbon-carbon bond in the initiation stage of the reaction.

The pyrolysis of chlorinated ethylenes was somewhat more complex than that of the ethanes. Vinyl chloride decomposed between 551-618°C, to give hydrogen chloride, ethylene, acetylene and methane[84]. The order of the reaction was 1.5 at time zero, increasing to 2.0 as the reaction proceeded.

A study of the thermal decomposition of 1,2-dichloroethylene[85], revealed a non-integral order of reaction, which changed from 1.5 in a packed vessel, to 1.0-1.5 in an empty vessel. Inhibition of the reaction by addition of propylene, n-hexane or n-pentane resulted in a first order reaction[86]. The following scheme appeared to explain the results obtained.

$$M + C_2H_2Cl_2 \longrightarrow M + C_2H_2Cl\cdot + Cl\cdot$$

$$Cl\cdot + C_2H_2Cl_2 \longrightarrow HCl + C_2HCl_2\cdot$$

$$C_2HCl_2\cdot + S \longrightarrow Cl\cdot + C_2HCl + S$$

$$M + C_2H_2Cl\cdot + Cl\cdot \longrightarrow M + C_2H_2Cl_2$$

where, M is any molecular species capable of transferring energy, and S is the surface area. The theoretical rate equation, derived under steady state conditions, predicted an order of 1.5 when S was large, and first order when S was small.

Trichloroethylene decomposed by a radical-chain mechanism to give hydrogen chloride and hexachlorobenzene in theoretical yield[87] The bimolecular reaction appeared to be inhibited by one of the products, and, since the effect did not decrease with time, hexachlorobenzene was thought to be responsible. The induction period was pressure dependent which suggested bimolecular chain initiation.

Dichloroacetylene and chlorine were the major products from the vapour phase decomposition of tetrachloroethylene[14,59,84], although hexachloroethane[14] and hexachlorobenzene[84] have also been reported. Hexachloroethane[14] was probably formed by chlorination of tetrachloroethylene, and hexachlorobenzene either from three tetrachloroethylene molecules with loss of chlorine, or by trimerization of dichloroacetylene.

Dechlorination was thought to occur on the surface of the reactor, since free chlorine could not be detected as a product when the reaction was studied by mass spectrometry[59].

$$C_2Cl_4\ (g) + C_{surface} \longrightarrow C_2Cl_2\ (g) + 2Cl(C_{surface})$$

CHAPTER 2

REACTIONS OF CHLOROFORM IN THE PRESENCE OF A BASE

2.I. THE HYDROLYSIS OF CHLOROFORM

The hydrolysis of chloroform was first reported by Geuther[88] in 1862, who suggested that chloroform existed as $CCl_2 \cdot HCl$, and that hydrogen chloride could be removed by alkali, to give dichlorocarbene, which decomposed to give carbon monoxide. Mossler[89], (1903), also cited dichlorocarbene as an intermediate in the reaction of chloroform vapour and air with solid potassium hydroxide, to give phosgene. Early kinetic studies showed that the overall hydrolysis reaction could be represented by the equation

$$CHCl_3 + 4KOH = 3KCl + 2H_2O + HCO_2K$$

and that the reaction was first order with respect to both chloroform[90] and hydroxide[91] in dilute solutions. This suggested that replacement of the chlorine atoms occurred in successive stages.

The first detailed investigation of this reaction was carried out by Hine and coworkers[92-99], between 1950 and 1958. They considered three possible mechanisms.

Mechanism I

$$CHCl_3 + OH^- \xrightleftharpoons{\text{fast}} CCl_3^- + H_2O$$

$$CCl_3^- \xrightarrow{\text{slow}} :CCl_2 + Cl^-$$

$$:CCl_2 \xrightarrow[H_2O]{OH^-,\ \text{fast}} CO + HCO_2^-$$

Mechanism II

$$\mathrm{CHCl_3 + OH^- \xrightleftharpoons{fast} CCl_3^- + H_2O}$$

$$\mathrm{H_2O + CCl_3^- \xrightarrow{slow} H_2\overset{+}{O}\text{-}\overset{-}{C}Cl_2 + Cl^-}$$

$$\mathrm{H_2\overset{+}{O}\text{-}\overset{-}{C}Cl_2 \xrightarrow[H_2O]{OH^-,\ fast} CO + HCO_2^-}$$

Mechanism III

$$\mathrm{CHCl_3 + OH^- \xrightarrow{slow} CHCl_2OH + Cl^-}$$

$$\mathrm{CHCl_2OH \xrightarrow[H_2O]{OH^-,\ fast} CO + HCO_2^-}$$

Of these three mechanisms, it is mechanism I which has been widely favoured, largely as a result of the supportive evidence which Hine has put forward, which will be outlined below.

The initial equilibrium has been investigated, and shown, by isotopic analysis[94,100-102], to be reached very rapidly compared to the rate of hydrolysis; an essential factor in mechanisms I and II.

The addition of neutral salts has been studied by many authors[92,93,103-107]. Equal concentrations of sodium nitrate, sodium fluoride and sodium perchlorate, at ionic strengths up to 0.20, had similar effects on the basic hydrolysis[93]. Other halide ions had a considerably greater effect, and the rate was decreased in the order $I^- > Br^- > Cl^-$. This was explained by the fact that the first group of salts contain anions which are less likely to recombine with an intermediate, so that the observed rate was in fact the rate of formation of the intermediate, which must therefore be independent of the nature of anions present. Chloride, bromide and iodide ions would readily recombine with the intermediate, resulting in the observed decrease in rate, the relative effects being as predicted by the relative nucleophilicities of the anions.

The salt effect was explained on the basis of mechanism I, in which the recombination of halide ions with the intermediate dichlorocarbene led to a reversal of the rate determining step (RDS), and hence to a retardation of the reaction.

$$:CCl_2 + X^- \longrightarrow CXCl_2^-$$

When bromide or iodide ions were added the resulting mixed haloforms reacted more readily than the original chloroform, resulting in an increase in the rate constant as the reaction proceeded. Mixed haloforms have been isolated from such mixtures[93,108,109], giving further evidence for dichlorocarbene as an intermediate.

Mechanism II does not offer a satisfactory explanation of the observed results, since nucleophilic attack would be expected to occur between halide ions and the trichloromethyl anion, rather than on the intermediate. If X^- was chloride the reactant would be regenerated, and the rate unaffected.

$$CCl_3^- + X^- \longrightarrow CXCl_2^- + Cl^-$$

In an attempt to provide more conclusive evidence for the formation of dichlorocarbene, Hine studied the reaction of chloroform with sodium thiophenolate[92], and showed that it was negligibly slow compared to that with hydroxide ions. Addition of sodium hydroxide increased the reaction, suggesting that hydroxide was necessary for the formation of an intermediate which then reacted with the thiophenolate. Since thiophenolate ions are more nucleophilic than hydroxide, it would seem unlikely that the reaction involved nucleophilic attack. However, since they are less basic than hydroxide, a slower reaction would be predicted from both mechanisms I and II.

Mechanism II predicts a competitive reaction between thiophenolate ions and water for the trichloromethyl anion.

$$CCl_3^- + C_6H_5S^- \xrightarrow{k_t} C_6H_5SCCl_2^- + Cl^-$$

$$CCl_3^- + H_2O \xrightarrow{k_w} H_2\overset{+}{O} - \bar{C}Cl_2 + Cl^-$$

If this were the case, addition of trichlorophenolate ions to a system containing chloroform and hydroxide might be expected to increase the rate of disappearance of chloroform, but experimentally this was not observed. Since the reaction between thiophenolate and trichloromethyl anions involves reaction between two negative ions, it would be expected to show a larger positive salt effect than that with a neutral water molecule. It might be expected therefore, that the ratio k_t/k_w would decrease with decreasing ionic strength, but again this was not the case.

It is interesting to compare the rate of hydrolysis of chloroform with those of other methyl halides. The relative reactivities of methyl chloride, dichloromethane and chloroform have been found to be 830 : 5.5 : 10,000 respectively[110]. In general, the replacement of a hydrogen atom attached to the α-carbon, by a halide, decreases SN_2 and increases SN_1 reactivity[92]. Whilst this could account for the decreased reactivity of dichloromethane relative to methyl. chloride, it does not explain the greater reactivity of chloroform. Similarly, the replacement of an α-hydrogen by fluorine should decrease SN_2 reactivity, but bromochlorofluoromethane was found to react 300,000 times faster than bromochloromethane[95]. The most important factor effecting the ease of carbanion formation ($CHI_3 \simeq CHBr_3 > CHCl_3$), has been shown to be d-orbital resonance[111]. Although inductive effects and polarizability may play a stabilizing role, these effects were thought to be minor.

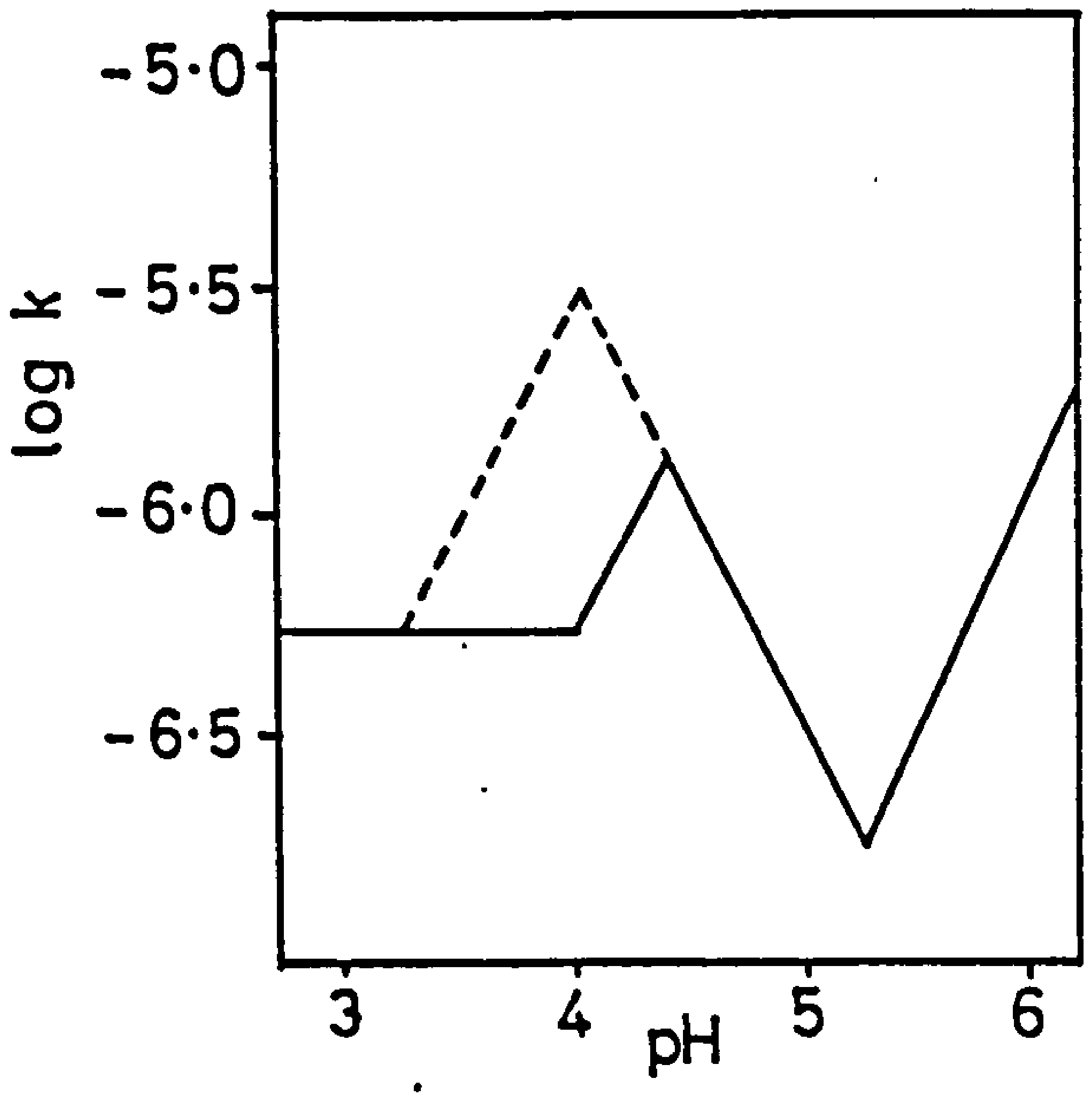
Hine[98] has examined the effects of structure on the relative stabilities of dihalocarbenes, and compared these to the reaction rates of the parent haloforms. He found that there were three factors controlling the rate (k_2), at which trihalomethyl anions lost a halide ion; a) the ease with which the departing halogen breaks away with its electron pair, b) the ability of the remaining halogens to stabilise the carbene produced, and c) the fact that the carbanion character of the reactant decreases in the transition state, so that whatever factors tend to stabilise a carbanion will lower the rate.

The formation of dihalocarbenes appeared to decrease in the order $F \gg Cl > Br > I$, and, since the carbenes are thought to be formed in a non-radical (singlet) state rather than a diradical (triplet) state, this was attributed to the relative abilities of the halogens to supply electrons to the carbon atom. The relative ability of the halogens to separate as anions (I>Br>Cl) was less significant.

An alternative mechanism has been suggested[103,105] to explain the formation of dichlorocarbene. The effect of pH on the rate of hydrolysis was investigated, and four different regions identified.

FIGURE 1

Effect of pH on the hydrolysis of chloroform[103]



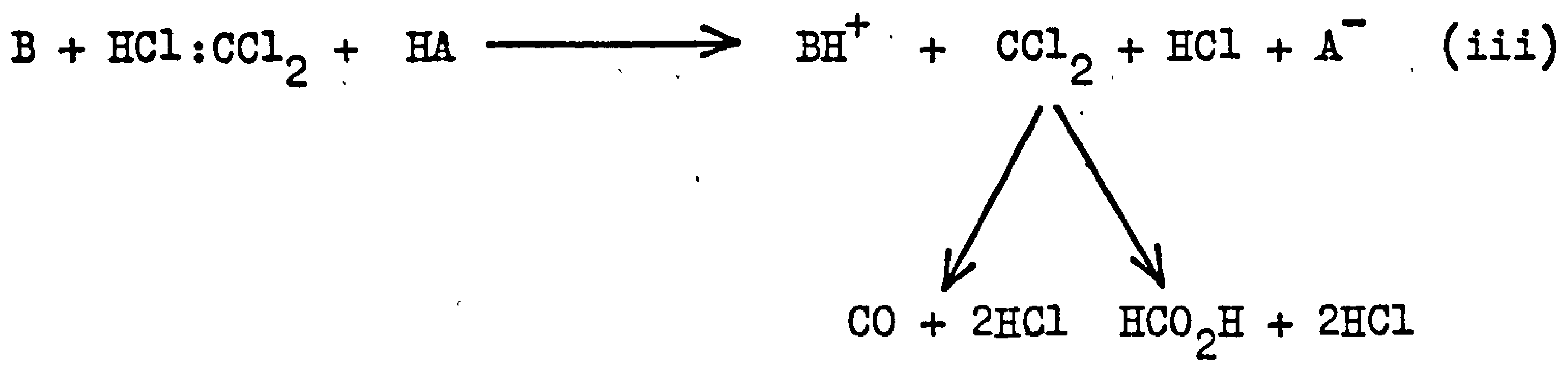
---- in absence of salts.

—— in presence of 0.01N sodium sulphate

Between pH 0.1–3.2 the hydrolysis rate was constant (5.0×10^{-7} mol. $l.^{-1}$ min^{-1}); it then rose to a maximum at pH 4.0 (3.2×10^{-6} mol. $l.^{-1} min^{-1}$), and fell to a minimum (5.0×10^{-8} mol. $l.^{-1}$ min^{-1}) at pH 5.2. Thereafter it continued to rise with increasing pH. The mechanism suggested to account for these observations is a follows, the proposed intermediate being the same as that suggested by Geuther[88] in 1862.

$$HCCl_3 + B \longrightarrow CCl_3^- + H^+B \qquad (i)$$

$$AH + CCl_3^- \longrightarrow A^- + HCl{:}CCl_2 \qquad (ii)$$



$$B + HCl{:}CCl_2 + HA \longrightarrow BH^+ + CCl_2 + HCl + A^- \qquad (iii)$$

$$CCl_2 \longrightarrow CO + 2HCl \qquad CCl_2 \longrightarrow HCO_2H + 2HCl$$

At low pH's the second step of the reaction is rate-controlling and for the line of zero slope, AH of step (ii) is the hydroxonium ion. As the pH increases, however, hydroxonium ion is gradually replaced by water as AH and the rate increases. By pH 4.0 the third step of the reaction, in which HA was hydroxonium ion and B water, has become so slow that it now becomes rate-controlling, and the rate decreases with increasing pH. At the point of minimum rate, at about pH 5.0, HA becomes water and B is hydroxide ion.

Hine[99] also investigated the effect of pH on hydrolysis, but observed no maximum or minimum as reported above[103]. His reactions were carried out in buffered solutions and he reported that at pH's below those at which the base catalysed reaction began, the hydrolysis of chloroform was first order with respect to chloroform, pH independent, and largely S_N2 in character.

In their investigation of the effect of added salts, Horiuti and Tanabe[103] found that the addition of 0.01N sodium sulphate to the reaction mixture decreased the reaction rate by a factor of six, but the profile observed in the absence of added salts was still apparent (see Fig.1). When the concentration of salt was increased to 0.2N, the variation of rate with pH was no longer observed. Since Hine's experiments were carried out at ionic strengths of 0.2, it has been suggested[103] that this was why he found the reaction to be independent of pH.

In an attempt to distinguish between the two proposed mechanisms, the rate of chlorine exchange has been studied[99,106]. According to Hine's mechanism, chlorine exchange would be expected to result from S_N2 attack by chloride ions on chloroform, in acid solution, and by recombination with dichlorocarbene in alkaline solution.

$$\overset{*}{Cl}^- + CHCl_3 \longrightarrow CHCl_2\overset{*}{Cl} + Cl^- \qquad \text{(acid soln.)}$$

$$:CCl_2 + \overset{*}{Cl}^- \longrightarrow CCl_2\overset{*}{Cl}^- \xrightleftharpoons{H_2O} CHCl_2\overset{*}{Cl} \qquad \text{(alkaline soln.)}$$

From Horiuti's mechanism,

$$CCl_3^- + \overset{*}{Cl} + HA \longrightarrow CCl_2\overset{*}{Cl}^- + Cl + HA$$

In acid solution HA was thought to be H_3O^+, and the rate of exchange was found to be independent of pH. Above pH 6, HA became water, and the rate of exchange increased linearly with increasing basicity. Hine[99] argued that the possibility of one mechanism being responsible for the reaction at all values of pH was unlikely.

The two mechanisms lead to different predictions on the effect of hydroxide ion concentration, and added salts on the ratio of the rates of chlorine exchange, to hydrolysis (U_s/V_d). Hine's theory predicts that U_s/V_d depends only on hydroxide ion concentration, and that both V_d and U_s will decrease by the same factor with increasing Cl^- and I^- concentrations, because of the decrease of the steady state concentration of dichlorocarbene. Horiuti's mechanism on the other hand, requires that U_s/V_d and $V_d/[OH^-]$ are independent of hydroxide, chloride and iodide ion concentrations, and this agreed with experimental observations[106].

It has been reported[90,112], that under conditions of high hydroxide concentration, the order of the reaction with respect to the base increases from one to two. Bose[112,113] has suggested that two simultaneous reactions occurred, the first predominating at temperatures below 45°, whilst above this the second reaction became more important.

$$CHCl_3 + 4KOH = HCO_2K + 3KCl + 2H_2O$$

$$CHCl_3 + 3KOH = 3KCl + 2H_2O + CO$$

The termolecular reaction observed was explained by the substitution of one of the chlorine atoms, as well as the extraction of a proton, by the hydroxide ions when these are present in excess.

$$CHCl_3 + 2OH^- \xrightleftharpoons{fast} C(OH)Cl_2^- + H_2O + Cl^-$$

$$C(OH)Cl_2^- \xrightarrow{slow} Cl^- + C(OH)Cl$$

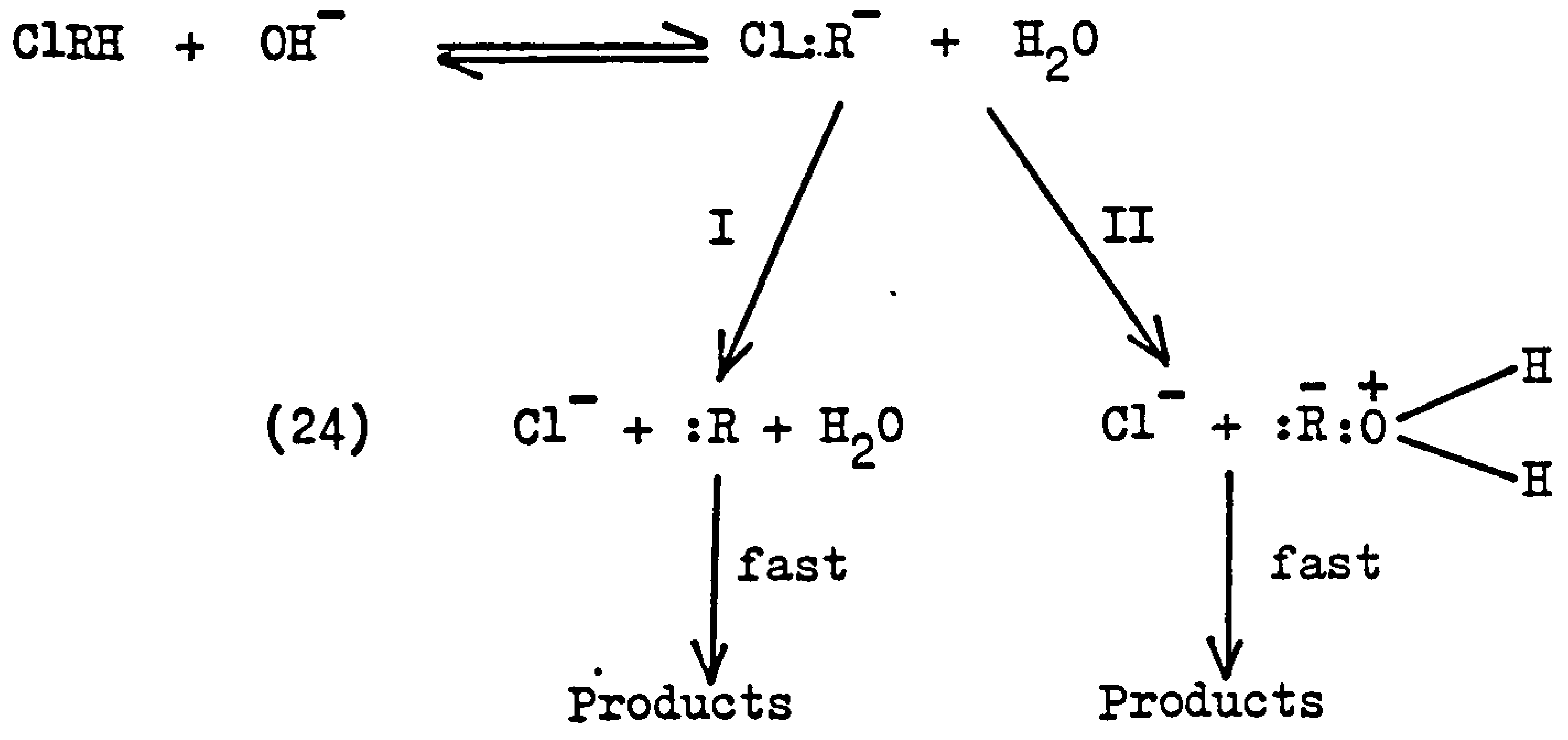
$$C(OH)Cl + OH^- \xrightarrow{fast} C(OH)_2 + Cl^-$$

$$C(OH)_2 \xrightarrow{isomerises} HCOOH$$

The "volume of activation" (ΔV^*), that is, the difference in molar volume between the transition states and the reactants, has been studied[114,115], to gain further insight into the nature of the intermediate in this reaction. A value of ΔV^* may be estimated. (± 0.5 ml.). From an experimental knowledge of the effect of hydrostatic pressure on the rate constant, from the relationship

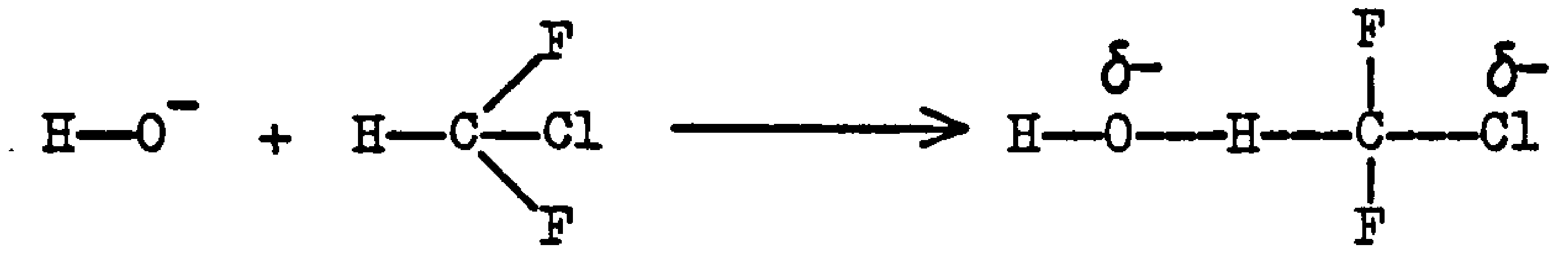
$$\Delta V^* = -RT \left(\frac{d \ln k}{dp}\right) \tag{4}$$

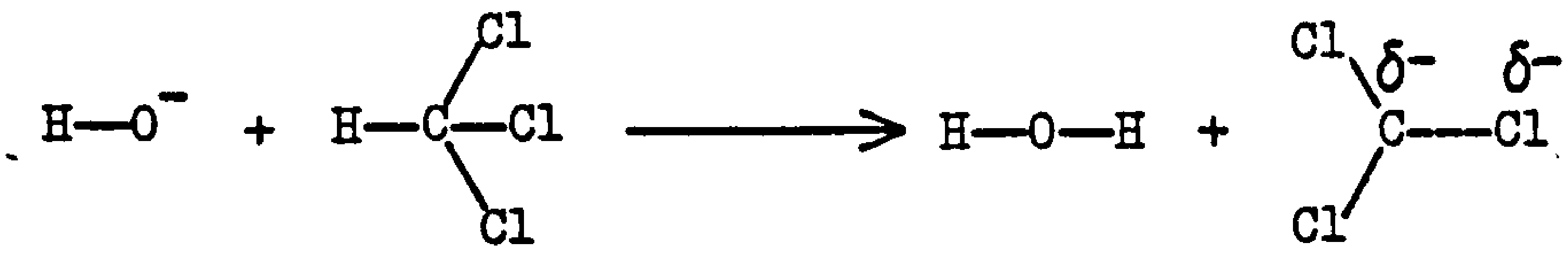
This may then be used to distinguish between transition states which include covalently bound solvent (23) and those in which solvent molecules remain at Van der Waals distances (24), such as those in mechanisms I and II suggested by Hine.[92-99]



(24) (23)

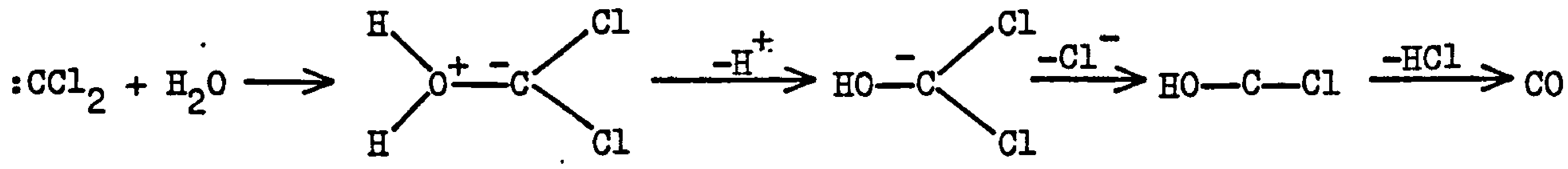
Mechanism I would be expected to have a larger ΔV^{*} than II, and by comparison with known values for similar reactions, values of $\Delta V^{*} = +15 \pm 5$ ml. mol.$^{-1}$, and -5 to -10 ml. mol.$^{-1}$, were predicted for mechanisms I and II respectively. The value determined for the hydrolysis of chloroform was $+16 \pm 1$ ml. mol.$^{-1}$, which is in good agreement with that predicted for a dihalocarbene intermediate. In the hydrolysis of difluorochloromethane a lower value was obtained ($+8.4$ ml. mol^{-1}) than that measured for chloroform. This supports the idea that hydrolysis of this halomethane proceeds by a concerted α-dehydrohalogenation, since the activated complex would be more compact than in the chloroform reaction.





Although much work has been devoted to elucidating the mechanism by which reaction intermediates are formed, little has been said about what happens to them thereafter. If, as it has been suggested[92-99,110,112,113] carbon monoxide and formate were formed simultaneously, the ratio of the products should remain constant throughout the reaction. However, the ratio of formate to carbon monoxide was found to be very small at the beginning of the reaction, and to increase as the reaction proceeded[116], suggesting that carbon monoxide was the primary product, and this then reacted further to give formate. The rate of formate formation was found to be proportional to the product of the concentrations of hydroxide and carbon monoxide.

On the basis of predicted salt effects[116], the most likely reaction of dichlorocarbene in aqueous solution was thought to be

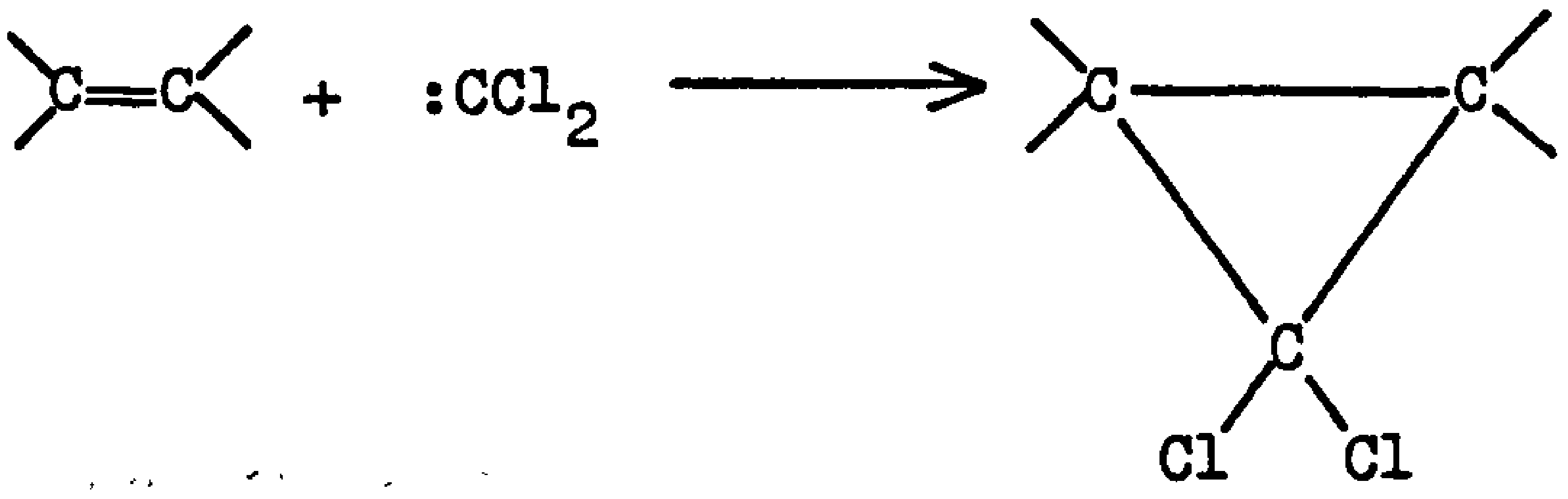


Carbon monoxide reacted in an aqueous alkaline solution by a second order reaction which showed no large salt effect[116]. It was proposed therefore, that the mechanism involved direct slow attack by a hydroxide ion on the carbon atom of the carbon monoxide, followed by a prototropic rearrangement.

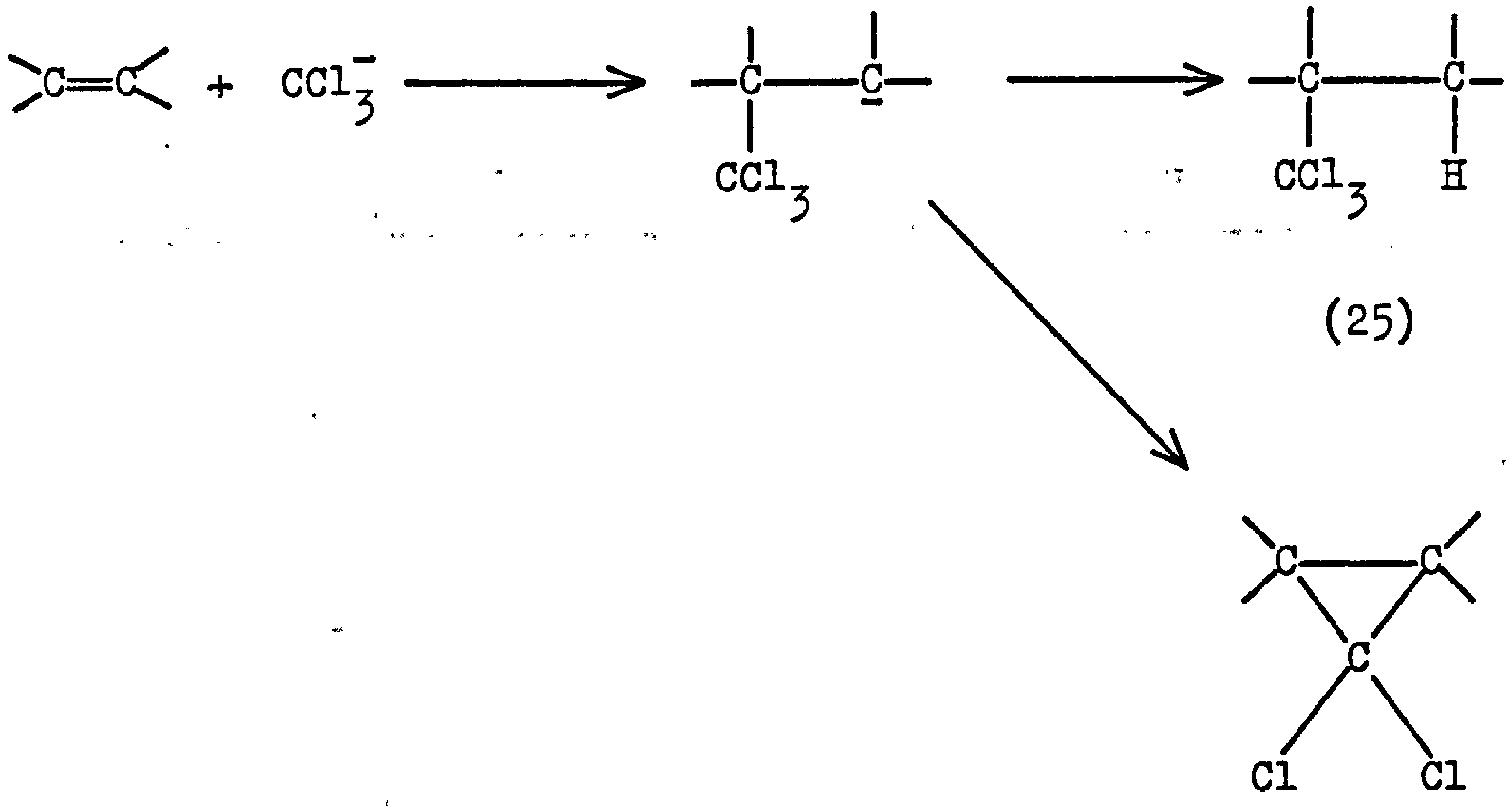
2.II. REACTIONS OF CHLOROFORM WITH A BASE IN THE PRESENCE OF A SUBSTRATE

The reactions of chloroform with a base in the presence of various substrates has been studied extensively. Many of these reactions give products analogous to those obtained from the same reactants in the gas phase.

Following the first report of the formation of a cyclopropane derivative, from olefins and chloroform in the presence of potassium t-butoxide[117], many authors have been engaged in this field, studying the mechanism of the reaction and extending its synthetic applications. As in the gas phase, the reaction is thought to involve dichlorocarbene as an intermediate[117] and is considered by some people, as the most conclusive evidence for its existence.

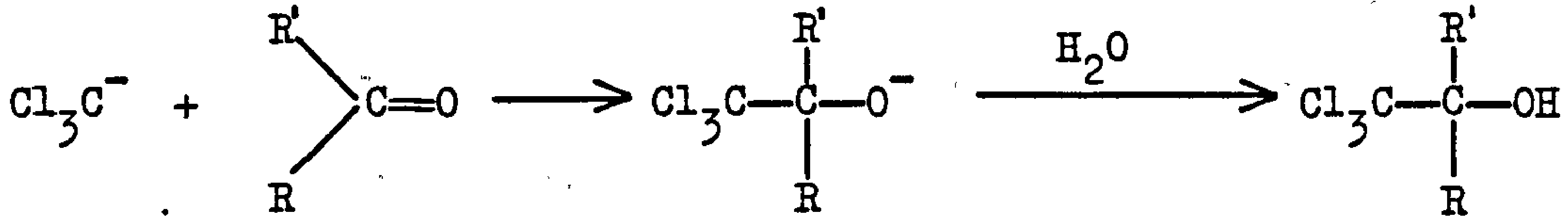


A mechanism[117,118] involving the addition of a trichloromethyl anion to the double bond to form a carbanion, from which cyclopropanes are formed by elimination was rejected. Carbanions are usually unreactive towards double bonds, and it has never been possible to isolate the saturated trichloromethyl derivative (25), from these reactions, which should be formed from the carbanion on addition of a proton.



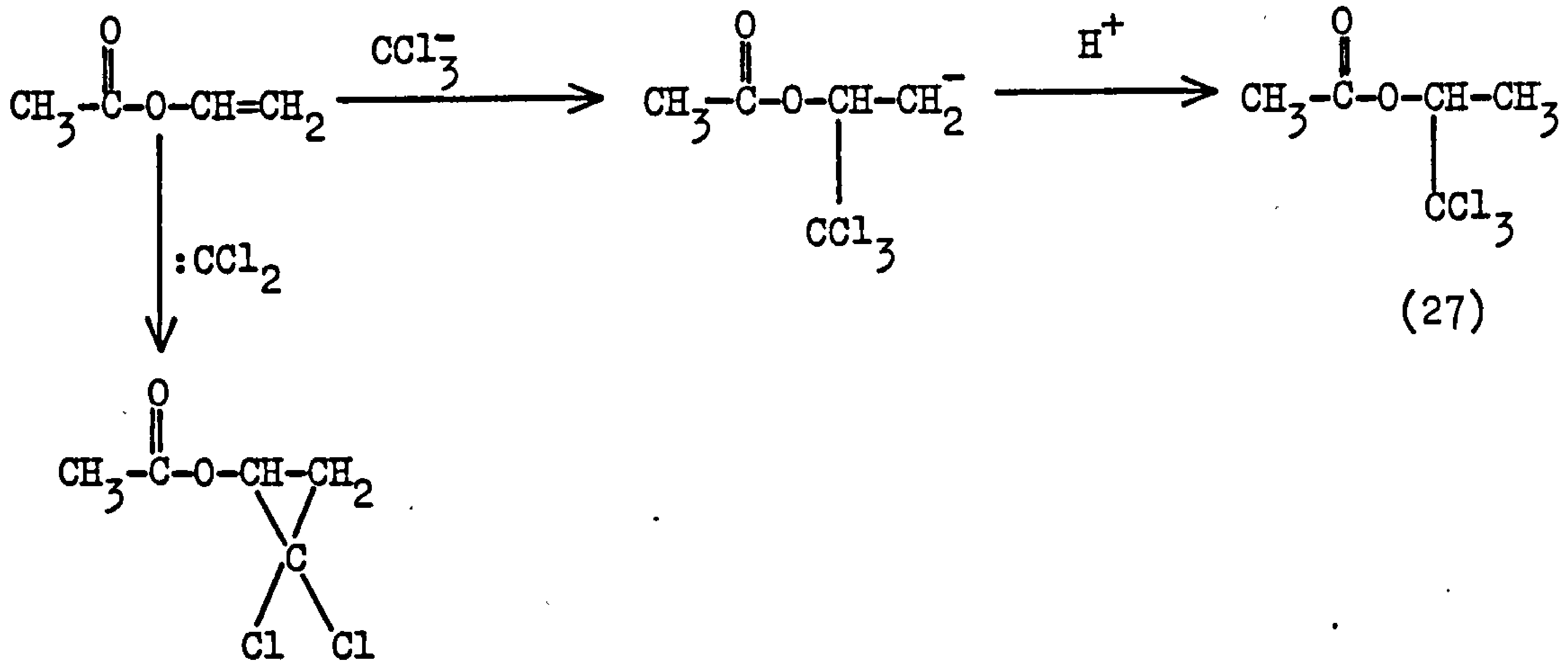
(25)

However, in the reaction between ketones, chloroform, and a base, trichloromethylcarbinols (26) have been shown to be formed[119-121].



(26)

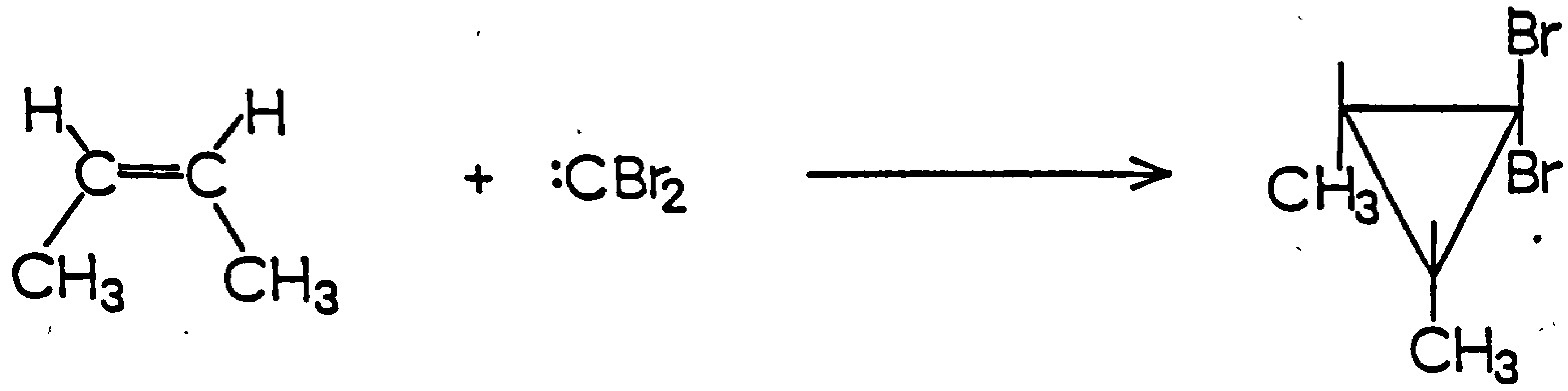
Similarly, 1,1,1-trichloro-2-propyl acetate (27) was obtained from vinylacetate when sodium trichloroacetate was used as a source of trichloromethyl anions[122]. This is thought to be formed by addition of CCl_3^- to the double bond, giving a primary carbanion, which then takes up a proton, the origin of which is not clear.



(27)

A second criticism of the trichloromethyl anion mechanism is that it does not explain the stereospecific characteristics of the reaction.

The reaction of bromoform with <u>cis</u>- or <u>trans</u>-2-butene has been shown to produce <u>cis</u>- (28) and <u>trans</u>-1,1-dibromo-2,3-dimethylcyclopropane (29) respectively, in 99 % purity[123,124].



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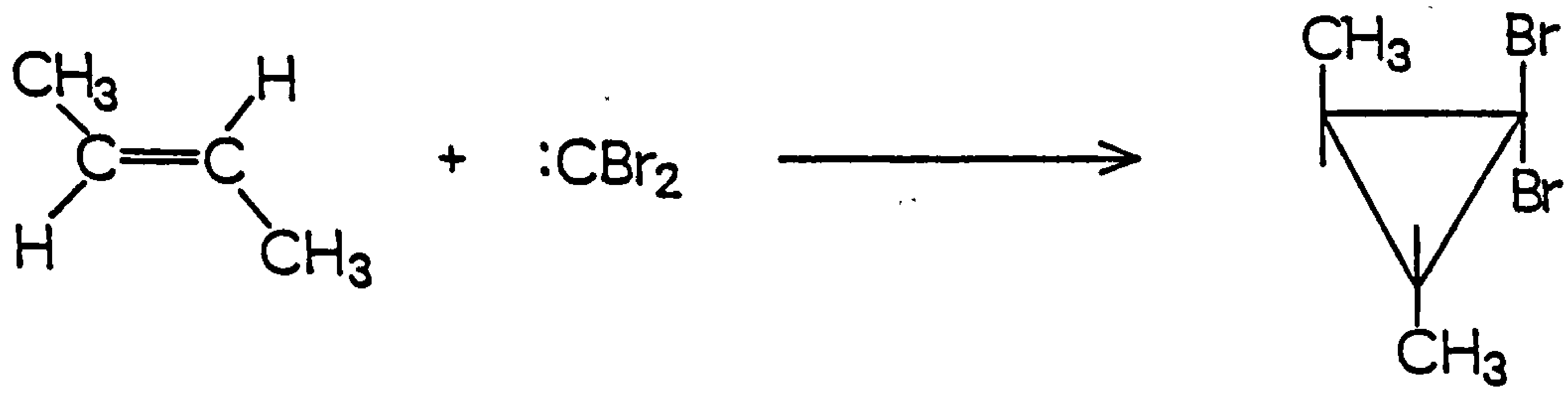


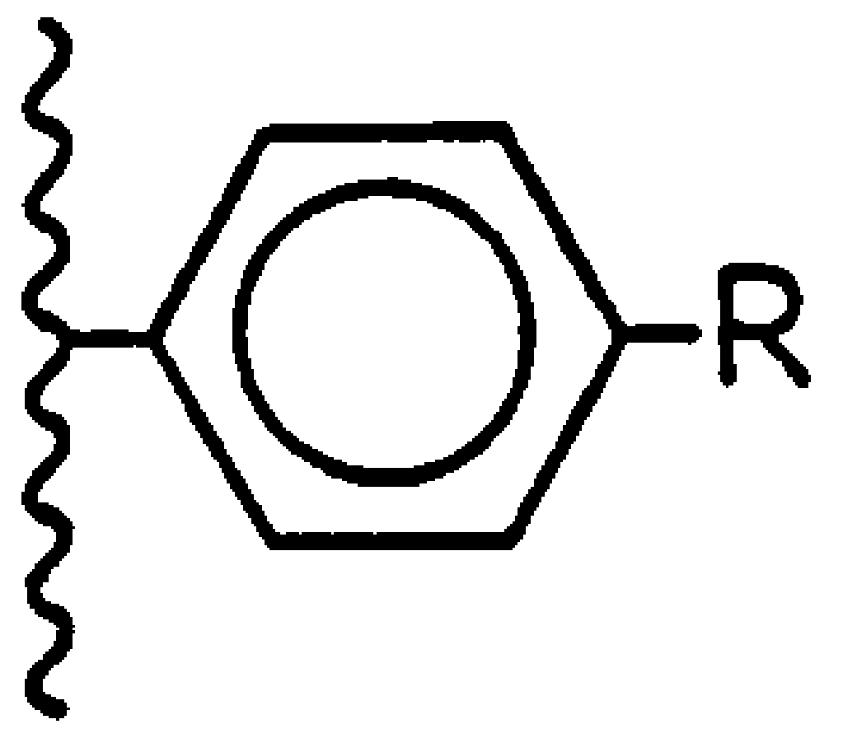
(29)

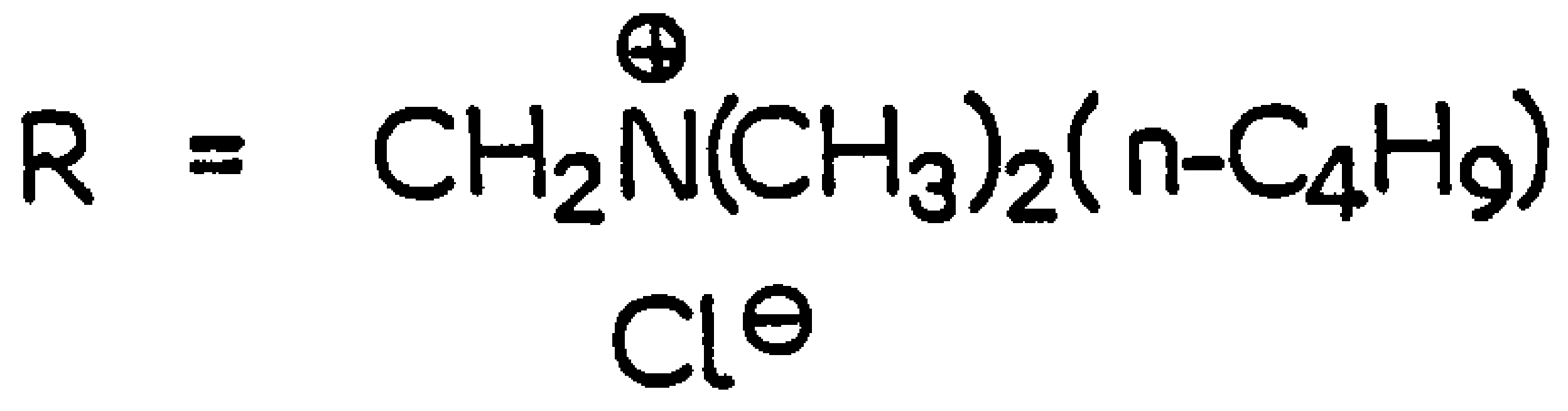
This supports the idea that a three-centre transition state is formed in the reaction. A stepwise process leading to a charge separated intermediate would require that the intermediate rearranged to the cyclopropane faster than rotation could occur about the carbon-carbon single bond.

The extent of reaction depends on the nucleophilicity of the olefin[125]. The increase in reactivity of olefins with increasing alkyl substitution can thus be explained by the ability of the substituents to donate electrons towards the double bond.

Potassium t-butoxide has been most frequently used as the base[117,125-129], since the highly hindered t-butanol formed in its reaction with chloroform would be fairly unreactive. Sodium methoxide[130], butyllithium[131], cyclopentadienylsodium[132] and potassium diphenylmethide[133] have also been employed.

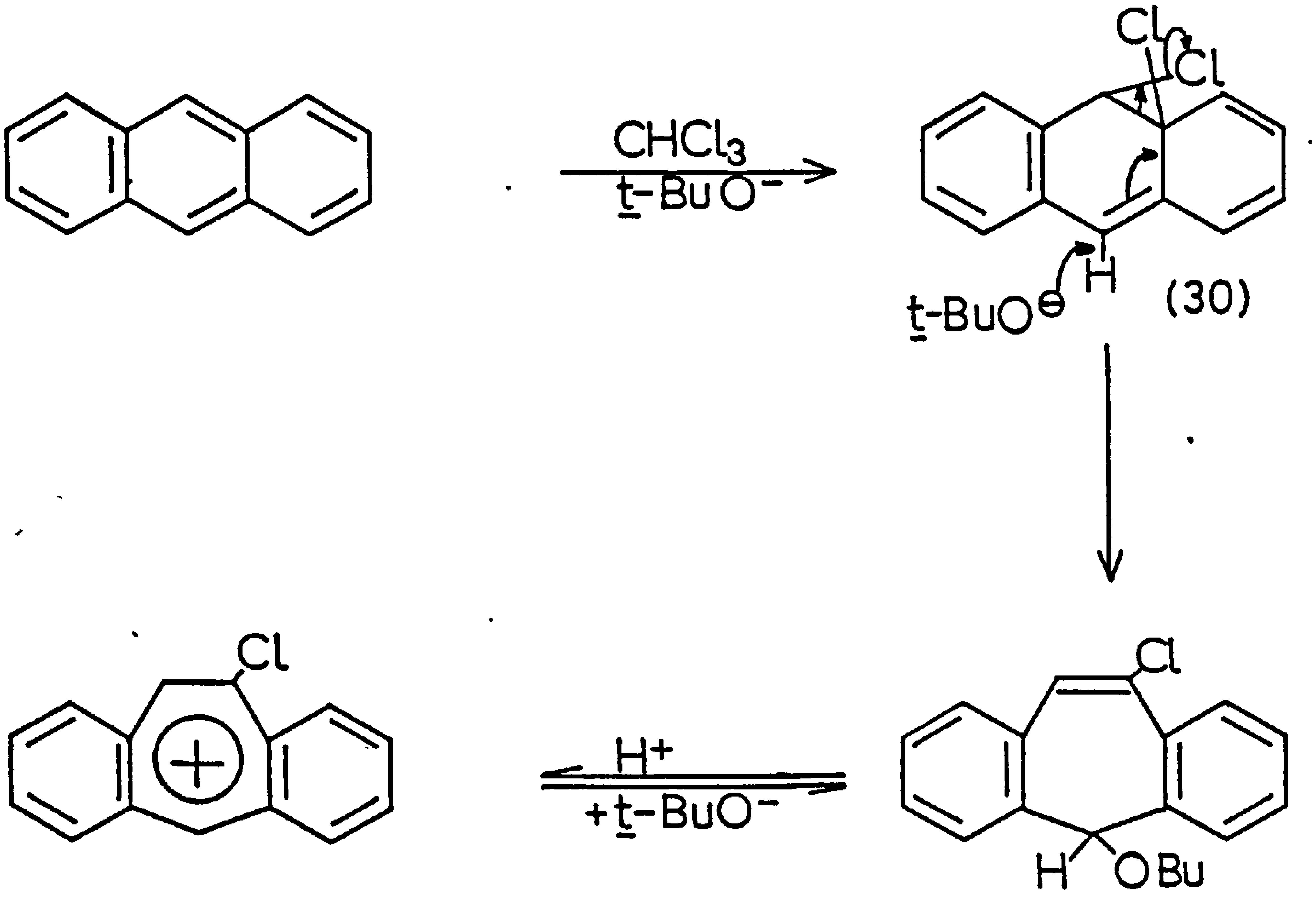
Until recently, the use of aqueous media had been avoided because of the competing hydrolysis reaction. Since the introduction of phase transfer catalysts however, increases in yields from 5 to 60 % have been reported in aqueous solutions[134]. Trialkylamines[135], quaternary ammonium compounds[134,136-139] and crown ethers[138] have been used in this context. Catalysis by quaternary ammonium compounds was thought to be due to the formation of ion pairs $\geqslant\overset{+}{N}< \quad \overset{-}{C}\leqslant$, which enable the trichloromethyl anion to be transported into the organic phase. Solid polystyrene resins have been used[140] as "triphase catalysts", in which both the catalyst and each one of the pair of reactants were located in separate phases.



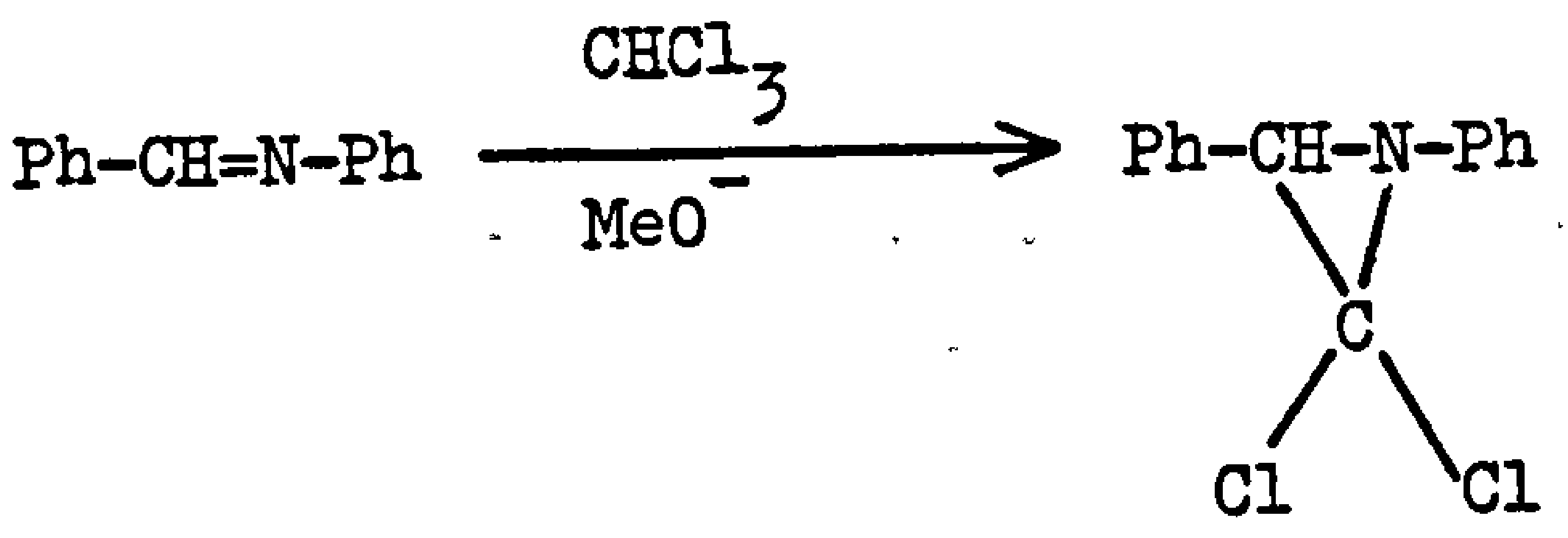

$R = CH_2\overset{\oplus}{N}(CH_3)_2(n\text{-}C_4H_9)\ Cl^{\ominus}$

Polystyrene resin

Most benzene derivatives are inert towards chloroform in the presence of a base, although anthracene afforded a product which may be derived from the hypothetical dichlorocarbene adduct (30) by displacement of a chloride ion by t-butoxide[141].

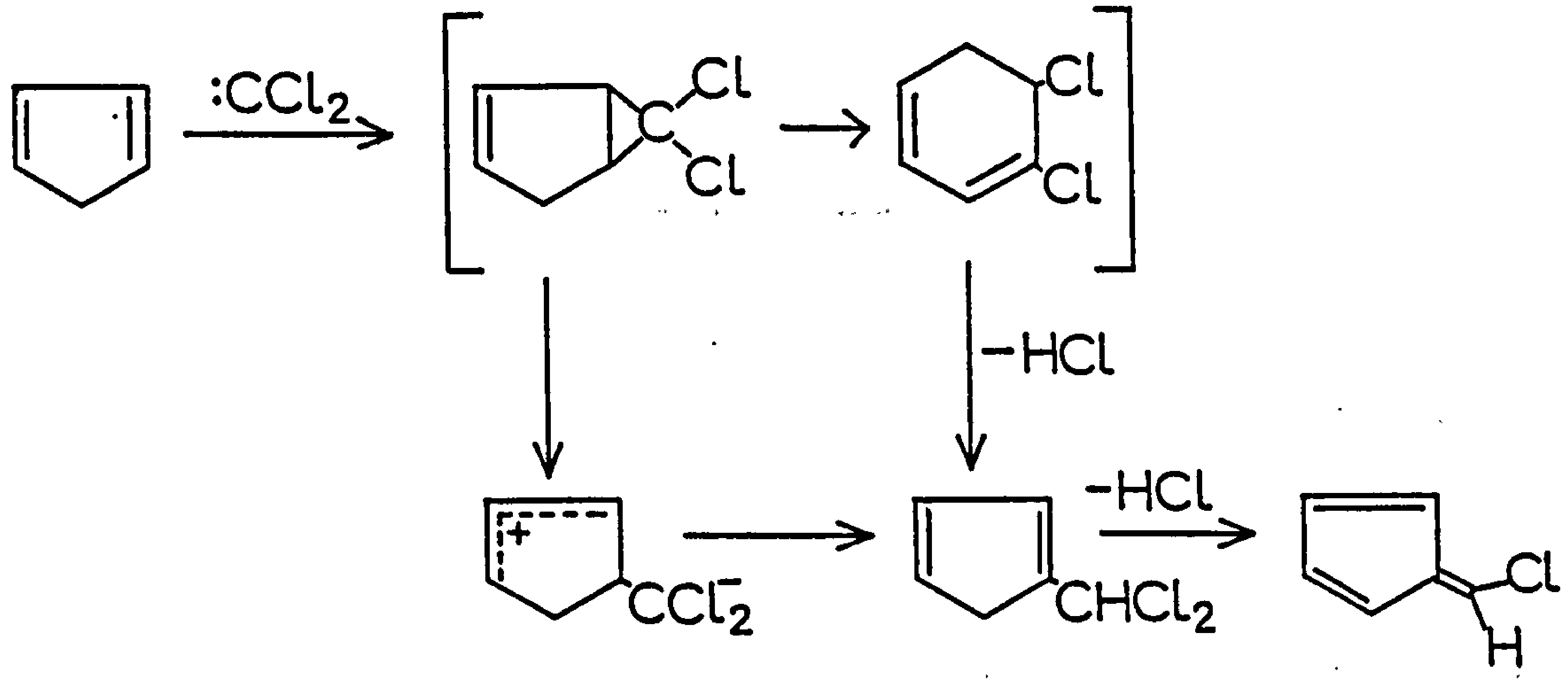


Addition to carbon-nitrogen double bonds has also been shown to take place. The reaction of N-benzylideneaniline with chloroform and sodium methoxide, gave 1,3-diphenyl-2,2-dichloroaziridine[142] (31).



(31)

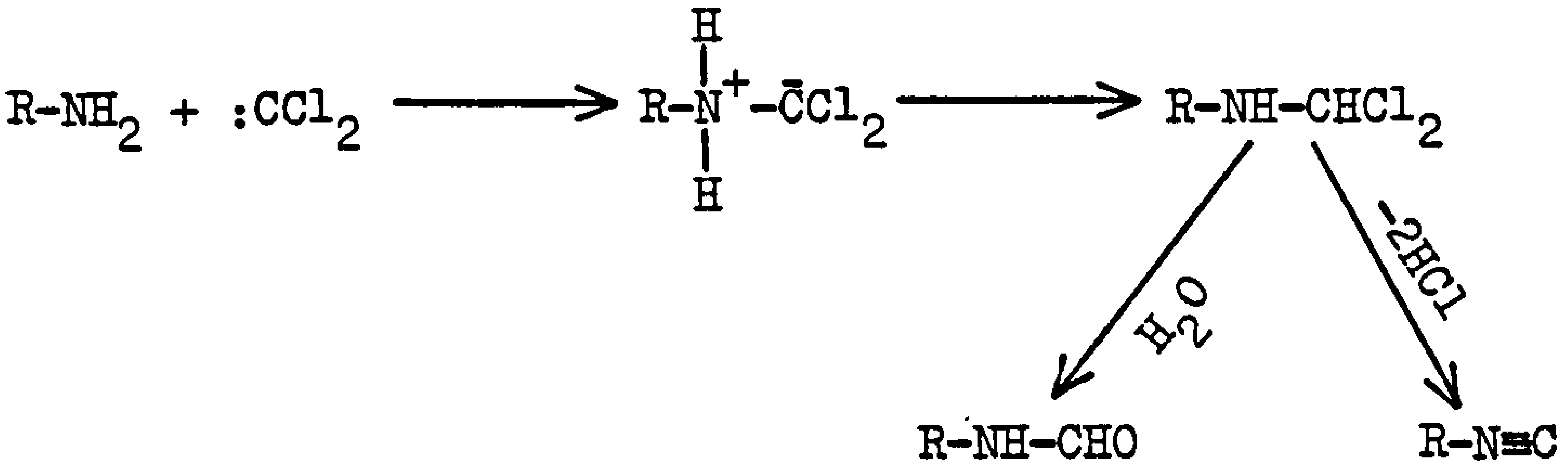
Ring expansion reactions analogous to those observed in the gas phase have been observed with pyrrole[143-145] and its derivatives[144-148], indole[149] and its derivatives[150,151], indene[152,153] and cyclopentadiene[129]. Cyclopentadiene gave not only the expected ring-expanded product, chlorobenzene, but also 6-chlorofulvene[129]. (32).



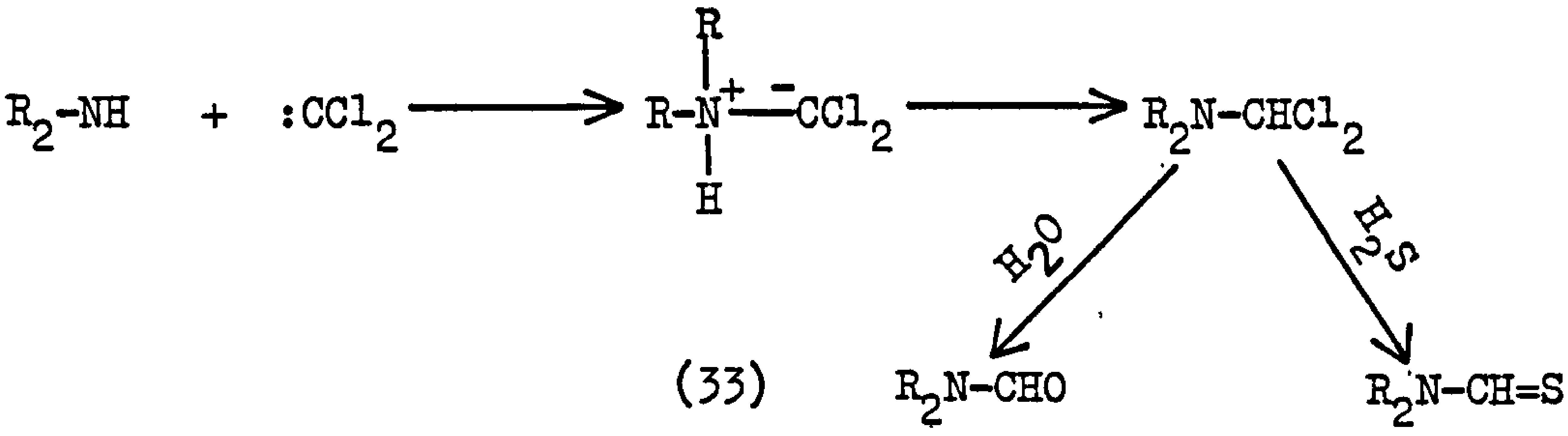
(32)

The most commonly employed base was the sodium compound of the reactant.

The action of alkali on a mixture of chloroform and a primary amine was first studied by Hoffman[154,155] in 1867, and has been widely used in synthesis and analysis, to distinguish between primary and secondary amines.



Secondary amines gave dialkylformamides (33) as the major products when reacted with chloroform and a base[156-158]. The formamides were thought to arise by hydrolysis of intermediate amidodichlorides (34), although these have not been isolated.



(34)

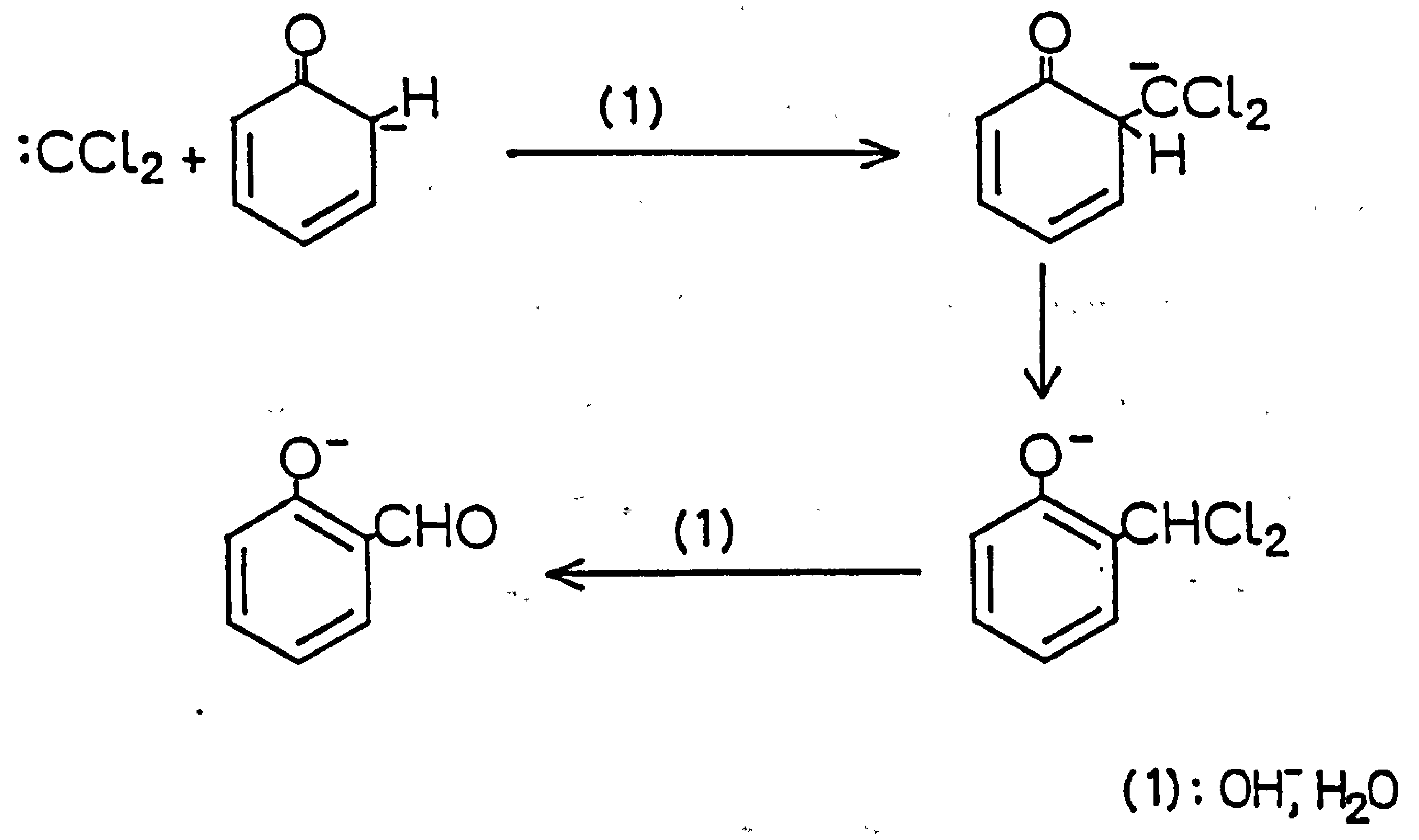
(33)

A variety of products were obtained from tertiary amines depending on the structure of the amine used[157]. When triethylamine was treated with chloroform and potassium t-butoxide, diethylformamide and N,N-diethyl-α-chloropropionamide were obtained[157].

Piperidine reacted with chloroform to give piperidine hydrochloride and dichloromethylpiperidine, which was readily hydrolysed to

N-formylpiperidine, but the reaction was slow in the absence of a strong base[159].

The Reimer-Tiemann synthesis of phenolic aldehydes[160-162] is also thought to involve attack of dichlorocarbene on the o- and p- position of phenoxide ions[163,164], since chloroform and sodium phenoxide are almost inert in the absence of sodium hydroxide.



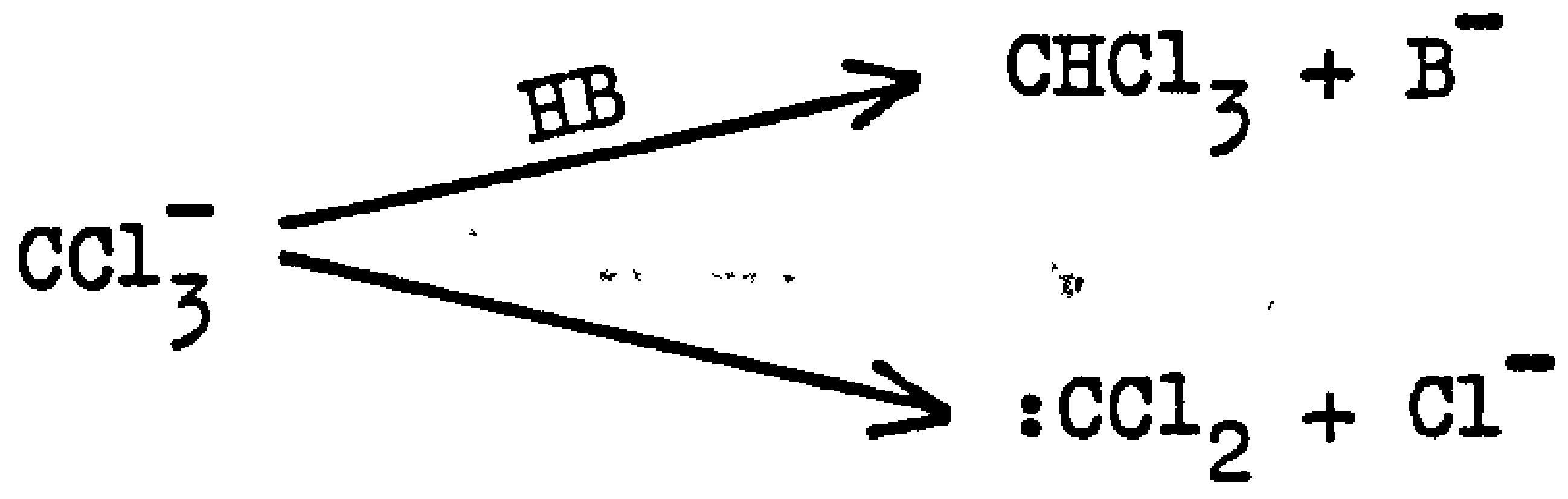
In aqueous solution, water and phenoxide ions compete for the carbene, and a study of the competition constants k_p/k_w has shown that the reaction involves the above mechanism rather than reaction between phenoxide and carbon monoxide formed from the hydrolysis of chloroform[116].

2.III. Reactions of some chloroform derivatives in the presence of a base

Many compounds which may be regarded as derivatives of chloroform, that is compounds in which either the hydrogen atom or a chlorine atom has been replaced by another group, undergo reactions similar to those of chloroform, when treated with a base. Again, dichlorocarbene has been postulated as the reaction intermediate.

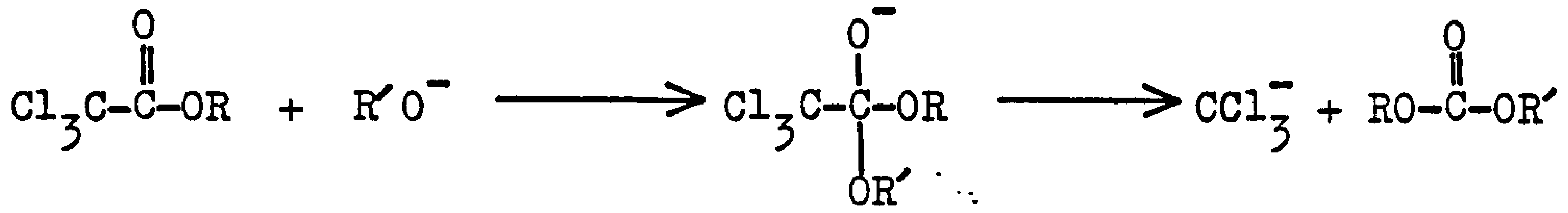
Trichloroacetic acid gave chloroform and carbon dioxide when heated with various bases[165,166]. Kinetic studies[166] of the decarboxylation showed that the reaction was first order and gave a trichloromethyl anion, which could either abstract a proton to give chloroform, or lose a chloride ion to give dichlorocarbene. In aqueous solutions the rate of hydrolysis was slow compared to the rate of protonation and chloroform was the main product.

$$Cl_3C-CO_2^- \longrightarrow CO_2 + CCl_3^-$$



The decarboxylation of salts of trichloroacetic acid in an aprotic solvent has also been used as a source of trichloromethyl anions and dichlorocarbene under neutral conditions[167-171]. The rates of decarboxylation were in the order K > Na > Li. In the presence of olefins dichlorocyclopropane derivatives were obtained in good yields.

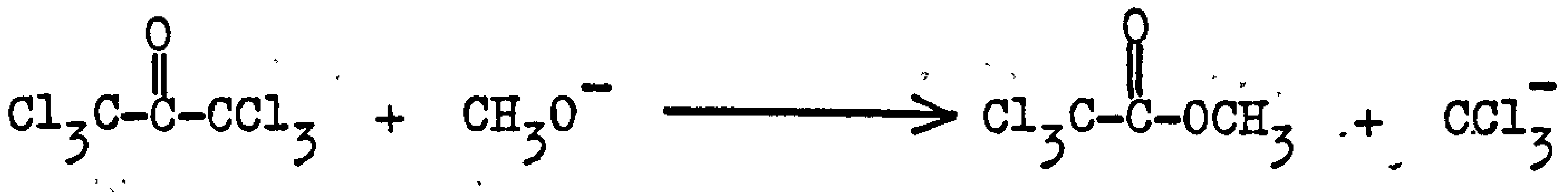
Esters of trichloroacetic acid reacted with alkoxides to give trichloromethyl anions which subsequently decomposed to dichlorocarbene[172,173]. The latter was trapped by stereospecific addition to olefins giving dichlorocyclopropane adducts in good yields regardless of the base used, (potassium t-butoxide, sodium ethoxide, sodium methoxide).



$$Cl_3C-\overset{\overset{O}{\|}}{C}-OR + R'O^- \longrightarrow Cl_3C-\overset{O^-}{\underset{OR'}{C}}-OR \longrightarrow CCl_3^- + RO-\overset{\overset{O}{\|}}{C}-OR'$$

$$CCl_3^- \longrightarrow :CCl_2 + Cl^-$$

As in alkyl trichloroacetates, the carbonyl group of hexachloroacetone is highly reactive towards nucleophiles, and readily yielded dichlorocarbene in an aprotic medium on treatment with a base, such as sodium methoxide[174,175]. The methyl trichloroacetate formed in the first step reacted further to give a second trichloromethyl anion, as shown above.



$$Cl_3C-\overset{\overset{O}{\|}}{C}-CCl_3 + CH_3O^- \longrightarrow Cl_3C-\overset{\overset{O}{\|}}{C}-OCH_3 + CCl_3^-$$

In the presence of olefins the expected addition products were obtained, together with some hexachloroisopropanol[174]. The latter was thought to arise by reduction of the ketone, the olefin being the source of protons.

The reactions of methyl trichloromethylsulphinate (35) and of trichloromethylsulphonyl chloride (36) with alkoxide are thought to proceed by the same mechanism, although yields of addition products were poor[176].

$$Cl_3C\text{-}SO_2CH_3 + RO^- \longrightarrow RO\text{-}SO_2CH_3 + CCl_3^-$$

(35)

$$Cl_3C\text{-}SO_2Cl + 2RO^- \longrightarrow RO\text{-}SO_2OR + CCl_3^- + Cl^-$$

(36)

Cycloaddition products have also been formed from olefins in the presence of trichloromethyllithium. This was prepared in situ by the action of alkyllithiums on tetrahalomethanes[177].

$$CCl_3X + RLi \longrightarrow CCl_3Li + RX$$

$$CCl_3Li \longrightarrow :CCl_2 + LiX$$

In the reaction between alkyllithiums and chloroform, the dichlorocarbene produced was trapped by triphenylphosphine, to give triphenylphosphinedichloromethylene (37)[178].

$$(C_6H_5)_3P + :CCl_2 \longrightarrow (C_6H_5)_3P{=}CCl_2$$

(37)

This has been used as an intermediate in the synthesis of substituted vinyl chlorides.

CHAPTER 3

THE YAGIL APPROACH

It has been shown by Bascombe and Bell[179,180], that the high acidities encountered in concentrated acid solutions are primarily due to the strong hydration of the proton in these solutions. Existence of the proton in a tetrahydrated form has been suggested and the following equilibrium put forward for an acid-base indicator.

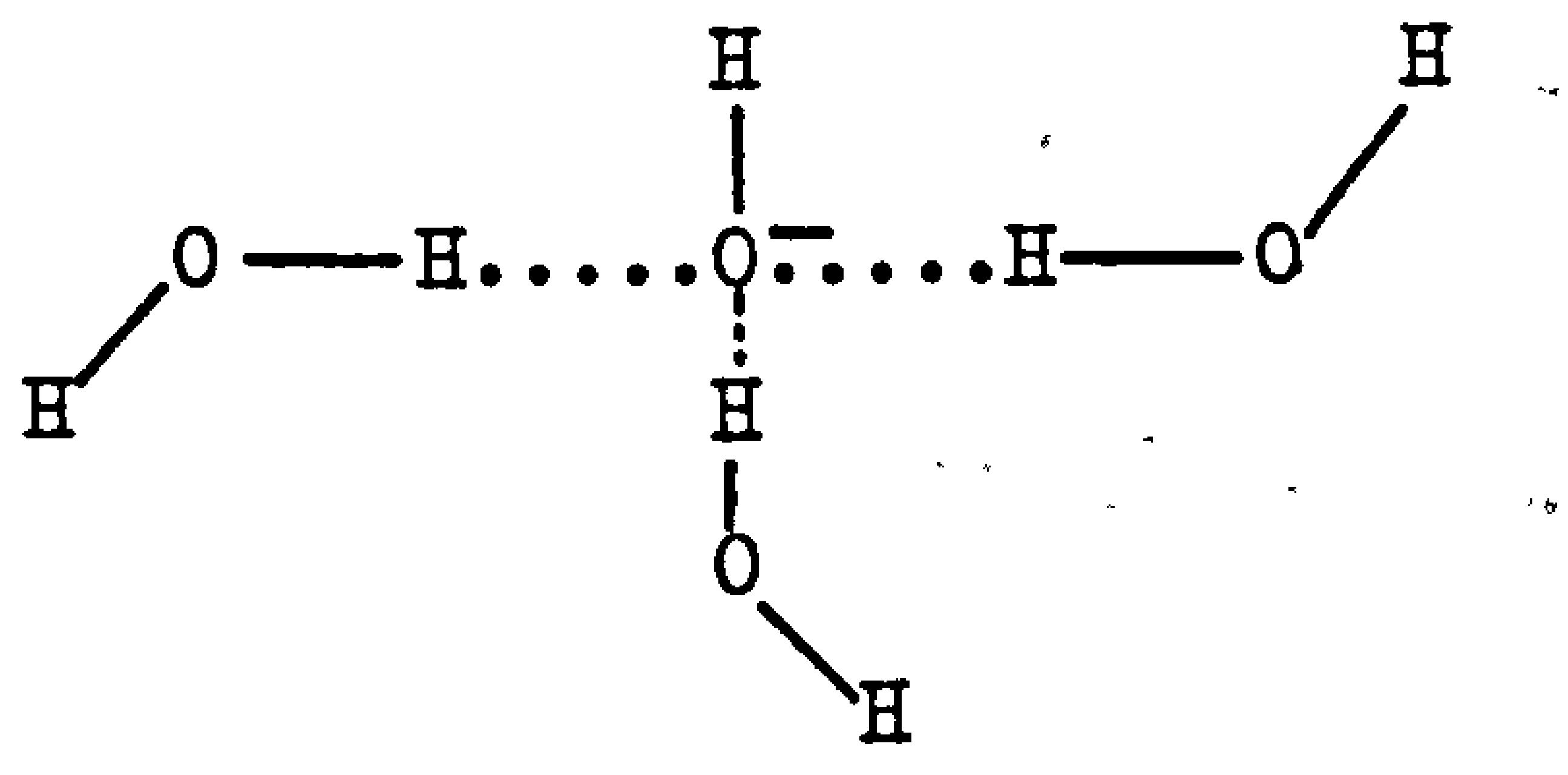
$$B + H(H_2O)_4^+ \rightleftharpoons BH^+ + 4H_2O \qquad (5)$$

The water on the right hand side of the equation is "free water", and its concentration will affect the equilibrium to the fourth power. Increasing the acid concentration results in a rapidly decreasing concentration of free water, thereby increasing the BH^+/B ratio, which determines the acidity function.

Yagil and coworkers[181], have applied the theory of Bascombe and Bell to alkaline solutions, since these exhibit similar behaviour. By analogy with acid solutions

$$BH + \overline{OH}(H_2O)_n \rightleftharpoons B^- + (n+1)H_2O \qquad (6)$$

The hydration number, n, has been found to have a value of three[181], and two possible structures have been proposed for the hydrated hydroxide ion (38 and 39).



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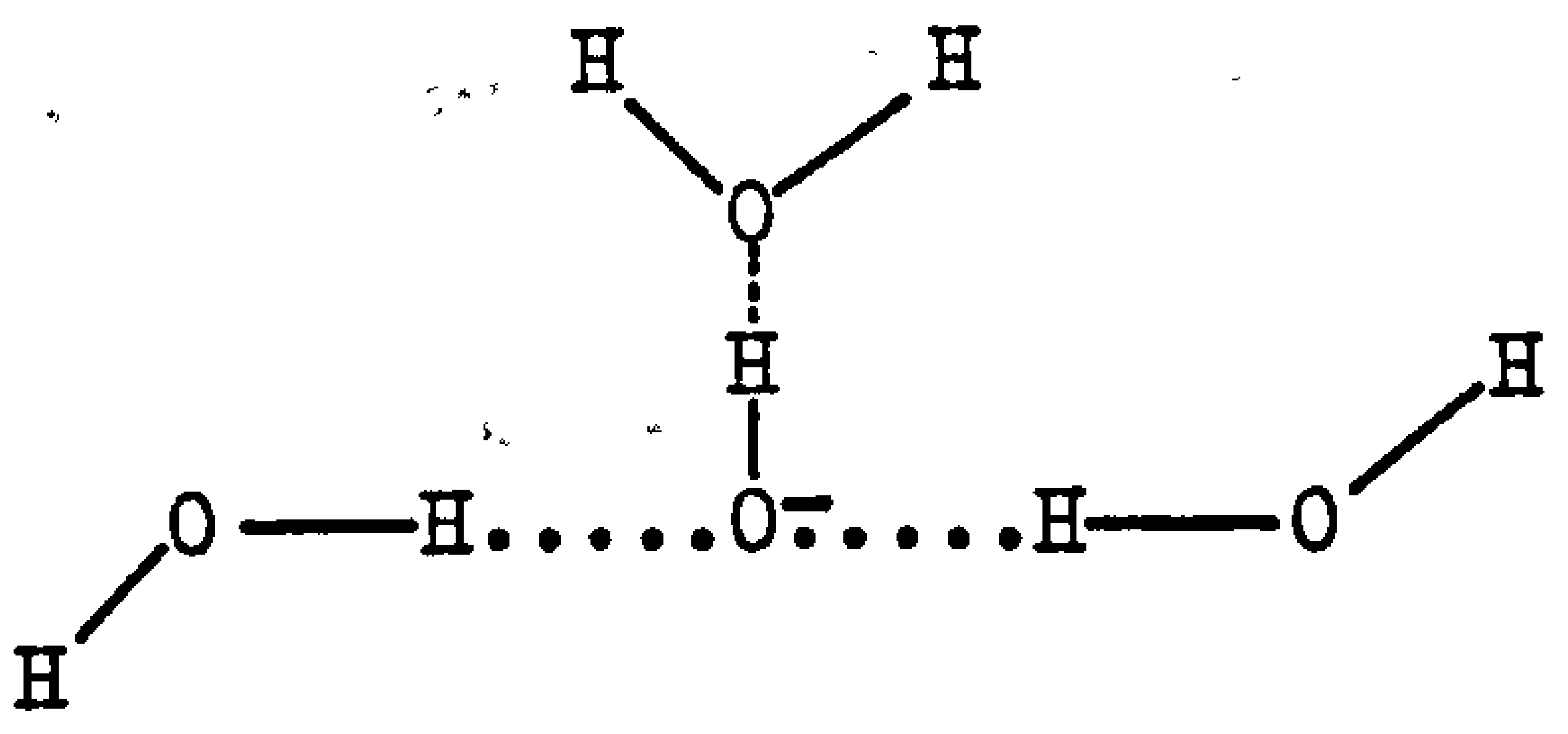


(39)

The strong basicity of OH^- means that it is more likely to form a hydrogen bond by accepting a proton (38) than by donating it (39).

In the study of reaction rates in alkaline solutions it is not unreasonable to expect that the hydroxide ion must lose its associated water before it can react with any other molecule. This idea has been applied to two reactions in which nucleophilic attack by OH^- takes place[182]. Plots of the observed rate constant ($\log_{10}k$) against ($H_- + \log_{10} C_w$), where C_w is the free water concentration, for the alkaline hydrolyses of chloramine and of ethyl iodide, gave straight lines with positive slopes of one. In terms of eq.(6), (n=3), this means that

$$\log_{10} k = \log_{10} (C_{OH^-} C_w^{-3}) + \text{constant} \qquad (7)$$

or

$$k = k' C_{OH^-} C_w^{-3} \qquad (8)$$

The hydrolysis of serine phosphate, an elimination reaction, gave similar results[182].

In the base catalysed substitution of chloramine by ammonia, the conjugated base $NHCl^-$, ("B^-") is formed in a pre-equilibrium step.

$$NH_2Cl + OH(H_2O)_3^- \rightleftharpoons NHCl^- + 4H_2O$$

$$NHCl^- + NH_3 \xrightarrow{\text{slow}} N_2H_4 + Cl^-$$

The governing rate constant is therefore

$$\log_{10} k = \log_{10} C_{OH^-} - 4 \log_{10} C_w + \text{constant} \qquad (9)$$

When $\log_{10} k/C_{OH^-}$ was plotted against V_w for this reaction, a straight line of slope -4 was obtained. V_w is the volume fraction of unbound water, and was used in preference to C_w in some cases, since it takes into account the differences in size between various species. Numerically the two values are very similar in hydroxide solutions.

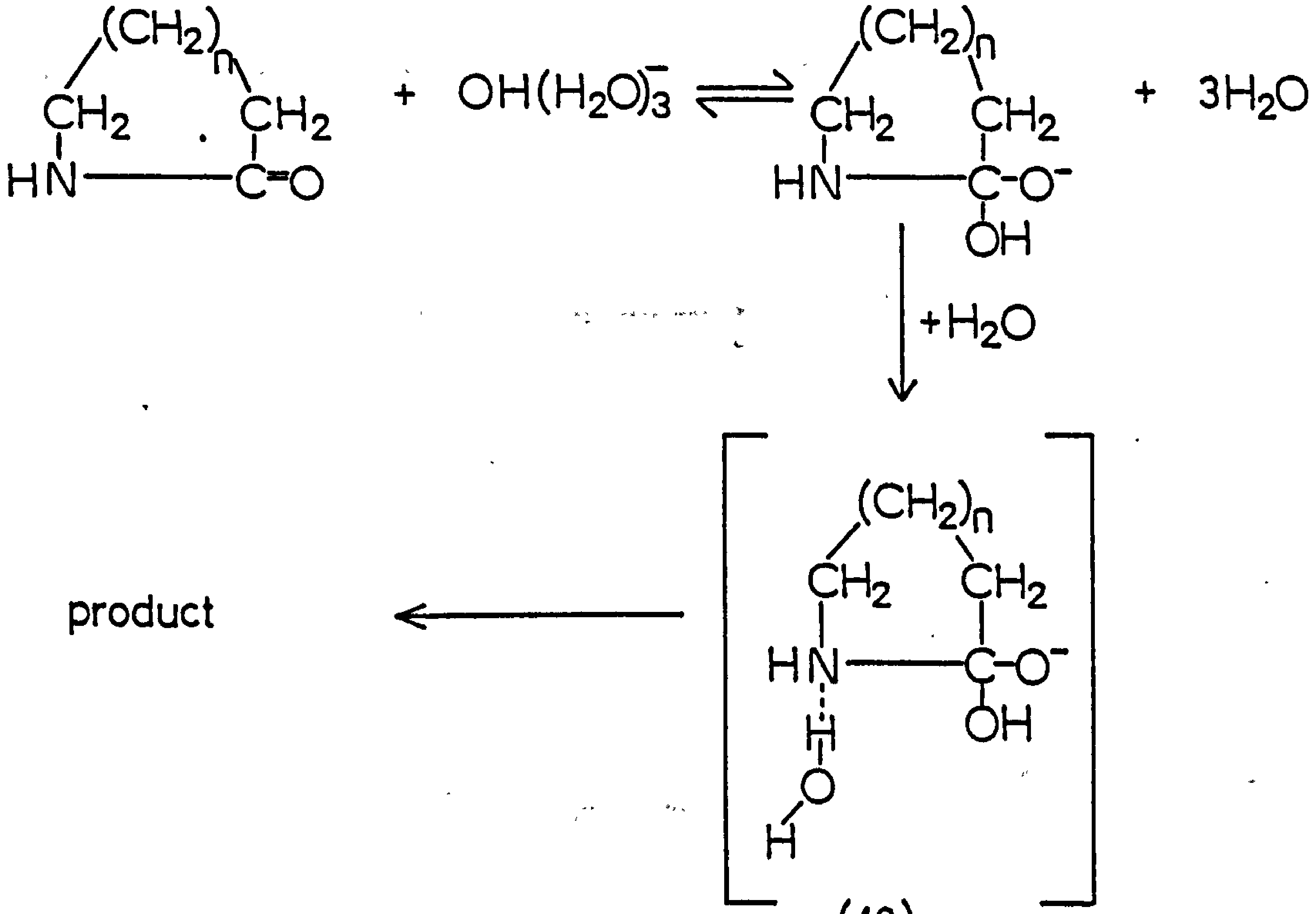
A general form of eq.(8) may be written

$$k = k' C_{OH^-} C_w^{-n} \qquad (10)$$

$$\log_{10} k/C_{OH^-} = n \log_{10} C_w + \text{constant} \qquad (11)$$

where n is the number of water molecules which are lost or gained during the formation of the transition state.

In the base catalysed cleavage of caprolactam, valerolactam and enantholactam a value of n = -2 was obtained[182]. Addition of a hydroxide ion to the carbonyl group prior to bond cleavage requires the loss of three water molecules, and a value of -3 might have been expected. It has been suggested, however, that bond cleavage is assisted by a water molecule acting as a general acid, donating the required hydrogen to the incipient amine (40), thus accounting for the observed value of -2.



(40)

This approach has been successfully applied to a wide range of reactions in acid solutions[182]. From the general equation

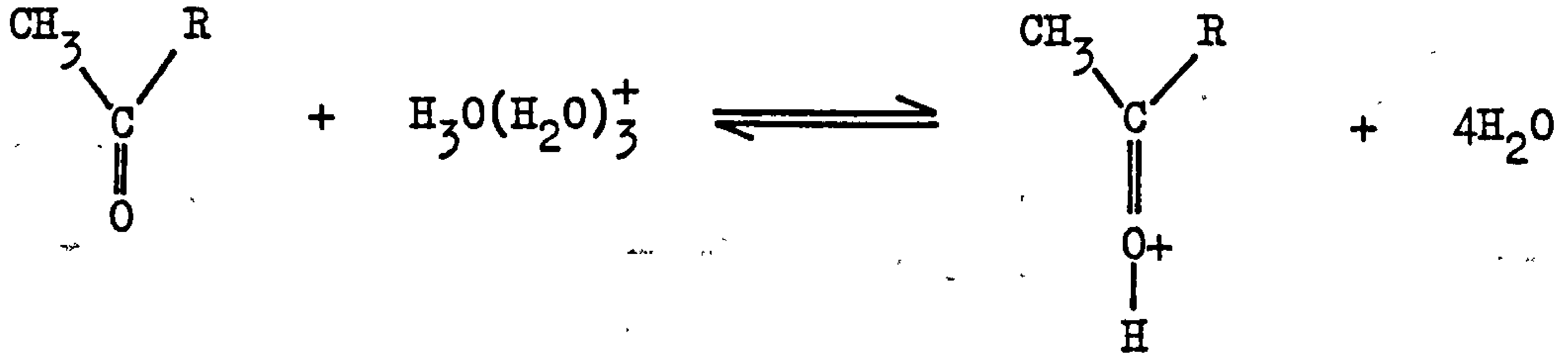
$$k = k' C_{H^+} C_w^{\,n} \, Q \qquad (12)$$

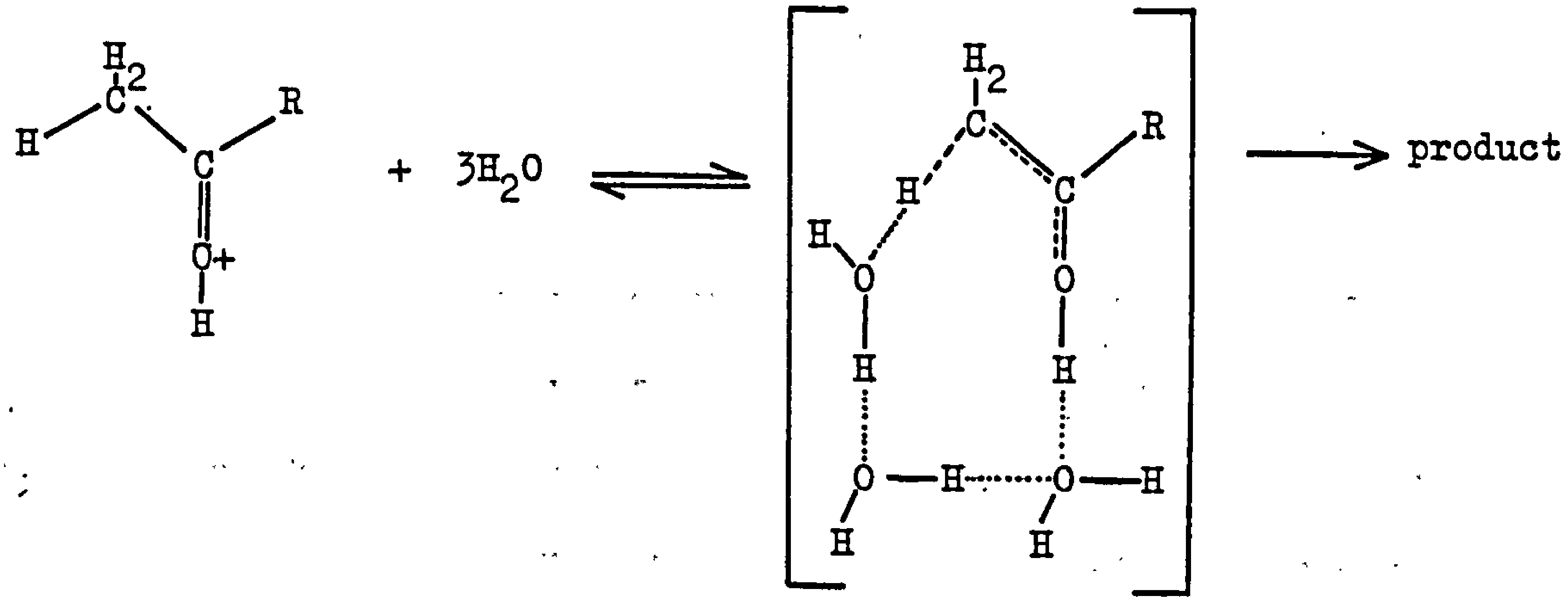
where

$$Q = \frac{f_s F_{H^+}}{f^{*} f_w^{\,n}} \qquad (13)$$

straight line plots of $\log_{10} k/C_{H^+}$ against $\log_{10} C_w$ or $\log_{10} V_w$ may be expected, as long as Q is unity or, at least, constant.

The enolisation of ketones gave straight line plots over a considerable concentration range, with slopes close to -1[182]. Abstraction of a proton from the oxygen-protonated ketone is known to be the rate determining step in this reaction. Since protonation of the ketone involves an increase of four water molecules to the medium, three water molecules must be assumed to participate in the formation of the transition state (41) to account for the overall order.

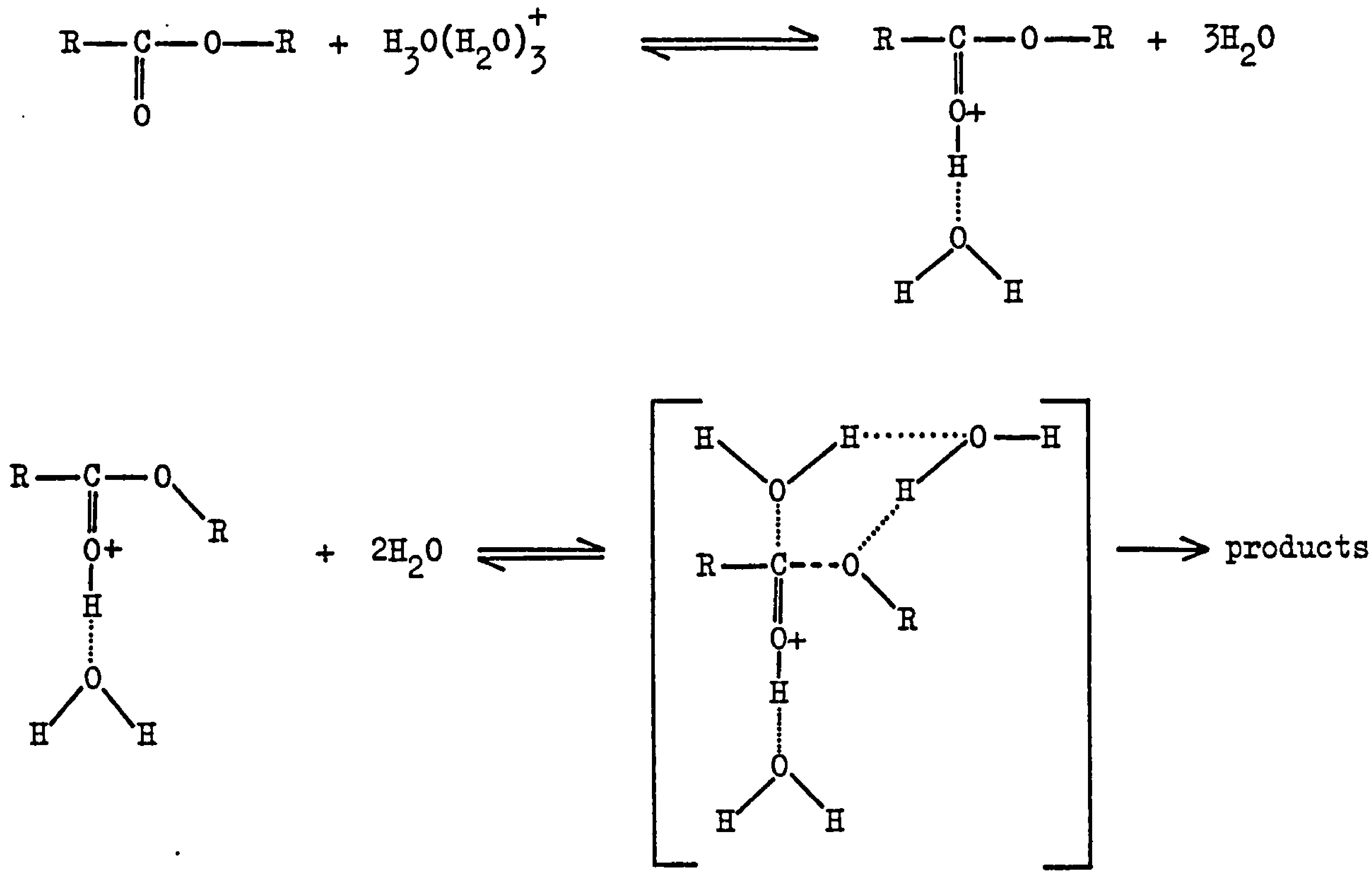




(41)

In the suggested transition state (41)one water molecule is thought to act as a base, ready to accept the C-H hydrogen, whilst a second solvates the acid proton to the carbonyl group. The exact role of the third water molecule is less certain.

Similarly, the value of -1 obtained for the hydrolysis of esters has been explained thus[182]:



The hydrolysis of aziridinium ions has been studied under conditions where the ion was already protonated over the acid concentration range of interest[183]. The reaction showed a first order dependence on water concentration[184]. Since the substrate was already protonated the loss of four water molecules during the protonation equilibrium did not contribute to n, and the relationship between the reaction rate and C_w is simplified.

$$k = k_o C_w^n \qquad (14)$$

or

$$\log_{10}k = \log_{10}k_o + n \log C_w \qquad (15)$$

CHAPTER 4

THE DETERMINATION OF THE HYDRATION NUMBER OF 1,4-DIOXANE

The number of water molecules associated with an organic solvent molecule has been determined for pyridine and dimethylsulphoxide (DMSO) as one and two respectively[185]. The method used compared the basicity (as expressed by the indicator scale H_-), of an aqueous hydroxide solution in the presence of the solvent, with its basicity in pure water. A considerable increase in H_- was observed in all cases as the solvent content was raised, and the rates of increase have been shown to be in the order pyridine $<$ sulpholane $<$ DMSO. The addition of DMSO to an aqueous hydroxide solution (0.011 M tetramethylammonium hydroxide), resulted in an increase in H_- from 12 in pure water to 26 in 99.5 % DMSO[186].

When the solvent composition was kept constant and the concentration of added base varied, the basicity of the solution was found[187] to increase according to the simple relationship

$$H_- = \log_{10} \frac{[OH^-]_a}{[OH^-]_b} \qquad (16)$$

where $[OH^-]_a$ and $[OH^-]_b$ are the concentrations of added base. This was shown to hold for aqueous pyridine, aqueous sulpholane and aqueous DMSO, provided the water concentration was not very low, in which case the basicity increased much more rapidly.

The observed change in H_- has been explained in terms of the equilibrium between the hydroxide ion and the indicator acid, HB,

$$OH(H_2O)_3^- + HB \rightleftharpoons B^- + 4H_2O \qquad (17)$$

in which the hydroxide ion is closely associated with three water molecules[179-181]. The effect of adding a non electrolyte is two-fold: it displaces some water molecules, and binds additional "free water" molecules. Both of these effects will tend to shift the equilibrium further over to the right, and so the hydroxide ions appear to be more basic than they would be in pure water.

4.I. EXPERIMENTAL DETERMINATION OF BASICITY

In order to compare the basicity of two solutions it is necessary to consider what is meant by basicity and to understand how it may be measured experimentally. The indicator acidity function H_- is a measure of the ability of a solution to remove a proton from a weak acid. It has been derived for aqueous alkali metal hydroxide solutions by Yagil and Anbar[181], in a similar manner to Bascombe and Bell's treatment[179,180] of the H_o function for concentrated acid solutions. The acid-base equilibrium involving the hydroxide ion may be generally expressed by

$$BH + OH(H_2O)_n^- \rightleftharpoons B^- + (n+1)H_2O \qquad (6)$$

where n is the hydration number of OH^-. The equilibrium constant for the equation will be

$$K = \frac{a_{B^-} a_{H_2O}^{n+1}}{a_{BH}\ a_{OH^-}}$$

Where a_{B^-}, a_{BH}, $a_{H_2O}^{n+1}$, a_{OH^-} are the activities of the ionised form of the acid, the unionised acid, the free water and the hydroxide ion respectively. By analogy with the treatment of Bascombe and Bell, the ratio of the activity coefficients has been assumed to be equal to unity and a molar equilibrium applied.

$$K_c = \frac{C_{B^-}\ C_{H_2O}^{n+1}}{C_{BH}\ C_{OH^-}} \qquad (19)$$

where C is the molar concentration.

The H_- indicator acidity function is defined[188]

$$H_- = \log_{10} \frac{C_{B^-}}{C_{BH}} + pK_a \tag{20}$$

where pK_a is the dissociation constant of the acid BH

$$BH \rightleftharpoons B^- + H^+ \tag{21}$$

$$K = \frac{a_{B^-}\, a_{H^+}}{a_{BH}} \tag{22}$$

$$\therefore \quad pK_a = -\log_{10} \frac{a_{B^-}\, a_{H^+}}{a_{BH}} \tag{23}$$

The acidity function of the solution may therefore be expressed by

$$H_- = -\log_{10} \frac{a_{H^+}\, f_{B^-}}{f_{BH}} \tag{24}$$

where f denotes the activity coefficients of the indicator. In dilute aqueous solutions where the activity of the hydrogen ion becomes equal to its concentration, and the activity coefficients of the indicator approach unity the function H_- becomes identical with pH.

Measurement of H_- is usually carried out using absorption spectrophotometric estimation of the acid and/or its conjugate anion. A suitable group of weak acids is required, which should have pK values in the range 12-19. The acid should lose a proton in dissociation and ionisation must be rapidly established. The compound should be sufficiently soluble in hydroxide solutions, stable against hydrolysis by alkali, and either the acid and/or base form should absorb light appreciably above 230 nm, where OH^- begins to absorb.

A wide range of compounds have been employed as acid indicators with varying degrees of success. Schwartzenbach and Sulzberger[189] were the first to attempt the construction of an H_- acidity scale using aqueous potassium and sodium hydroxide solutions, and indigo derivatives as their acid indicators.

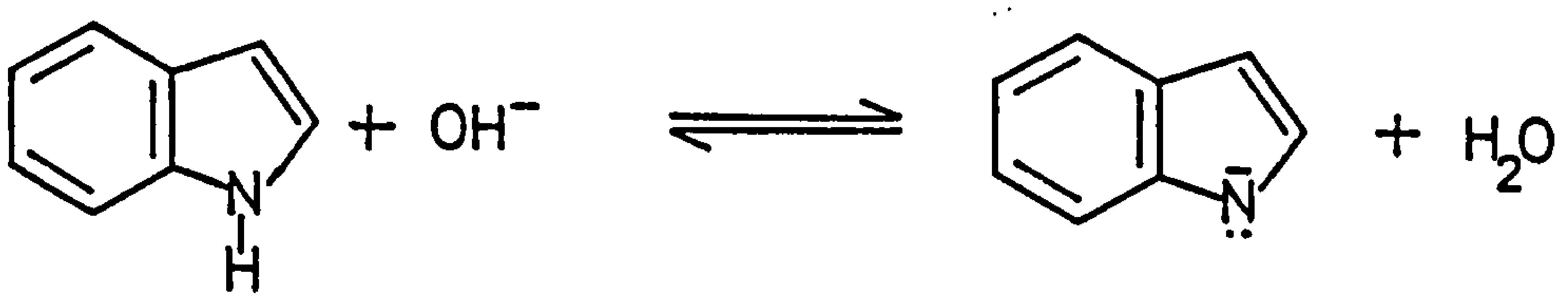
One group of commonly used compounds are the nitro derivatives of aniline, which have been employed in several solvent systems including hydrazine[190-192], ethylene diamine[192], methanol[193-196], ethanol[197], DMSO[198-200], sulpholane[200], pyridine[201] and others. It has been suggested however, that the ionisation of these compounds may proceed by losing a proton from the ring in some cases, whilst in others, an OH^- or RO^- ion is added to the ring. It has been reported[185] that the red colours of trinitrobenzene and 2,4-dinitroaniline were not formed in aqueous solutions, unless traces of alcohol were present suggesting involvement of RO^- in base formation. The use of these compounds has also been criticized because the reaction has not always been found to be reversible, nor was the base form always stable.

Another group of compounds with suitable pK values for use as indicators is the alcohols. Aliphatic alcohols, however, do not absorb above 230 nm and phenols reach pK 13-14 only if they are internally hydrogen bonded, or substituted with a bulky group in the ortho position[202,203].

The use of carboxylic acids is also limited because of difficulties in determining pK accurately. The ions formed from suitable acids showed a tendency to undergo unusual spectral shifts as the degree of ionisation changed which may have been due to the formation of radical anions[204]. Poor solubility in water further complicated the derivation of valid H_-

scales anchored in water.

Derivatives of indole have also been used as acid indicators[185,205]. In alkaline solutions a new absorption generally occurred between 310 and 320 nm. Single ring heterocyclic compounds such as imidazole and pyrrole were rejected because they did not absorb at a high enough wavelength. Ionisation was believed to proceed thus:



Abstraction of a proton from the ring has been ruled out, by determining the pK of derivatives in which almost every hydrogen has been substituted. No abnormalities were observed in the values of pK, or, in the spectrum of the ionised acid. Addition of OH^- to the ring is also unlikely, because resonance stabilisation is greater in the indolate anion (eight possible structures), compared to the eight possible OH^- adducts (two or three possible resonance structures).

In order that the H_- scale be an extension of the conventional pH scale, the pK of the most acid indicator must be determined by measuring the ionisation ratio within the pH region. Indicators most frequently used for this purpose include 3-formylindole and benzimidazole[185], and 2,4,6-trinitroaniline[198]. The ionisation ratio (r) of the indicator is measured in aqueous buffers and sodium hydroxide, and a plot of $\log_{10}$ r against $\log_{10} C_{OH^-}$ constructed. This should give a straight line of unit slope, indicating that the activity coefficient ratio $f_{B^-}f_w/f_{BH}\,f_{OH^-}$ is very close to unity, so that correction of this term, (by determining the pK at several constant ionic strengths, and extrapolating to zero ionic strength), is unnecessary. Considerable variation in this term would not be expected, since both the numerator and the denomenator contain a single negative charge, so that the electrostatic contribution is largely cancelled. The pK of the indicator can be determined from the value of C_{OH^-} at which $\log_{10} r$ is zero, that is $C_{B^-} = C_{BH}$

$$pK = 14.00 - \log_{10} C_{OH^-}^{r=1} \qquad (25)$$

Construction of the H_- scale begins by deriving the pK of an "overlapping" indicator, from the relationship

$$pK_2 = pK_1 + (\log_{10} r_2 - \log_{10} r_1) \qquad (26)$$

This expression holds at each value of C_{OH^-}, provided that $(f_{B^-}/f_{BH})_1 = (f_{B^-}/f_{BH})_2$, that is, provided that plots of $\log_{10} r$ against $\log_{10} C_{OH^-}$ for the series of indicators, run parallel, which is a basic assumption of the indicator acidity concept. The difference in $\log_{10} r$ between two overlapping indicators at several hydroxide concentrations may be averaged, and this value of ΔpK used to determine pK of the second indicator, and hence, H_-. The process can then be repeated to determine the pK values of increasingly less acidic indicators, until values have been assigned to the whole series.

From the calculated pK values and ionisation ratios, H_- may be calculated from the relationship which defines the scale,

$$H_- = pK + \log_{10} r \qquad (27)$$

Several values of H_- are obtained at each value of C_{OH^-} , since there are several indicators for which $0.1 < r < 10$ at each hydroxide concentration.

Determination of H_- in a mixed solvent in which C_{OH^-} is kept constant as the concentration of organic solvent is increased is carried out in a similar manner[198]. Once again the pK of the most acid indicator is determined in aqueous buffers in order to anchor the scale to the pH region. The ionisation ratio of this indicator is then measured in solutions containing known amounts of organic solvents. The H_- values of these solutions are thus considered known. By comparing the ionisation ratios with those of an overlapping indicator in solutions of the same composition, the pK of the second indicator is determined. This may be used to measure H_- for new solvent mixtures and to determine the pK of the next overlapping indicator.

Once the difference in basicity of the aqueous solvent mixture is known relative to pure water at the same hydroxide ion concentration, the hydration number of the solvent molecule can be calculated[206], by dividing the molarity of bound water, (total water: n_1 - bulk water; n_w) by the molarity of the solvent present (n_2).

$$\text{hydration number:} \quad h = \frac{n_1 - n_w}{n_2} \qquad (28)$$

The number of moles of bulk water present in one litre is given by

$$n_w = 55.40\ V_w \qquad (29)$$

assuming that the partial molar volume of bulk water remains 18.05 ml. at all compositions. The volume fraction scale is used because of the considerable difference in size between water and the solvent molecule, particularly when the latter is hydrated. V_w, the volume fraction of bulk water is calculated from the equation

$$\Delta H_- = -4 \log_{10} V_w \qquad (30)$$

It has been shown, using this method, that in aqueous solutions of DMSO below concentrations of 52 % the number of water molecules bound to DMSO is almost constant[206]. The value obtained was very close to two, in good agreement with values previously suggested. At higher concentrations of DMSO the hydration number decreased, presumably due to a deficiency of water molecules. Pyridine has similarly been shown to have a hydration number of one.

CHAPTER 5

PLUG FLOW REACTORS IN CHEMICAL KINETICS[207]

Plug flow reactors are characterized by the fact that the orderly flow of fluid through the reactor allows no element of fluid to overtake any other element. Consequently, there should be no diffusion or mixing of fluid along the flow path, (although there may be lateral diffusion), and all elements of fluid should have the same velocity. A necessary condition for plug flow is that the residence time in the reactor is the same for all elements of fluid.

The relationship between the feed rate F_{AO},

$$F_{AO} = \frac{\text{moles of reactant A entering}}{\text{time}} \tag{31}$$

and reactor volume V, is conveniently expressed in a flow system by the terms space time and space velocity, which are defined

$$\text{Space time} = \tau = \frac{1}{S} = \begin{array}{l}\text{time required to process one reactor}\\ \text{volume of feed measured at specific}\\ \text{conditions}\end{array}$$

$$= \text{time} \tag{32}$$

$$\text{Space velocity} = S = \frac{1}{\tau} = \frac{\text{(Vol. of entering feed at specified conditions/time)}}{\text{void volume of reactor}}$$

$$= \text{time}^{-1} \tag{33}$$

Thus a space time of five seconds means that every five seconds one reactor volume of feed at specified conditions, is being treated in the reactor. The corresponding space velocity would be 0.20 sec^{-1}, that is, 0.20 reactor volumes of feed at the same conditions are being fed into the reactor every second.

The conditions of temperature, pressure and state (gas, liquid or solid), at which the values for space time or space velocity are measured are arbitrary. If, as is most usual, they are those of the stream entering the reactor, the relation between τ or S and V/F_{AO} is

$$\tau = \frac{1}{S} = \frac{C_{AO}\,V}{F_{AO}} = \frac{\left(\frac{\text{moles of A entering}}{\text{volume of feed}}\right)\left(\text{volume of reactor}\right)}{\left(\frac{\text{moles of A entering}}{\text{time}}\right)} \qquad (34)$$

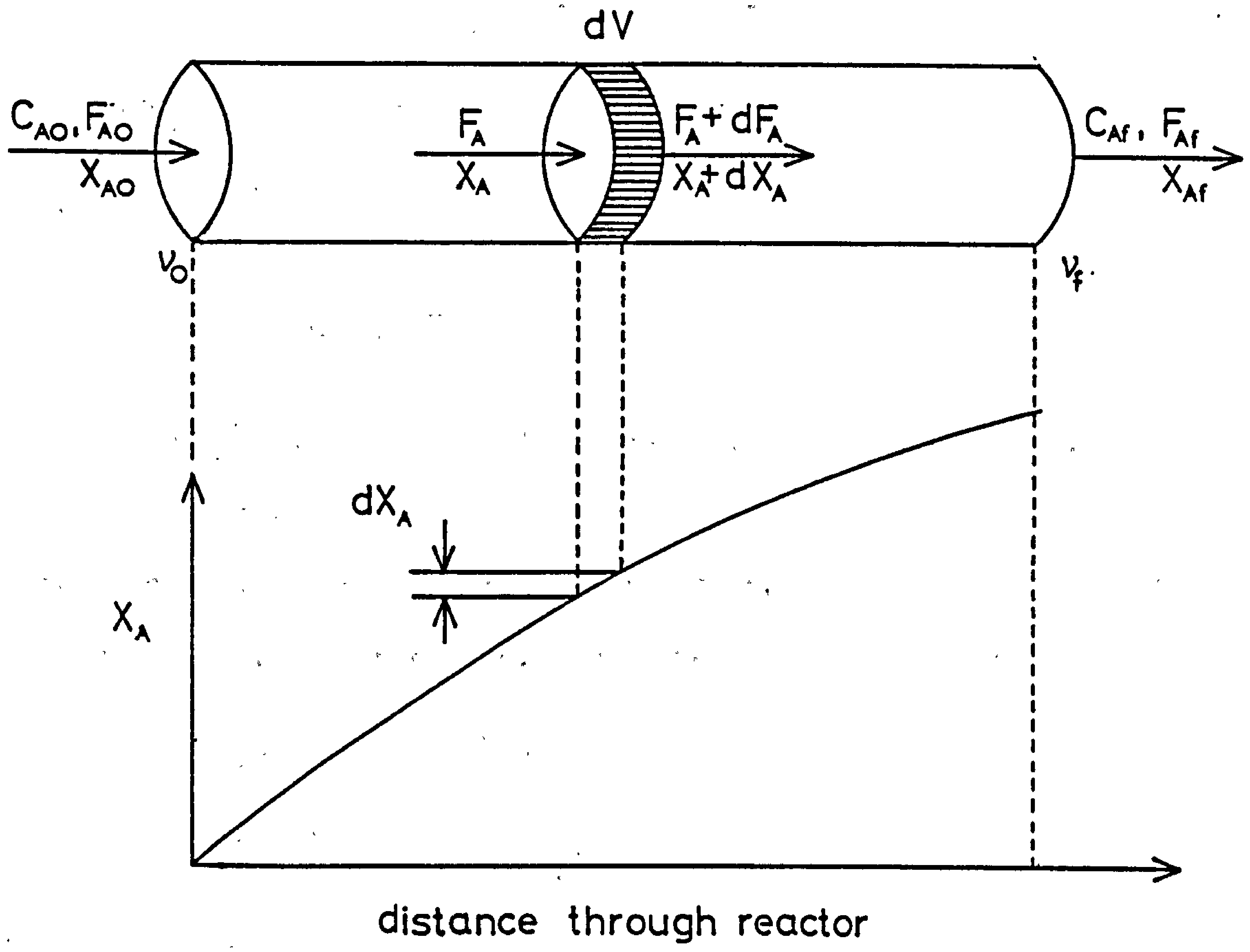
$$= \frac{V}{v_0} = \frac{\text{reactor volume}}{\text{volumetric feed rate}} \qquad (35)$$

The material balance for a reaction component must be made for a differential volume dV, since the composition of fluid varies from position to position along the flow path. Thus for a component A we obtain,

$$\text{input} = \text{output} + \text{disappearance by reaction} \qquad (36)$$

FIGURE 2

Variables for a plug flow reactor



From Fig.2. we see that for volume dV

Input of A (mol.time^{-1}) $= F_A$ (37)

Output of A (mol.time^{-1}) $= F_A + dF_A$ (38)

Disappearance of A by reaction (mol.time^{-1}) $= (-r_A)dV$

$$= \left[\frac{\text{moles of A reacting}}{(\text{time})\ (\text{volume of reacting fluid})}\right] \times \left[\begin{array}{l}\text{volume of fluid in} \\ \text{section of reactor} \\ \text{considered}\end{array}\right] \quad (39)$$

Introducing these three terms into equation (36) we obtain

$$F_A = (F_A + dF_A) + (-r_A)dV \tag{40}$$

Since

$$dF_A = d\,[F_{A0}(1 - X_A)] = -F_{A0}dX_A \tag{41}$$

where X_A is the fraction of A which has reacted.

By substitution into (40)

$$F_{A0}dX_A = (-r_A)dV \tag{42}$$

Equation (42) accounts for A in the differential volume dV. For the reactor as a whole the expression must be integrated. The feed rate F_{A0} is constant, but r_A, the rate of reaction, depends on the concentration of materials, or conversion. Grouping the terms accordingly we get

$$\int_0^V \frac{dV}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A} \tag{43}$$

Hence

$$\frac{V}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A} \tag{44}$$

or

$$\tau = \frac{V}{\nu_0} = C_{A0}\int_0^{X_A} \frac{dX_A}{-r_A} \tag{45}$$

C_{AO} being the initial concentration of A, given by

$$C_{AO} = \frac{\text{total moles of A in feed}}{\text{(volume of feed)(time of pyrolysis)}} \tag{46}$$

The plug flow reactor can be used for kinetic studies. Graphical analysis of data differs from that of static systems since the appropriate rate expression must account for the changing fluid density. The fractional change in volume of the system between zero conversion and complete conversion is expressed by ε_A.

$$\varepsilon_A = \frac{V_{XA=1} - V_{XA=0}}{V_{XA=0}} \tag{47}$$

For example, in the isothermal gas phase reaction

$$A \longrightarrow 4R$$

By starting with pure reactant A,

$$\varepsilon_A = \frac{4-1}{1} = 3$$

but with 50 % inert gas present, two volumes of reactant mixture yield on complete conversion five volumes of product mixtures, thus

$$\varepsilon_A = \frac{5-2}{2} = 1.5$$

Hence, ε_A accounts for both the reaction stoichiometry and the presence of inert gases.

For irreversible reactions of order n

$$\tau = C_{AO}\int_0^{X_A} \frac{dX_A}{kC_A^{\,n}} \tag{48}$$

allowing for expansion proportional to conversion

$$C_A = \frac{N_A}{V} = \frac{N_{AO}\ (1-X_A)}{V_0\ (1+\varepsilon_A X_A)} = \frac{C_{AO}\ (1-X_A)}{(1+\varepsilon_A X_A)} \tag{49}$$

Therefore

$$\tau = \frac{1}{kC_{AO}^{\,n-1}}\int_0^{X_A} \frac{(1+\varepsilon_A X_A)^n\ dX_A}{(1-X_A)^n} \tag{50}$$

For zero order reactions this becomes

$$k\tau = C_{AO}X_A \tag{51}$$

For irreversible first order reactions

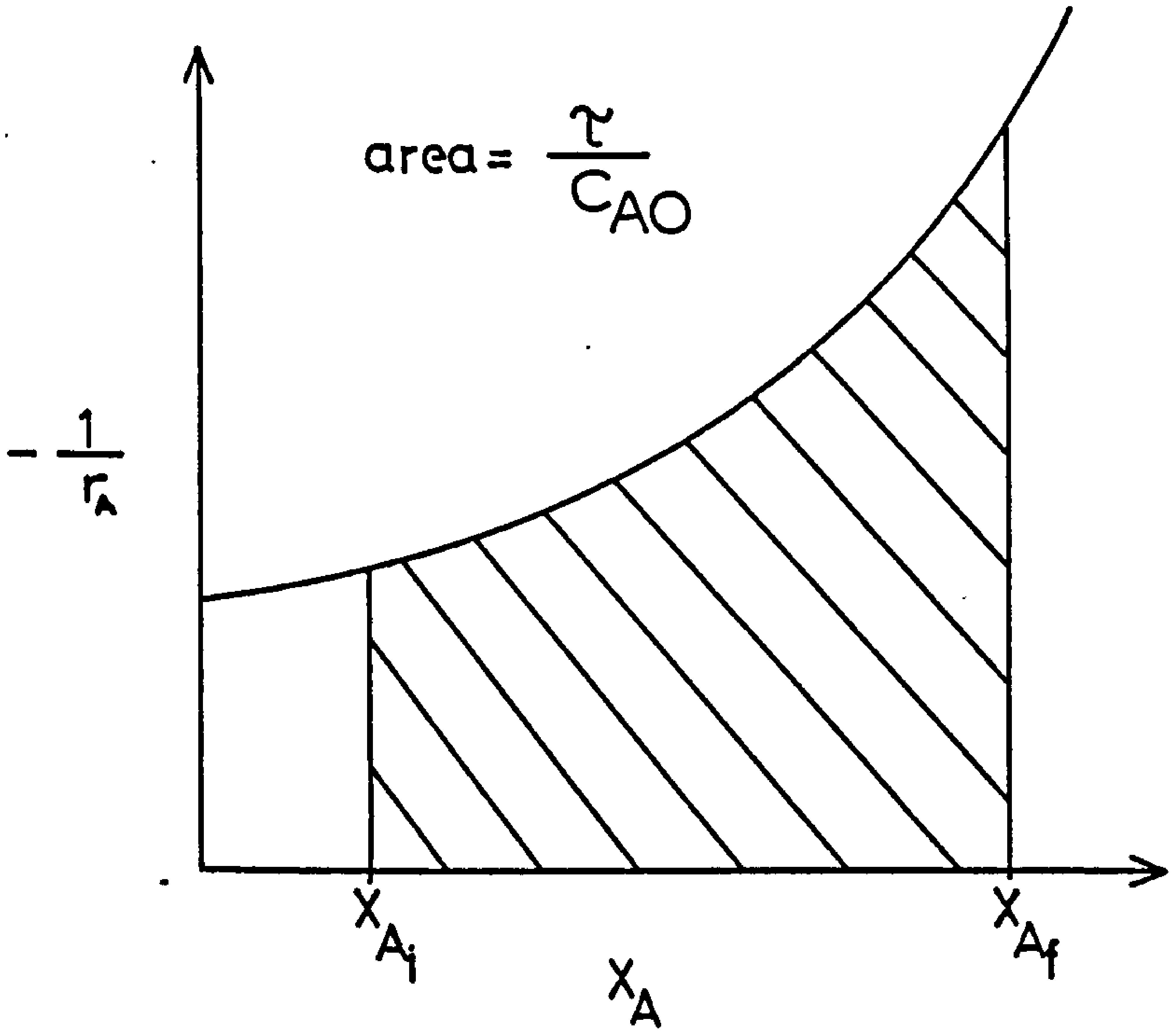
$$k\tau = (1+\varepsilon_A)\ \ln\frac{1}{(1-X_A)} - \varepsilon_A X_A \tag{52}$$

For irreversible second order reactions with one reactant A, or two reactants of equal concentrations

$$C_{AO}k\tau = 2\varepsilon_A(1+\varepsilon_A)\ \ln(1-X_A) + \varepsilon_A^2 X_A + (\varepsilon_A+1)^2\frac{X_A}{(1-X_A)} \tag{53}$$

For higher or fractional orders graphical integration is recommended. This is done by plotting $-1/r_A$ against X_A and evaluating the area under the curve between the appropriate limits, as shown in Fig.3.

FIGURE 3



To study the kinetics of a reaction using plug flow conditions a number of runs must be carried out at different space times. Each run, with a specific τ value may be compared with one particular instant of time in the static system. Consequently kinetic studies carried out in such systems are found to be much more time consuming, than studies carried out in static systems.

PART TWO

EXPERIMENTAL AND RESULTS

CHAPTER 6

THE PYROLYSIS OF CHLOROFORM

6.I GENERAL PROCEDURE FOR PYROLYSIS EXPERIMENTS

APPARATUS

i) FURNACE: A Carbolite furnace was used at an angle of 10°, to ensure that the chloroform ran into the preheater.

ii) PREHEATER: The preheater consisted of a pyrex tube (71 cm. long, 1.9 cm. i.d.), closely wound with electrothermal heating tape. A rheostat was used to control the temperature at approximately 160°C, thus vapourising the chloroform before it entered the reaction tube.

iii) REACTION TUBE: Pyrolysis was carried out in a silica tube (44.0 cm. long, 1.9 cm. i.d.).

iv) NITROGEN GAS FLOWMETER: A 'Quickfit' gas flowmeter was used to control the flow rate of the nitrogen carrier gas, (British Oxygen Company Ltd., white-spot, oxygen free nitrogen). The manometer, which contained dibutyl phthalate as the manometric fluid, was adjusted to give a flow rate of 19.30 $l.h^{-1}$. (22°C).

v) PURIFICATION AND DRYING OF NITROGEN: The nitrogen was purified and dried by passing it through a series of Dreschel bottles containing the following reagents.

a) Fieser's solution: Traces of oxygen present in the gas were removed by Fieser's solution[208].

b) Safety trap: The nitrogen passed through an empty bottle before it was bubbled through concentrated sulphuric acid, to prevent the acid coming into contact with the alkaline Fieser's solution in the event of sucking back.

c) Concentrated sulphuric acid: Passing the nitrogen through conc. sulphuric acid removed any basic impurities and traces of water.

d) Drying tower: Soda-lime was used to ensure that the nitrogen was dry when it entered the furnace.

e) Mercury safety tube: A safety tube containing mercury was present to release any pressure which might build up as the result of a blockage in the apparatus.

vi) COOLING TRAPS: The reaction products emerging from the reactor were collected, and separated from the carrier gas, by condensing them in a series of cooling traps.

a) Trap one: Most of the products were retained in the first trap which consisted of a 2-litre round-bottomed flask kept at 0°C by immersion in an ice/water mixture.

b) Traps two and three: Tubular traps cooled to -78°C by a mixture of cardice and acetone.

c) Trap four: A spiral trap cooled to -190°C by liquid nitrogen.

viii) BUBBLER: The effluent gases (nitrogen and hydrogen chloride) were passed through dibutyl phthalate and then vented to the atmosphere. The bubbler was used to indicate any leaks or blockages that occurred in the apparatus.

ANALYSIS

Products were analysed both qualitatively and quantitatively by gas liquid chromatography (g.l.c.). A Pye 104 or a Pye Unicam G.C.D. chromatograph fitted with flame ionisation detectors were used, with nitrogen carrier gas (45 mls. min.^{-1} unless otherwise stated). The G.C.D. instrument was attached to a Pye-Unicam DP 88 computing integrator. Where preparative g.l.c. was required, a Pye 105 instrument was used with manual operation. The analytical columns used in this work are given below. All columns were made of glass, 4 mm. i.d., 1.5 m. in length.

Column 1: Apiezon 'L', (5 %) on Diatomite 'M' (60-80 mesh), acid washed and treated with dimethyldichlorosilane.

Column 2:. Tricresyl phosphate (5 %) on Diatomite 'C' (60-80 mesh), acid washed and treated with dimethyldichlorosilane

Column 3: Carbowax 20M (15 %) on Diatomite 'C' (60-80 mesh), acid washed and treated with dimethyldichlorosilane.

Mass spectral analysis was carried out using a combined gas chromatograph/ mass spectrometer. A Perkin-Elmer model 881 gas chromatograph was linked to a Hitachi-Perkin-Elmer RMS 4 mass spectrometer.

EXPERIMENTAL PROCEDURE

The silica reaction tube was cleaned prior to each run to remove any carbonaceous deposit from the previous experiment. This was done by passing a stream of oxygen through the tube, whilst heating it to a

Fig. 4 Pyrolysis Apparatus

high temperature, thus oxidising the carbon. It was hoped that by treating the tube in this way, the reaction tube surface would be reproduced as closely as possible for each experiment.

The apparatus was set up as shown in Fig.4. taking care that no stresses built up. Nitrogen was passed through the system, the furnace and preheater were switched on and left for two hours to allow equilibration at the operating temperature (510°C, 783 K).

The chloroform (British Drug Houses, analar grade) was introduced dropwise into the preheater from a pressure-equalising dropping funnel, and the time taken to introduce the chloroform recorded. It was very important that the drop-rate was constant in order to maintain plug flow conditions, particularly in kinetic studies. The chloroform was vapourised in the preheater and swept into the reaction tube, by the nitrogen, where pyrolysis occurred. The products and unreacted chloroform condensed in the cooling traps. When the addition was complete, the furnace and preheater were switched off, the nitrogen flow rate reduced, and the cooling baths removed. Once the traps had warmed to room temperature the products were transferred into a volumetric flask, to which the chloroform washings from the traps and reaction tube were added. The solution was made up to the required volume with chloroform and analysed by g.l.c. .

CALCULATION OF SPACE TIME

The space time (τ) is given by the formula

$$\tau = \frac{T_p \times V}{N}$$

where: T_p = Time of pyrolysis (sec.)

V = The internal volume of the reaction tube in the furnace (ml.)

N = Total number of moles of reactant (chloroform) and nitrogen passed through the reaction tube, as a volume at the operating temperature and pressure (ml.).

A worked example of the calculation of space time is given below, for a typical run.

Temperature of pyrolysis = 783 K.

Pressure of reactor = 770 mmHg.

Diameter of reaction tube = 1.9 cm.

Length of reaction tube inside the furnace = 44.0 cm.

$\therefore$ Volume of reaction tube $= \pi r^2 l = 3.142 \times 0.95^2 \times 44.0$ ml.

$= 124.8$ ml.

Moles of chloroform = 0.25 mol.

Volume of chloroform (783 K, 770 mmHg) = 15.86 l.

Time of pyrolysis = 971 sec.

Nitrogen flow rate = 19.30 l.h^{-1} (295 K, 760 mmHg).

Volume of nitrogen passed in 971 sec. (783 K, 770 mmHg) $= \frac{19.30}{3600} \times 971 \times \frac{783}{295} \times \frac{760}{770}$ l.

$= 13.64$ l.

Total volume of feed = (15.86 + 13.64) l. = 29500 ml.

$$\text{Space time, } \tau = \frac{124.8 \times 971}{29500} \text{ sec.}$$

$$\tau = 4.11 \text{ sec.}$$

6.I.i. PYROLYSIS OF CHLOROFORM AT 510°C

Chloroform (29.85 g, 0.25 mol.) was pyrolysed at 510°C, and the products of the reaction analysed by g.l.c. and g.l.c./mass-spectrometry. Products were identified by comparing their g.l.c. retention times and mass spectral breakdown patterns with those of authentic samples. The compounds present were commercially available, apart from pentachlorobutadiene which was prepared according to the method given in the literature[209].

The following compounds were identified in the product mixture.

TABLE 4

Products from chloroform pyrolysis at 510°C

Compound	Approx.molar % of products	Retention time (sec.) Column 1 (110°C)	Retention time (sec.) Column 2 (70°C)
Dichloromethane	14.2	46	34
Carbon tetrachloride	10.2	62	48
Trichloroethylene	8.5	70	77
Tetrachloroethylene	18.4	120	137
sym-Tetrachloroethane	< 1	196	—
Pentachloroethane	24.3	308	1060
Hexachloroethane	20.3	576	1323
Pentachlorobutadiene	< 2	1080	—
Hexachlorobutadiene	< 2	1342	—

TABLE 5

Mass spectra of products from chloroform pyrolysis

Compound	Molecular ion m/e	Mass-spectral breakdown pattern m/e (relative abundance)
Dichloromethane	84	49(100), 43(85.9), 84(49.4), 58(25.9), 47(20.0), 40(18.8), 44(14.1), 29(14.1).
Carbon tetrachloride	152	117(100), 119(97.3), 47(50.1), 35(48.7), 121(32.4), 82(29.0), 84(18.7), 37(15.1).
Trichloroethylene	130	95(100), 130(91.9), 60(50), 83(35.7).
Tetrachloroethylene	164	166(100), 129(80), 164(77.3), 131(75.1), 94(50.8), 168(47.6), 47(36.2), 96(31.9).
Pentachloroethane	200	117(100), 119(99.9), 165(99.9), 163(87.2), 167(67.2), 83(61.3), 60(52.6), 130(50.5).
Hexachloroethane	234	117(100), 119(99.9), 201(99.9), 203(74.4), 199(71.8), 166(64.1), 164(61.8), 94(58.5).
Pentachlorobutadiene	224	191(100), 189(77.7), 226(54.2), 193(48.6), 84(33.3), 228(31.9), 224(31.9), 154(30.6)
Hexachlorobutadiene	258	225(100), 227(70.5), 223(69.2), 190(50.0), 118(44.8), 188(39.7), 260(34.6),141(33.3).

Since the amount of chloroform which had reacted could not be measured directly, it was determined from the amount of products formed. The stoichiometry of the reaction was based on the number of carbon atoms present in the product molecule. Thus, for every mole of carbon tetrachloride or dichloromethane, one mole of chloroform was assumed to have reacted, and two moles of chloroform for every mole of tetrachloroethylene, pentachloroethane, etc.. The concentration of each product was calculated from a calibration curve of peak area against concentration, which was determined for each compound present in the mixture. A typical result from a pyrolysis run is shown below.

TABLE 6

Quantitative analysis of products from the pyrolysis of chloroform at 510°C

Compound	Peak area	Concentration (mol.l.$^{-1}$ x 10^2)	Moles formed x 10^3	Moles chloroform reacted x 10^3
CH_2Cl_2	5275	0.65	0.33	0.33
CCl_4	4014	0.10	0.05	0.05
C_2HCl_3	23938	0.80	0.40	0.80
C_2Cl_4	73763	4.60	2.30	4.60
C_2HCl_5	78539	7.36	3.68	7.36
C_2Cl_6	113338	4.60	2.30	4.60
C_4HCl_5	2758	0.075	0.038	0.15
C_4Cl_6	4955	0.120	0.060	0.24

Total amount of chloroform which had reacted = 0.01813 mol.

Total amount of chloroform used = 0.25 mol.

∴ Fraction of chloroform reacted (X_A) = 0.0725

6.I.ii. ANALYSIS OF EFFLUENT GAS FOR THE PRESENCE OF HYDROGEN AND CHLORINE

The effluent gas was analysed chemically for the presence of chlorine, and by g.l.c. for the presence of chlorine and hydrogen.

Chemical analysis for chlorine

Chlorine gas can be detected and determined quantitatively by bubbling the gas through potassium iodide solution. The reaction of chlorine with potassium iodide results in the liberation of iodine which may be determined either by titration with standard sodium thiosulphate solution, or colourimetrically, by measuring the absorbance of the solution at 350 nm.

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

Chlorine gas (British Oxygen Co. Ltd.), was bubbled through a solution of potassium iodide (4 %, weight/volume), which was shaken vigorously. Two aliquots (25 ml.) were removed and titrated against sodium thiosulphate solution (1.04×10^{-3} M) which had previously been standardised against a potassium iodate solution. On obtaining a pale straw colour, fresh starch indicator was added and the titration continued until the blue solution became colourless.

The absorbance of a third aliquot was measured (360 nm) relative to distilled water, using a Pye-Unicam S.P.600 spectrophotometer. Measurements were made at 360 nm. as opposed to the wavelength of maximum absorbance, 350 nm, since the latter was the limit of the instrument's range, and measurements at this wavelength might have given rise to inaccuracies.

The experiment was repeated, bubbling chlorine through the potassium iodide solution for different lengths of time. From the concentration of iodine liberated, the concentration of chlorine in the solution could be determined. A calibration curve of absorbance against concentration of chlorine could then be plotted.

Example of calculation: Solution 1.

Volume of sodium thiosulphate soln. used = 68.93 ml.

Concentration of sodium thiosulphate soln. = 1.04×10^{-3} mol. $l.^{-1}$

1 mole of I_2 reacts with 2 moles of $Na_2S_2O_3$

$$\therefore \text{concentration of iodine soln.} = \frac{68.93 \times 1.04 \times 10^{-3}}{25 \times 2} \text{ mol. } l.^{-1}$$

$$= 1.432 \times 10^{-3} \text{ mol. } l.^{-1}$$

1 mole of iodine is displaced by 1 mole of chlorine

$$\therefore \text{concentration of } Cl_2 = 1.432 \times 10^{-3} \text{ mol. } l.^{-1}$$

$$= 0.10153 \text{ g. } l.^{-1}$$

$$= 101.5 \text{ ppm.}$$

TABLE 7

Calibration curve for chlorine concentration against absorbance at 360 nm.

Solution No.	Sodium thiosulphate used (ml.)	Concentration chlorine (ppm)	Absorbance (360 nm. 1 mm. path length)
1	68.93	101.5	1.661
2	24.50	36.1	0.667
3	109.15	160.8	2.0
4	43.20	63.7	1.108
5	5.03	7.4	0.253
6	65.95	97.2	1.603
7	14.50	21.4	0.312

To determine whether the absorbance due to iodine was affected by nitrogen bubbling through the solution, an aliquot of solution 4 was taken and nitrogen passed through it for 15 minutes. The absorbance was remeasured and found to be unchanged.

Analysis of effluent gas

Chloroform (29.85 g) was pyrolysed in the usual manner and the effluent gas was passed through two Dreschel bottles containing potassium iodide solution (150 ml, 4 % w/v and 150 ml, 2 % w/v respectively), instead of the normal dibutyl phthalate bubbler. At the end of the run the cold traps were allowed to warm up to room temperature so that any gases which had condensed in the traps would vapourise and be swept through the potassium iodide solutions. The space time of the reaction was 5.87 sec..

The absorbance of the solutions was measured at 360 nm. relative to distilled water. No absorbance was observed for either solution, even when the path length of the cells was increased to 1 cm. Aliquots were taken from each solution and starch indicator added, but no blue colouration due to the presence of iodine developed.

Chromatographic analysis for chlorine and hydrogen

Apparatus

A Perkin-Elmer F17 gas chromatograph, with a katharometer detector (100°C) and nitrogen carrier gas (11 ml. min.$^{-1}$) was used. The columns were glass, 2 m. long, 3 mm. i.d.

Column 4: Molecular sieve 5A

Column 5: Poropak Q

TABLE 8

Identification of hydrogen and chlorine
by gas chromatography

Gas	Retention time (sec.) Column 4 (50°C)	Retention time (sec.) Column 5 (50°C)
Hydrogen	69	54
Chlorine	—	378

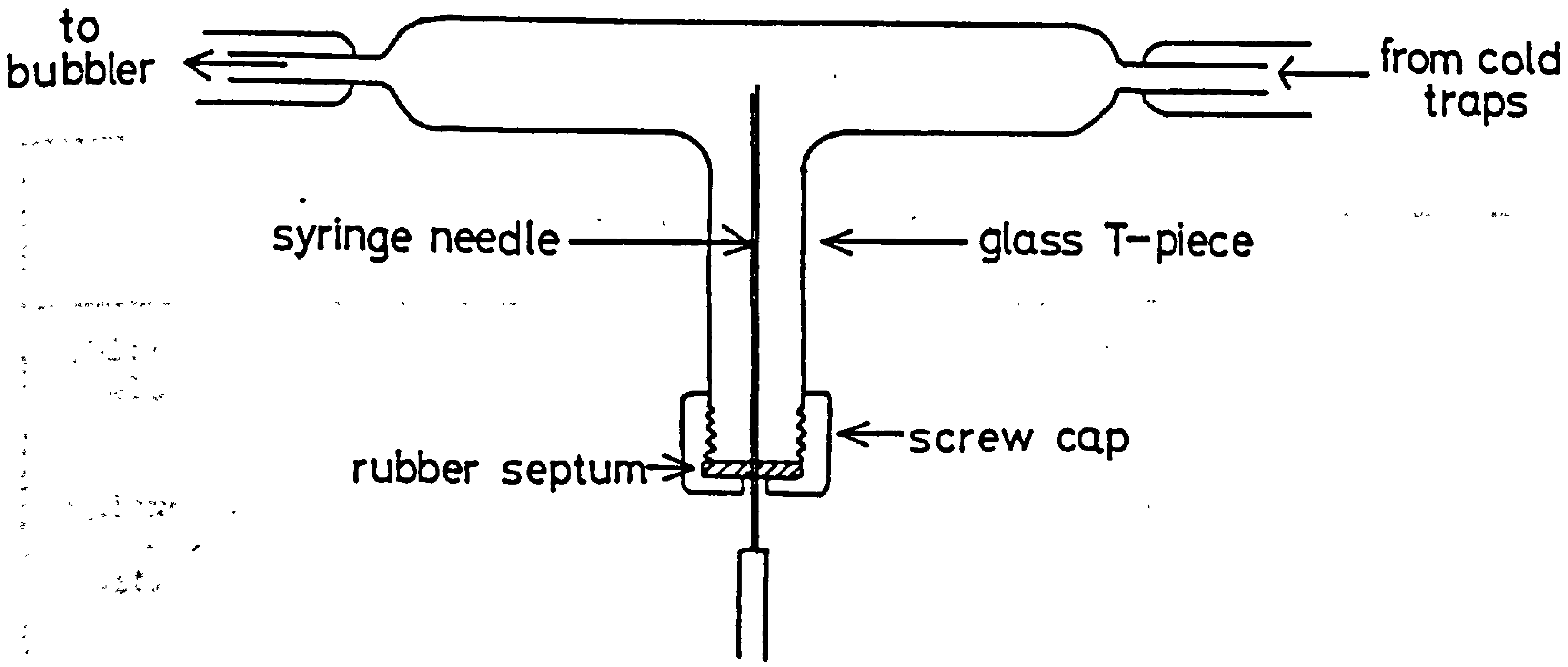
The lower limit of detection for the two gases was found to be 500 ppm.

Analysis of effluent gas

A glass T-piece was connected between the last cold trap of the pyrolysis apparatus and the dibutyl phthalate bubbler. The third arm of the T-piece was sealed with a rubber septum, through which it was possible to withdraw samples from the main gas stream using a syringe.

FIGURE 5

Glass T-piece used in sampling effluent gas



Chloroform (29.85 g) was pyrolysed in the usual manner with a space time of 7.23 sec.. Samples (1 ml.) of the effluent gas were withdrawn every 15 minutes and analysed on the gas chromatograph. On completion of the run the traps were allowed to warm to room temperature and samples of the effluent gas were taken at frequent intervals.

No chlorine or hydrogen was detected in any of the gas samples analysed.

6.I.iii TO DETERMINE THE EFFECT OF A RADICAL INITIATOR ON THE PYROLYSIS OF CHLOROFORM

Azobisisobutyronitrile (30 mg) was added to chloroform (29.85 g, 0.25 mol.) and the mixture shaken until the initiator had dissolved. The chloroform solution was then pyrolysed in the usual manner. Products were analysed by g.l.c. using Column 1 (110°C) and Column 2 (70°C).

TABLE 9

Effect of adding a radical initiator on the pyrolysis of chloroform

	Average τ (sec)	Moles of products formed (x 10^3) *						% $CHCl_3$ reacted
		CH_2Cl_2	CCl_4	C_2HCl_3	C_2Cl_4	C_2HCl_5	C_2Cl_6	
Chloroform alone	4.45	0.62	1.46	0.44	0.93	2.40	0.42	4.18
Chloroform + initiator	4.29	0.63	1.40	0.51	1.05	2.64	0.40	4.49
Effect of initiator		+1.6%	-4.1%	+15.9%	+12.9%	+10.0%	-4.8%	+7.4%

* All values are the average from three runs

6.I.iv. TO DETERMINE THE EFFECT OF A RADICAL INHIBITOR ON THE PYROLYSIS OF CHLOROFORM

Phenol (0.60 g) was dissolved in chloroform (29.85 g, 0.25 mol.) and the solution pyrolysed at 510°C. Analysis of the products by g.l.c. (Column 1, 110°C; Column 2, 70°C), showed additional peaks to those obtained from the usual pyrolysis products. These compounds were identified by combined g.l.c. - mass spectrometry (Column 1, 110°C).

The experiment was repeated using increasing amounts of phenol.

TABLE 10

Effect of adding a radical inhibitor on the pyrolysis of chloroform

Run No.	τ (sec)	% phenol w/w	Moles of products formed (x 10^3)						% $CHCl_3$ reacted
			CH_2Cl_2	CCl_4	C_2HCl_3	C_2Cl_4	C_2HCl_5	C_2Cl_6	
9	4.45	0	0.62	1.46	0.44	0.93	2.40	0.42	4.18
13A	4.16	2	0.41	4.75	0.38	0.63	2.48	0.34	5.13
13B	4.33	3	0.52	6.52	0.36	0.65	2.56	0.68	6.22
13C	3.97	4	0.62	7.14	0.18	0.40	1.66	0.19	5.05
13D	3.90	5	1.24	7.86	0.72	1.45	3.67	0.73	8.90
13E	4.28	6	0.31	5.47	0.21	0.26	2.57	0.18	4.89
13F	4.23	7	0.52	10.16	0.47	0.63	2.56	0.06	7.25

Of the other products from these experiments two were identified as chlorobenzene and trichlorcmethyl phenyl ether. The third was thought to be either diphenyl ether or dibenzofuran, but could not be identified more specifically due to the poor quality of the spectrum obtained.

TABLE 11

Mass-spectral breakdown patterns of products from the pyrolysis of chloroform with phenol

Compound	Molecular ion (m/e)	Mass spectral breakdown pattern m/e (relative abundance)
Chlorobenzene	112	112(100), 77(69.0), 114(33.6), 51(29.9), 50(26.5), 38(12.3), 74(11.7), 75(10.4)
Trichloromethyl phenyl ether	270	77(100), 65(46.1), 175(42.2), 119(32.4), 156(31.4), 117(30.4), 177(28.4), 63(28.4)

6.I.v. TO DETERMINE THE EFFECT OF SURFACE AREA ON THE PYROLYSIS OF CHLOROFORM

To increase the surface area of the reaction tube small silica rings were placed inside it. The dimensions of a number of rings were measured and average values determined. The average weight of one ring was determined by weighing several batches of ten rings. Thus, an approximate relationship between weight and surface area of the rings made it possible to increase the surface area of the reaction vessel by a known amount, by adding the required weight of rings. The rings were placed on the bottom of the tube prior to the experiment, which was carried out in the usual way. By placing the rings on the bottom of the tube, and not packing the tube to any great extent it was hoped to avoid turbulance and maintain plug flow conditions as far as possible.

Average dimensions of rings: 1.5 mm. in depth
5.0 mm. internal diameter
7.0 mm. external diameter

$\therefore$ Average surface area of one ring = 96.26 mm^2

Average weight of one ring = 0.0783 g.

Internal surface area of reaction tube = 38,202 mm^2

$\therefore$ To increase surface area by 50 % requires $\frac{38,202}{2 \times 96.26}$ rings

$$= \frac{38,202 \times 0.0783}{2 \times 96.26} \text{ g. of rings}$$

$$= 15.54 \text{ g. of rings}$$

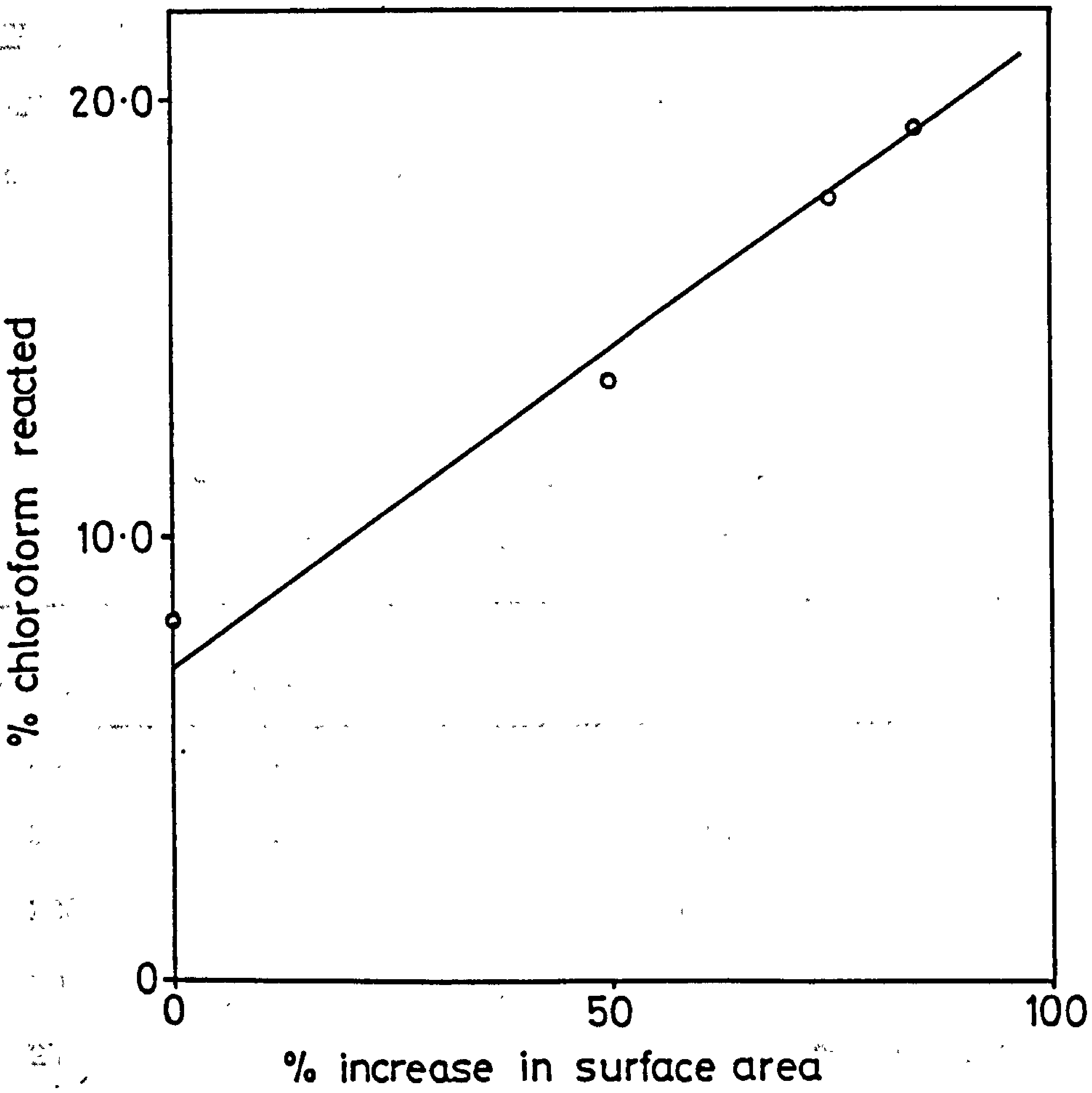
TABLE 12

The effect of surface area on the pyrolysis of chloroform

Run No.	τ (sec)	% increase in surface area	Moles of products formed (x 10^3)						% $CHCl_3$ decomposed
			CH_2Cl_2	CCl_4	C_2HCl_3	C_2Cl_4	C_2HCl_5	C_2Cl_6	
16	3.89	0	0.41	0.81	2.64	1.71	4.34	0.87	8.14
18	4.57	50	0.40	2.39	5.75	3.39	5.52	0.96	13.61
20	4.34	75	0.52	3.55	7.50	4.80	6.57	1.20	17.68
21	4.67	85	0.59	3.89	8.26	5.39	7.06	1.25	19.26

FIGURE 6

The effect of surface area on the extent of reaction in the pyrolysis of chloroform



6.I.vi. TO DETERMINE THE EFFECT OF PRETREATING THE TUBE ON THE PYROLYSIS OF CHLOROFORM

The reaction tube was pretreated in various ways to see whether the catalytic activity of the silica could be changed.

Run 207: Steam was passed down the reaction tube for 2 hours. The tube was then dried by heating it in the reaction furnace (510°C) in a stream of nitrogen.

Run 208: The reaction tube was soaked in distilled water for 70 hours and then dried as above.

Run 210: The reaction tube was soaked in ethylenediaminetetra-acetic acid (EDTA) solution (0.01M) for 20 hours. It was then rinsed and allowed to stand in distilled water for 30 minutes, before drying as above.

TABLE 13

The effects of pretreating the reaction tube
on the pyrolysis of chloroform

Run No.	τ (sec.)	Pretreatment of tube	% $CHCl_3$ reacted
201	3.69	None	7.25
207	3.82	Steaming for 2 h.	9.72
208	3.81	Soaking in water 70 h.	8.80
209	3.68	None, new tube	8.47
210	4.11	New tube, soaked in EDTA soln. 20 h.	10.38

6.I.vii. TO DETERMINE THE EFFECTS OF IMPURITIES AND AGEING ON THE CATALYTIC ACTIVITY OF SILICA

To determine the effect of impurities present in the silica of the reaction tube, on its catalytic properties, the pyrolysis of chloroform was carried out in reaction tubes made of different types of silica. One was made of very high purity grade silica, the other was of the same silica which had been used in previous experiments. The impurities present in the two materials are given in Table 14.

TABLE 14

Comparison of the impurities present in 'Heralux' and 'Suprasil' silicas

Impurities present (ppm)	HERAEUS, 'Heralux', fused silica from quartz crystal	HERAEUS, 'suprasil' synthetic fused silica
Aluminium	10-50	0.1
Boron	<0.1	<0.01
Gold	0.0003	not detected
Iron	0.8	0.2
Potassium	0.8	<0.001
Calcium	0.8-3	0.1
Copper	0.07	0.004
Lithium	0-2	<0.05
Sodium	0-2	0.04
Phosphorus	0.1	0.01-0.1
Titanium	0.8	<0.1
OH	130-180	1200
H_2O	65-90	600

The effect of ageing on the reaction tube, could be determined by comparing the extent of reaction in the new impure silica tube, with that in the old tube.

TABLE 15

The effect of different types of silica on the pyrolysis of chloroform

Run No.	τ(sec.)	Reaction tube	% $CHCl_3$ reacted
201	3.69	Old tube, 'Herelux' (impure) silica	7.25
209	3.68	New tube, 'Herelux' (impure) silica	8.47
206	3.75	New tube, 'Suprasil' (pure) silica	9.63

6.I.viii. THE PYROLYSIS OF CHLOROFORM AND TRICHLOROETHYLENE

Temperature of furnace:	510°C
Time of pyrolysis:	848 sec.
Nitrogen flow rate:	16.59 $l.h.^{-1}$ (22°C, 760 mmHg)
Wt. of chloroform:	29.85 g. (0.25 mol.)
Wt. of trichloroethylene:	3.29 g. (0.025 mol.)
Space time:	3.82 sec.

Products were analysed using Column 1 (110°C and 160°C) and Column 3 (75°C, N_2 flow rate 20 $ml. min^{-1}$).

6.I.ix. THE PYROLYSIS OF TRICHLOROETHYLENE

Temperature of furnace:	510°C
Time of pyrolysis:	834 sec.
Nitrogen flow rate:	43.18 $l. h.^{-1}$ (22°C, 760 mmHg)

Wt. of trichloroethylene: 3.29 g. (0.025 mol.)

Space time: 3.75 sec.

Products were analysed using Column 1 (110°C) and Column 3 (75°C, N_2 flow rate 20 ml. min^{-1})

No products were detected in the reaction mixture, only unreacted trichloroethylene. It was noted that negligible carbonisation had occurred on the reaction tube.

6.I.x. THE PYROLYSIS OF CHLOROFORM AND TETRACHLOROETHYLENE

Temperature of furnace 510°C

Time of pyrolysis: 770 sec.

Nitrogen flow rate: 16.59 l. $h.^{-1}$ (22°C, 760 mmHg)

Wt. of chloroform: 29.85 (0.25 mol.)

Wt. of tetrachloroethylene: 4.15 g. (0.025 mol.)

Space time: 3.59 sec.

Products were analysed using Column 1 (110°C and 160°C) and Column 3 (75°C, N_2 flow rate 20 ml. min^{-1}).

6.I.xi. THE PYROLYSIS OF TETRACHLOROETHYLENE

Temperature of furnace: 510°C

Time of pyrolysis: 805 sec.

Nitrogen flow rate: 43.18 l. $h.^{-1}$ (22°C, 760 mmHg)

Wt. of tetrachloroethylene: 4.15 g. (0.025 mol.)

Space time: 3.74 sec.

Products were analysed using Column 1 (110°C) and Column 3 (75°C, N_2flow rate 20 ml. min^{-1}).

No products were detected in the reaction mixture and again the amount of carbonisation was negligible.

TABLE 16

The effect of added trichloroethylene and tetrachloroethylene on the pyrolysis of chloroform

τ (sec)	Compound added	Moles of product formed (x 10^3)								% $CHCl_3$ reacted
		CH_2Cl_2	CCl_4	C_2HCl_3	C_2Cl_4	C_2HCl_5	C_2Cl_6	C_4HCl_5	C_4Cl_6	
3.69	none	0.33	0.05	0.40	2.30	3.68	2.30	0.04	0.06	7.25
3.82	10% C_2HCl_3	-	0.10	-	1.73	1.00	5.10	1.84	0.41	9.90
3.59	10% C_2Cl_4	-	0.05	1.10	-	2.34	4.55	0.06	0.70	7.62

6.II. KINETIC EXPERIMENTS

A kinetic investigation of the pyrolysis of chloroform was carried out with the aim of determining the order of the reaction. This involved carrying out a number of runs at different space times. All reactions were carried out under the following conditions.

Temperature of furnace:	510°C
Temperature of preheater:	160°C
Nitrogen flow rate:	19.30 l. h^{-1} (22°C, 760 mmHg)

Column 1 (110°C) and Column 2 (70°C) were used for g.l.c. analysis of the products.

Estimation of ε_A

To account for the fractional change in volume it was necessary to estimate the factor ε_A. Since the exact stoichiometry of the reaction was unknown this could not be done with any great accuracy. However from the relative amounts of products formed it was calculated that 286 volumes of products were obtained from 252 volumes of chloroform.

$$\varepsilon_A = \frac{\left[\left(\text{Vol. of } CHCl_3 \times \frac{286}{252}\right) + \text{Vol. of } N_2\right] - \left[\text{Vol. of } CHCl_3 + \text{Vol. of } N_2\right]}{\left[\text{Vol. of } CHCl_3 + \text{Vol. of } N_2\right]}$$

For example: Run 26

Wt. of chloroform = 29.85 g.

= 0.25 mol. = 15.86 l. (783 K, 770 mmHg)

Time of pyrolysis = 579 sec.

$$\text{Volume of nitrogen} = \frac{19.30}{3600} \times 579 \times \frac{783}{295} \times \frac{760}{770} \text{ l.}$$

$$= 8.13 \text{ l. } (783 \text{ K}, 760 \text{ mmHg})$$

$$\varepsilon_A = \frac{\left[\left(15.86 \times \frac{286}{252}\right) + 8.13\right] - \left[15.86 + 8.13\right]}{\left[15.86 + 8.13\right]}$$

$$= \frac{26.13 - 23.99}{23.99}$$

$$\varepsilon_A = 0.0892$$

Since the value of ε_A is small and it always occurs with X_A, the fraction of chloroform which has reacted, which is also small, <0.2, it was thought that any error in its estimation would have a negligible effect on the calculation of the order and rate of the reaction.

Zero, first, second and third order rate plots were constructed. Of these, the experimental data appeared to fit a first order plot considerably better than the other three, the second and third order plots giving definite curves. The reaction was therefore assumed to be first order with respect to chloroform.

It can be seen in the first order rate plot, that the majority of the points approximate to a straight line, from which the rate constant and the induction period were calculated.

$$\text{Gradient of line} = 31.87 \pm 0.40 \text{ sec.}$$

$$\therefore k_1 = \frac{1}{31.87} = 3.14 \pm 0.04 \times 10^{-2} \text{ sec.}^{-1}$$

$$\text{Intercept,} \quad \tau = 2.63 \pm 0.04 \text{ sec.}$$

TABLE 17

Results of kinetic experiments

Run No.	τ (sec.)	Time of pyrolysis (sec.)	Volume of feed (l.)	ε_A	Wt. of $CHCl_3$ used (g.)	Fraction of $CHCl_3$ reacted: X_A
1	3.01	579	23.99	0.0892	29.85	0.0180
2	3.19	632	24.74	0.0865	29.85	0.0196
3	5.49	1825	41.49	0.0516	29.85	0.0876
4	4.52	1171	32.31	0.0662	29.85	0.0403
5	4.86	1363	35.00	0.0611	29.85	0.0581
6	4.06	949	29.19	0.0733	29.85	0.0481
7	4.29	1054	30.66	0.0698	29.85	0.0485
8	3.82	851	27.81	0.0769	29.85	0.0436
9	4.60	1215	32.93	0.0650	29.85	0.0594
10	5.58	1907	42.64	0.0502	29.85	0.0549
11	7.17	2280	39.69	0.0260	14.44	0.1292
12	3.57	600	20.95	0.0805	23.59	0.0334
13	7.21	2700	46.71	0.0254	16.55	0.1458
14	7.67	2400	39.04	0.0183	10.05	0.1453
15	8.05	3974	61.59	0.0126	10.88	0.1526
16	6.69	3435	64.10	0.0334	29.85	0.0963
17	6.18	2582	52.12	0.0411	29.85	0.0760
18	6.35	2833	55.65	0.0385	29.85	0.0436
19	6.70	3455	64.39	0.0332	29.85	0.0888
20	7.33	5312	90.44	0.0235	29.85	0.1071
21	7.66	7041	114.72	0.0185	29.85	0.1143
22	7.93	9342	147.02	0.0145	29.85	0.1107
C.T.8	3.96	907	28.60	0.0748	29.85	0.0391
C.T.12	4.92	1399	35.51	0.0602	29.85	0.0783
C.T.16	4.77	1309	34.24	0.0625	29.85	0.0705
C.T.23	4.97	1430	35.94	0.0595	29.85	0.0633

TABLE 18

First order rate plot for the pyrolysis of chloroform at 510°C

Run No.	X_A	$\frac{1}{(1-X_A)}$	ε_A	$(1+\varepsilon_A)\ln\frac{1}{(1-X_A)} - \varepsilon_A X_A$	τ(sec.)
1	0.0180	1.018	0.0892	0.0176	3.01
2	0.0196	1.020	0.0865	0.0198	3.19
3	0.0876	1.096	0.0516	0.0921	5.49
4	0.0403	1.042	0.0662	0.0412	4.52
5	0.0581	1.062	0.0611	0.0603	4.86
6	0.0481	1.051	0.0733	0.0499	4.06
7	0.0485	1.051	0.0698	0.0499	4.29
8	0.0436	1.046	0.0769	0.0450	3.82
9	0.0594	1.063	0.0650	0.0613	4.60
11	0.1292	1.148	0.0260	0.1382	7.17
12	0.0334	1.035	0.0805	0.0345	3.57
13	0.1458	1.171	0.0254	0.1546	7.21
14	0.1453	1.170	0.0183	0.1572	7.67
15	0.1526	1.180	0.0126	0.1657	8.05
16	0.0963	1.131	0.0334	0.1240	6.69
C.T.8	0.0391	1.041	0.0748	0.0400	3.96
C.T.12	0.0783	1.085	0.0602	0.0817	4.92
C.T.16	0.0705	1.076	0.0625	0.0733	4.77
C.T.23	0.0633	1.068	0.0595	0.0655	4.97
10	0.0594	1.058	0.0502	0.0565	5.58
17*	0.0760	1.082	0.0411	0.0790	6.18
18*	0.0436	1.046	0.0385	0.0450	6.35
19*	0.0888	1.097	0.0332	0.0930	6.70
20*	0.1071	1.120	0.0235	0.1133	7.33
21*	0.1143	1.129	0.0185	0.1215	7.66
22*	0.1107	1.125	0.0145	0.1174	7.93

* Runs carried out at a later date.

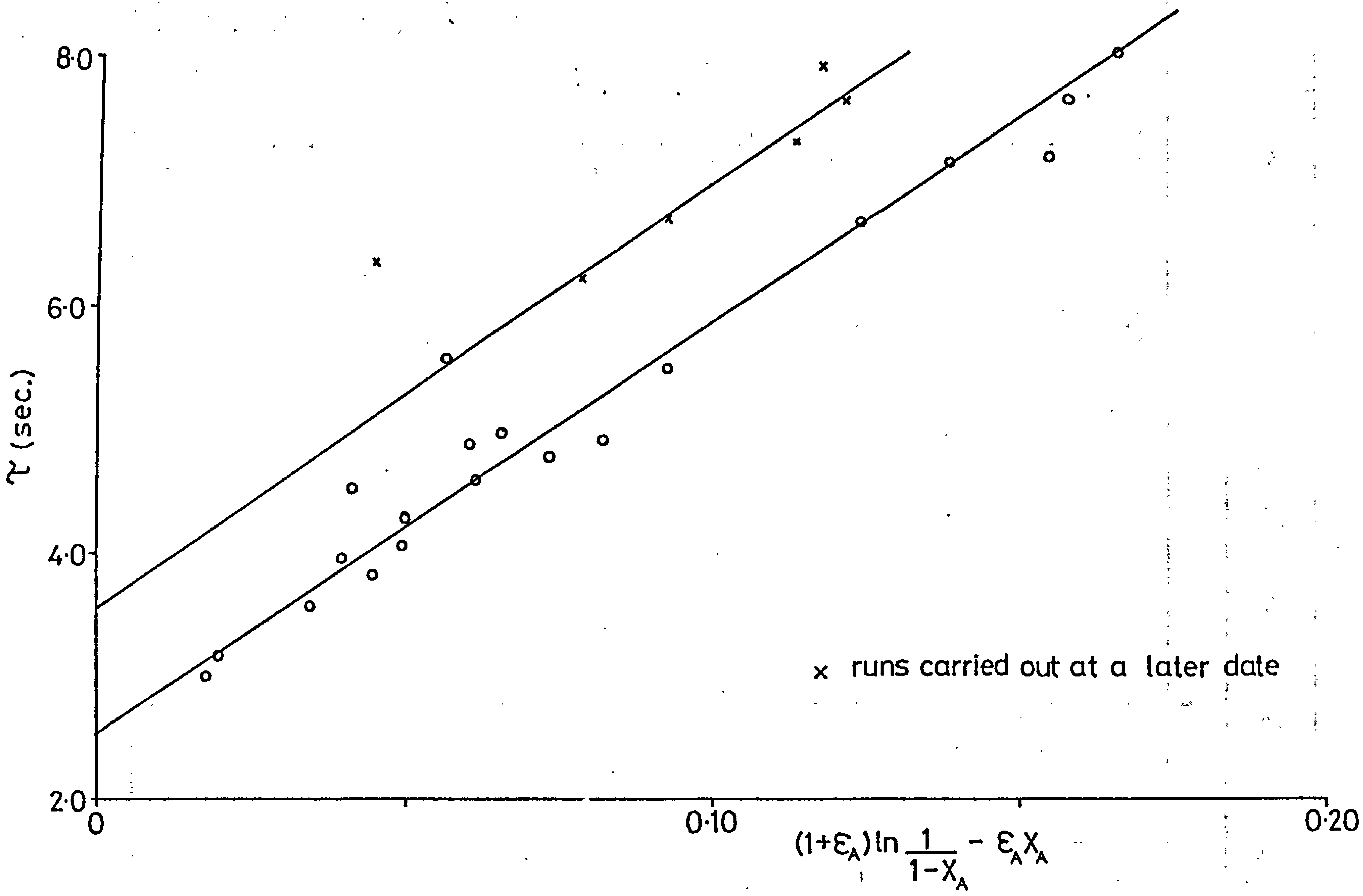


Fig. 7 First order rate plot - non carbonised tube

TABLE 19

Zero and second order rate plots for the pyrolysis of chloroform at 510°C

Run No.	τ (sec.)	$C_{A0}X_A(\times 10^4)$	$\dfrac{2\varepsilon_A(1+\varepsilon_A)\ln(1-X_A) + \varepsilon_A^2 X_A + \dfrac{(\varepsilon_A+1)^2 X_A}{(1-X_A)}}{C_{A0}}$
1	3.01	1.88	1.8
2	3.19	1.98	2.0
3	5.49	5.28	16.0
4	4.52	3.12	5.4
5	4.86	4.15	8.7
6	4.06	4.12	6.0
7	4.29	3.95	6.3
8	3.82	3.92	5.1
9	4.60	4.51	8.4
10	5.58	3.48	10.8
11	7.17	3.93	49.0
12	3.57	3.15	3.7
13	7.21	4.32	58.0
14	7.67	3.12	79.3
15	8.05	2.26	121.9
16	6.69	3.76	27.4
17	6.18	3.65	17.2
18	6.35	1.96	10.2
19	6.70	3.45	25.2
20	7.33	2.96	43.6
21	7.66	2.49	76.7
22	7.93	1.88	73.3
C.T.8	3.96	3.59	4.5
C.T.12	4.92	5.86	11.4
C.T.16	4.77	5.45	9.9
C.T.23	4.97	4.67	10.3

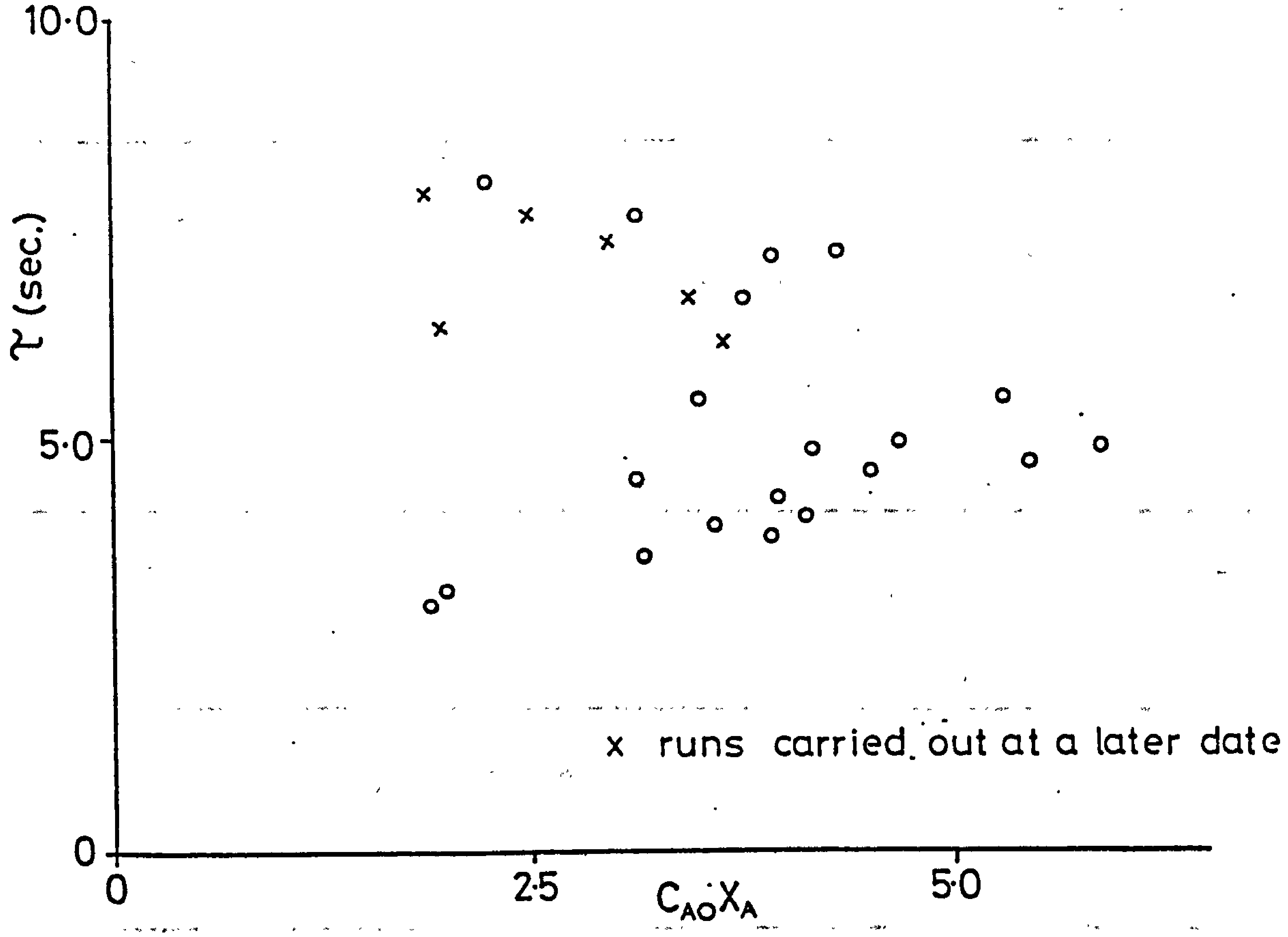


Fig.8 Zero order rate plot

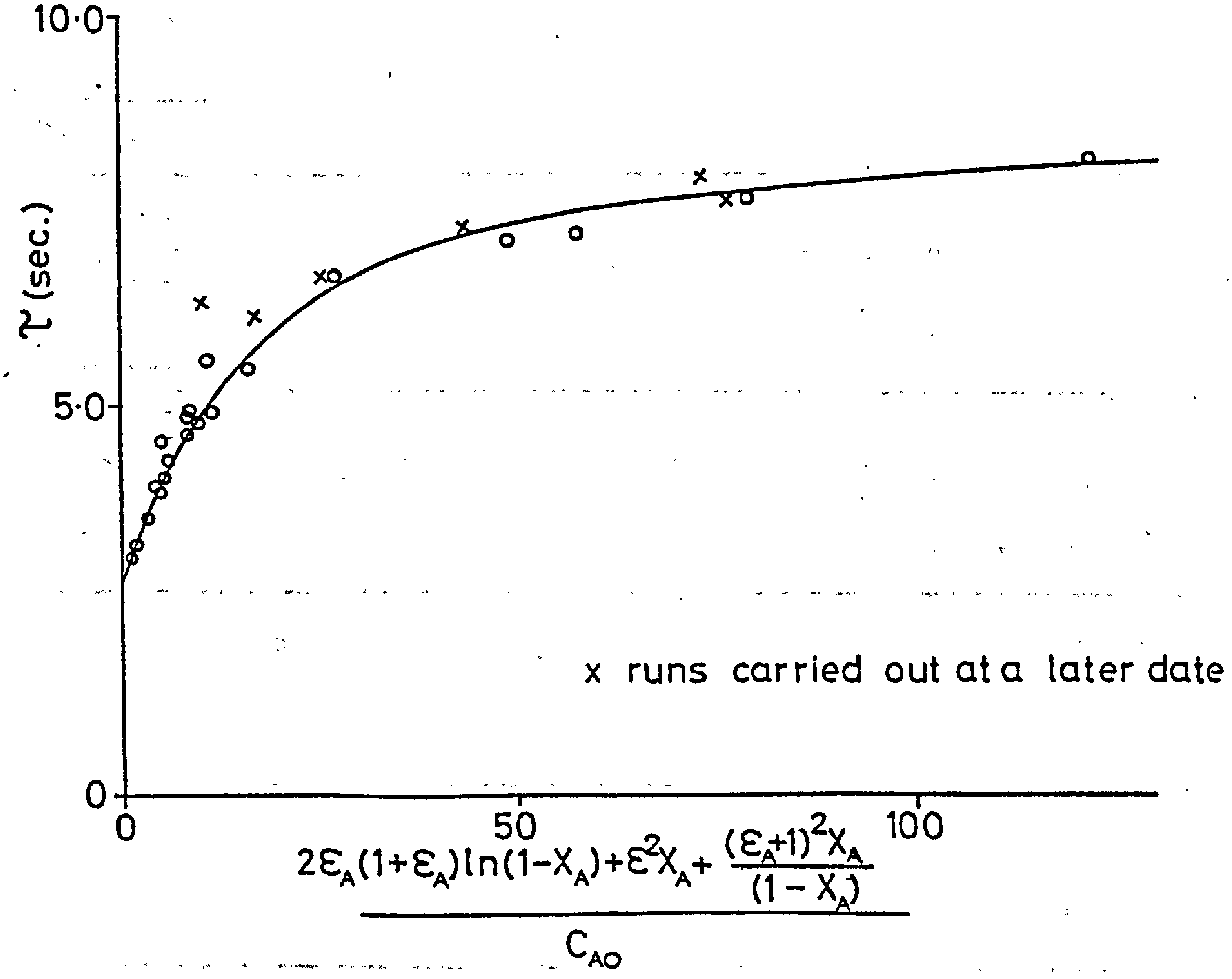


TABLE 20

Third order rate plot for the pyrolysis of chloroform at 510°C

Run No.	X_A	$\frac{(1+\varepsilon_A X_A)}{(1-X_A)}$	$\left\{\frac{(1+\varepsilon_A X_A)}{(1-X_A)}\right\}^3$	$\int_0^{X_A}\left\{\frac{(1+\varepsilon_A X_A)}{(1-X_A)}\right\}^3 dX_A$	C_{AO}	$\frac{1}{C_{AO}^2}$	$\frac{1}{C_{AO}^2}$ x integral (x 10^{-3})	τ (sec.)
1	0.0180	1.0200	1.0612	0.0186	0.01042	9,210	0.17	3.01
2	0.0196	1.0217	1.0665	0.0203	0.01011	9,784	0.20	3.19
3	0.0876	1.1009	1.3343	0.1013	0.00603	27,502	2.79	5.49
4	0.0403	1.0448	1.1405	0.0431	0.00774	16,692	0.72	4.52
5	0.0581	1.0659	1.2109	0.0642	0.00714	19,616	1.26	4.86
6	0.0481	1.0542	1.1717	0.0522	0.00856	13,647	0.71	4.06
7	0.0485	1.0545	1.1727	0.0527	0.00815	15,055	0.79	4.29
8	0.0436	1.0491	1.1546	0.0470	0.00899	12,373	0.58	3.82
9	0.0594	1.0673	1.2157	0.0658	0.00759	17,359	1.14	4.60
10	0.0549	1.0611	1.1946	0.0603	0.00586	29,121	1.75	5.58
11	0.1292	1.1523	1.5417	0.1614	0.00304	108,206	17.47	7.17
12	0.0334	1.0373	1.1162	0.0353	0.00942	11,269	0.40	3.57
13	0.1458	1.1750	1.6222	0.1867	0.00465	46,248	8.63	7.21
14	0.1453	1.1732	1.6148	0.1867	0.00535	34,938	6.52	7.67

TABLE 20 (cont'd)

Run No.	X_A	$\frac{(1+\varepsilon_A X_A)}{(1-X_A)}$	$\left\{\frac{(1+\varepsilon_A X_A)}{(1-X_A)}\right\}^3$	$\int_0^{X_A}\left\{\frac{(1+\varepsilon_A X_A)}{(1-X_A)}\right\}^3 dX_A$	C_{A0}	$\frac{1}{C_{A0}^2}$	$\frac{1}{C_{A0}^2}$ x integral ($\times 10^{-3}$)	τ (sec.)
15	0.1526	1.1823	1.6527	0.1965	0.00148	456,537	89.69	8.05
16	0.0963	1.1077	1.3590	0.1120	0.00390	65,746	7.36	6.69
17	0.0760	1.0856	1.2794	0.0858	0.00480	43,403	3.72	6.18
18	0.0436	1.0474	1.1489	0.0527	0.00449	49,603	2.61	6.35
19	0.0888	1.1006	1.3332	0.1013	0.00388	66,426	6.73	6.70
20	0.1071	1.1227	1.4151	0.1293	0.00276	131,275	16.98	7.33
21	0.1143	1.1314	1.4483	0.1399	0.00218	210,420	29.44	7.66
22	0.1107	1.1263	1.4288	0.1344	0.00170	346,021	46.52	7.93
C.T.8	0.0391	1.0437	1.1369	0.0418	0.00917	11,892	0.50	3.96
C.T.12	0.0783	1.0901	1.2954	0.0899	0.00748	17,873	1.61	4.92
C.T.16	0.0705	1.0806	1.2618	0.0797	0.00773	16,736	1.33	4.77
C.T.23	0.0633	1.0716	1.2305	0.0706	0.00739	18,311	1.29	4.97

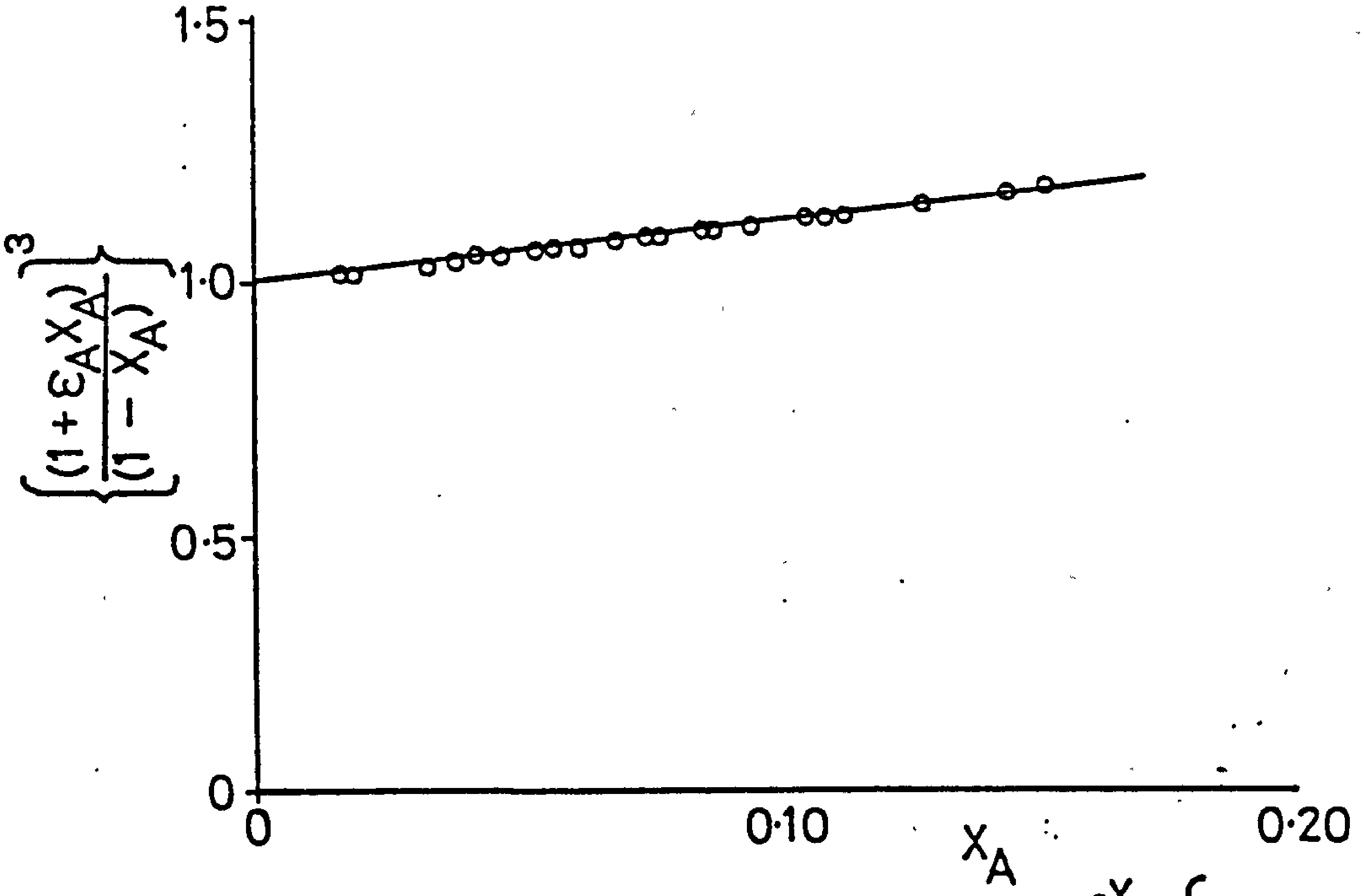


Fig. 10 Determination of $\int_0^{X_A} \left\{\frac{(1+\varepsilon_A X_A)}{(1-X_A)}\right\}^3 dX_A$

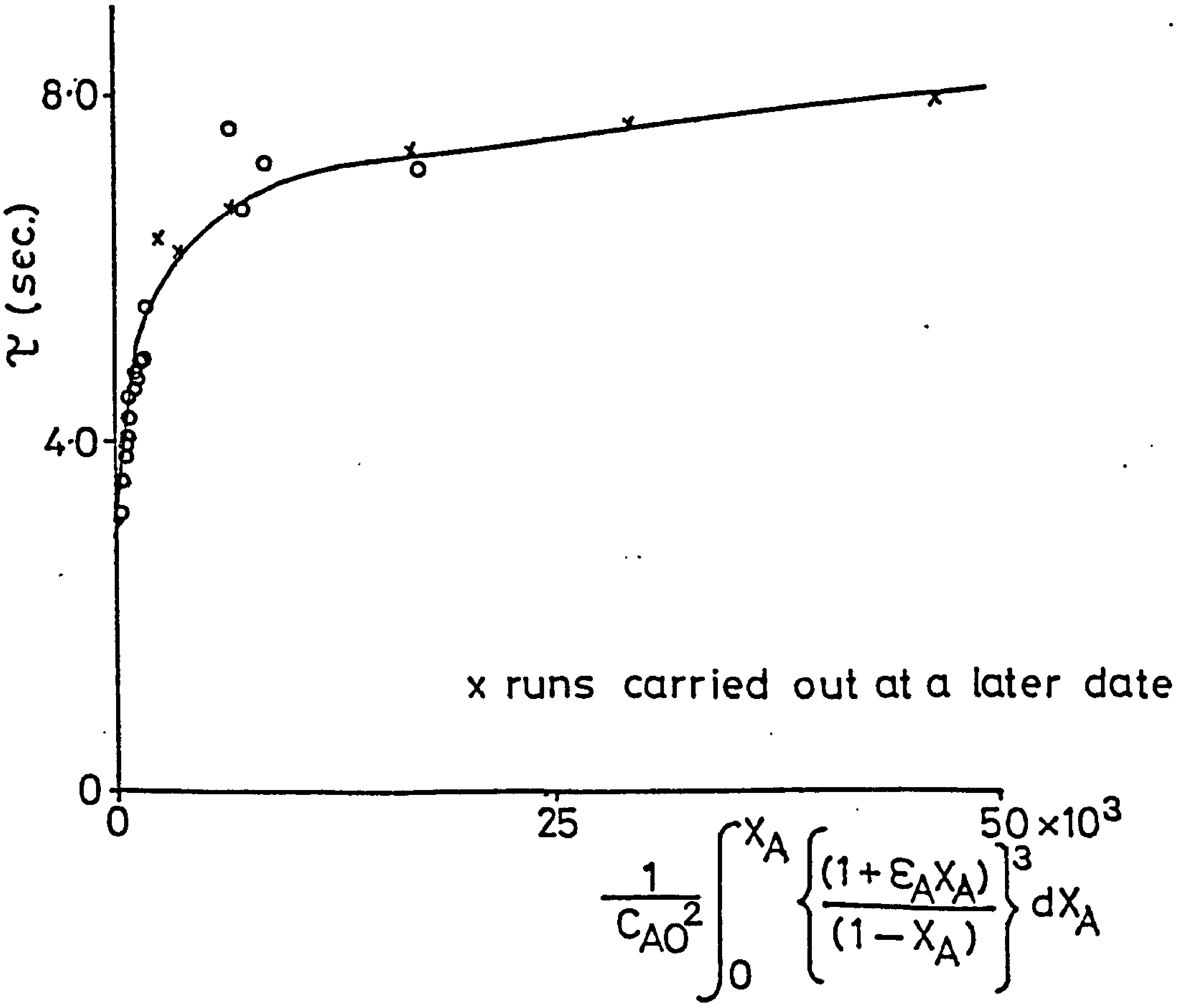


Fig. 11 Third order rate plot

The remaining points (10,17-22), most of which (17-22) were determined at a later date to the others, appeared to fit a second straight line, which gave a similar value of rate constant $k_1 = 2.87 \pm 0.19 \times 10^{-2}$ sec.$^{-1}$), but a larger intercept (3.52 ± 0.11 sec.).

The third order rate plot is constructed by plotting

$1/C_{A0}^{2} \int_0^{X_A} \left\{ \frac{(1+\varepsilon_A X_A)}{(1-X_A)} \right\}^3 dX_A$ against τ. The integral, $\int_0^{X_A} \left\{ \frac{(1+\varepsilon_A X_A)}{(1-X_A)} \right\}^3 dX_A$

may either be determined graphically, by plotting $\left\{ \frac{(1+\varepsilon_A X_A)}{(1-X_A)} \right\}^3$ against X_A, and calculating the area under the curve between the limits X_A and zero for each value of X_A, or it may be determined numerically. The graphical method was found to be the easiest to calculate and this is shown in Fig.11. The numerical calculation of the third order rate plot is given in Appendix 1.

6.III. THE PYROLYSIS OF CHLOROFORM USING A CARBONISED TUBE

A series of runs were carried out using a carbonised tube, that is, one in which the carbonaceous deposit was not removed from the surface of the tube between runs. The aim of the investigation was to determine whether the carbon layer affected the amount of reaction taking place, and to see whether the reproducibility from one run to another was improved, and continued to improve as the carbon layer built up. The runs were carried out under the conditions used for the kinetic runs in the previous section.

TABLE 21

Determination of reproducibility using
a carbonised tube

Day	Order of runs	τ (sec.)	% Chloroform reacted
1	1	2.95	10.34
1	2	2.99	9.85
2	3	2.94	15.10
2	4	2.94	9.83
2	5	2.90	8.98
2	6	2.90	10.30

The results in Table 21 show that for a 3.1 % variation in space time, there was a corresponding variation of 13.8 % in the amount of chloroform which had reacted (excluding run 3). There was a surprising increase (53 %) in the extent of reaction in the case of run 3. This run was the first, on the second day of the series, and the carbon layer which had built up from the two previous runs, had become cracked and broken as the tube cooled down overnight. The observed increase in reaction was therefore attributed to the presence of a highly irregular carbon surface, which was more active than either the clean silica surface, or the smooth carbonised surface.

Kinetic Runs.

Kinetic runs were carried out under the conditions used for kinetic runs in the clean silica tube, except that the tube was cleaned only at the end of each day. The first run of each day was not included in the results, having been carried out in a clean tube.

Zero, first, second and third order rate plots were constructed as before. Unlike the previous set of results however, the difference between the plots was less marked owing to the amount of scatter in the results. It was decided that the data approximated most closely to a straight line in the first order rate plot, the second order plot showing some curvature, although this was less obvious than in the third order plot.

From the first order rate plot:

$$\text{Gradient} = 20.10 \pm 1.02 \text{ sec.}$$

$$\therefore k_1 = 4.98 \pm 0.25 \times 10^{-2} \text{ sec.}^{-1}$$

$$\text{Intercept} = \tau = 4.05 \pm 0.09 \text{ sec.}$$

TABLE 22

Results from kinetic experiments using a carbonised tube

Run No.	τ (sec.)	Time of pyrolysis (sec.)	Volume of feed (l.)	ε_A	Wt.of $CHCl_3$ used (g.)	Fraction of $CHCl_3$ reacted; X_A
C.T.9	5.41	1760	40.58	0.0527	29.85	0.0504
C.T.10	4.69	1264	33.61	0.0636	29.85	0.0554
C.T.11	5.41	1757	40.54	0.0528	29.85	0.0453
C.T.13	5.70	2017	44.19	0.0484	29.85	0.0885
C.T.14	6.14	2521	51.27	0.0417	29.85	0.1099
C.T.15	5.89	2220	47.04	0.0455	29.85	0.0805
C.T.17	5.24	1620	38.61	0.0554	29.85	0.0807
C.T.19	6.33	2797	55.14	0.0388	29.85	0.0966
C.T.20	7.03	4276	75.92	0.0282	29.85	0.1286
C.T.21	6.77	3618	66.67	0.0321	29.85	0.1302
C.T.24	5.70	2023	44.27	0.0483	29.85	0.0821
C.T.25	6.18	2573	52.00	0.0411	29.85	0.0977
C.T.27	5.29	1662	39.20	0.0546	29.85	0.0664
C.T.28	6.43	2952	57.32	0.0373	29.85	0.0920
C.T.31	4.82	1341	34.69	0.0617	29.85	0.0571
C.T.32	5.48	1813	41.32	0.0518	29.85	0.0620
C.T.33	6.09	2461	50.42	0.0424	29.85	0.0797

TABLE 23

First order rate plot for the pyrolysis of chloroform in a carbonised tube at 510°C

Run No.	X_A	$\frac{1}{(1-X_A)}$	ε_A	$(1+\varepsilon_A)\ln\frac{1}{(1-X_A)} - \varepsilon_A X_A$	τ (sec.)
C.T.9	0.0504	0.9496	0.0527	0.05178	5.41
C.T.10	0.0554	0.9446	0.0636	0.05710	4.69
C.T.11	0.0453	0.9547	0.0528	0.04641	5.41
C.T.13	0.0885	0.9115	0.0484	0.09287	5.70
C.T.14	0.1099	0.8901	0.0417	0.11669	6.14
C.T.15	0.0805	0.9195	0.0455	0.08408	5.89
C.T.17	0.0807	0.9193	0.0554	0.08880	5.24
C.T.19	0.0966	0.9034	0.0388	0.10178	6.33
C.T.20	0.1286	0.8714	0.0282	0.13791	7.03
C.T.21	0.1302	0.8698	0.0321	0.13979	6.77
C.T.24	0.0821	0.9179	0.0483	0.08584	5.70
C.T.25	0.0977	0.9023	0.0411	0.10302	6.18
C.T.27	0.0664	0.9336	0.0546	0.06883	5.29
C.T.28	0.0920	0.9080	0.0373	0.09668	6.43
C.T.31	0.0571	0.9429	0.0617	0.05890	4.82
C.T.32	0.0620	0.9380	0.0518	0.06411	5.48
C.T.33	0.0797	0.9203	0.0424	0.08320	6.09

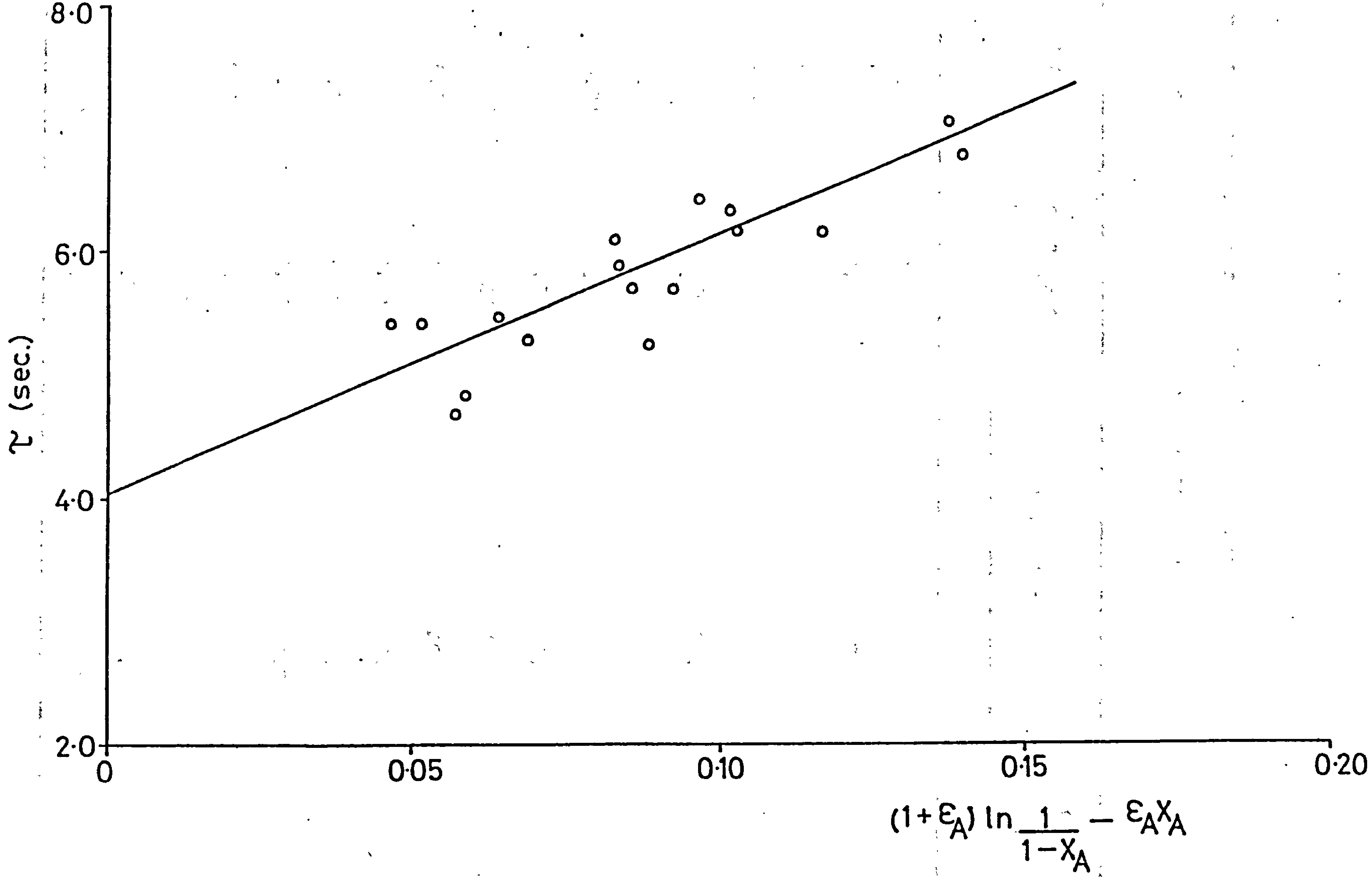


Fig. 12 First order rate plot — carbonised tube

TABLE 24

Zero and second order rate plots for the pyrolysis of chloroform (510°C) in a carbonised tube

Run No.	τ (sec.)	$C_{A0}X_A(\times 10^4)$	$\frac{2\ {}_A(1+\ {}_A)\ln(1-X_A)+\varepsilon_A^2X_A+\frac{(1+\varepsilon_A)^2X_A}{(1-X_A)}}{C_{A0}}$
C.T.9	5.41	3.10	8.6
C.T.10	4.69	4.12	7.9
C.T.11	5.41	2.80	7.7
C.T.13	5.70	5.01	17.2
C.T.14	6.14	5.36	25.4
C.T.15	5.89	4.27	16.5
C.T.17	5.24	5.23	15.1
C.T.19	6.33	4.38	22.7
C.T.20	7.03	4.23	45.0
C.T.21	6.77	4.88	40.1
C.T.24	5.70	4.64	15.9
C.T.25	6.18	4.70	22.6
C.T.27	5.29	4.24	11.2
C.T.28	6.43	4.01	23.3
C.T.31	4.82	4.12	8.4
C.T.32	5.48	3.75	11.0
C.T.33	6.09	3.95	17.5

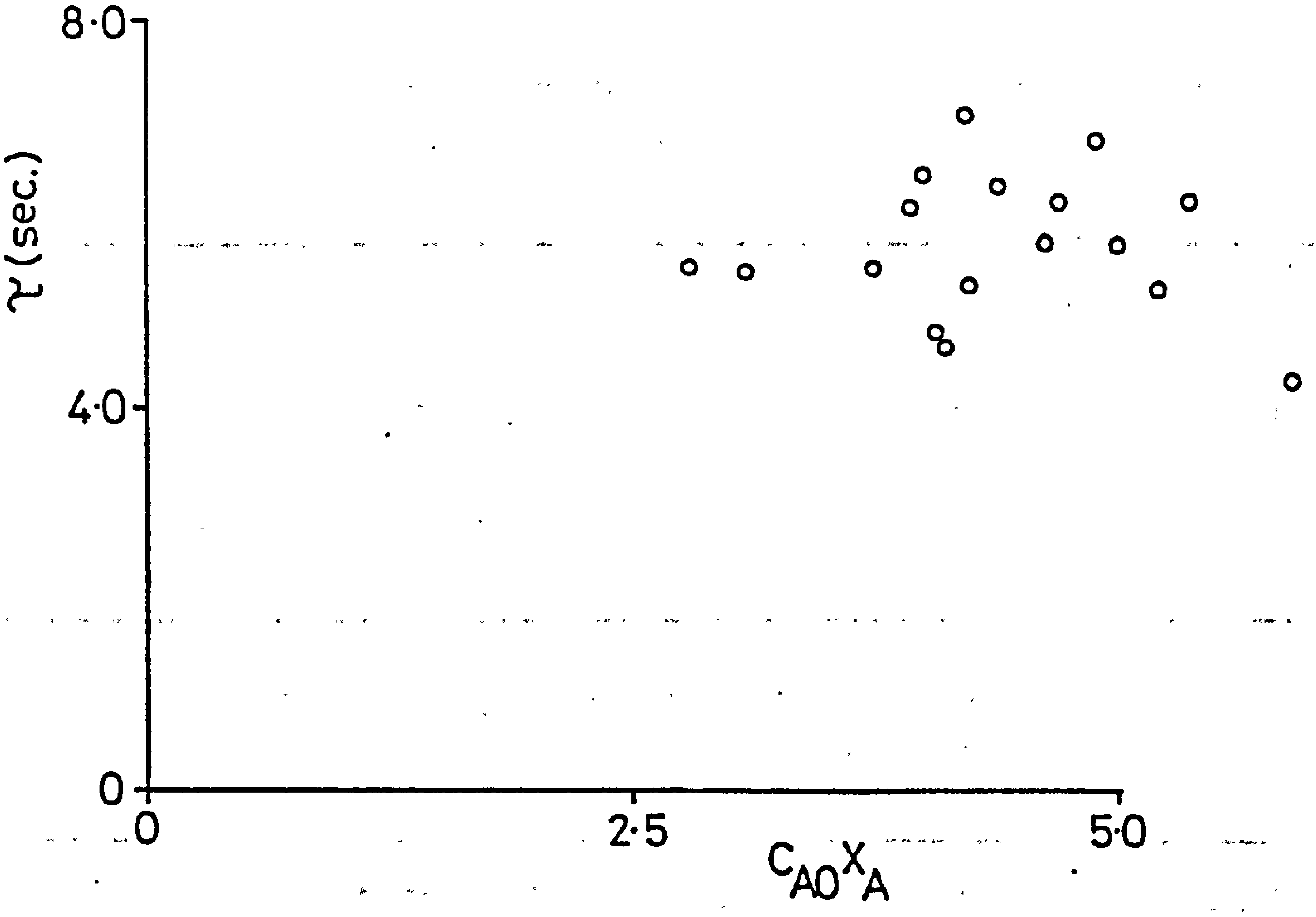


Fig. 13 Zero order rate plot– carbonised tube

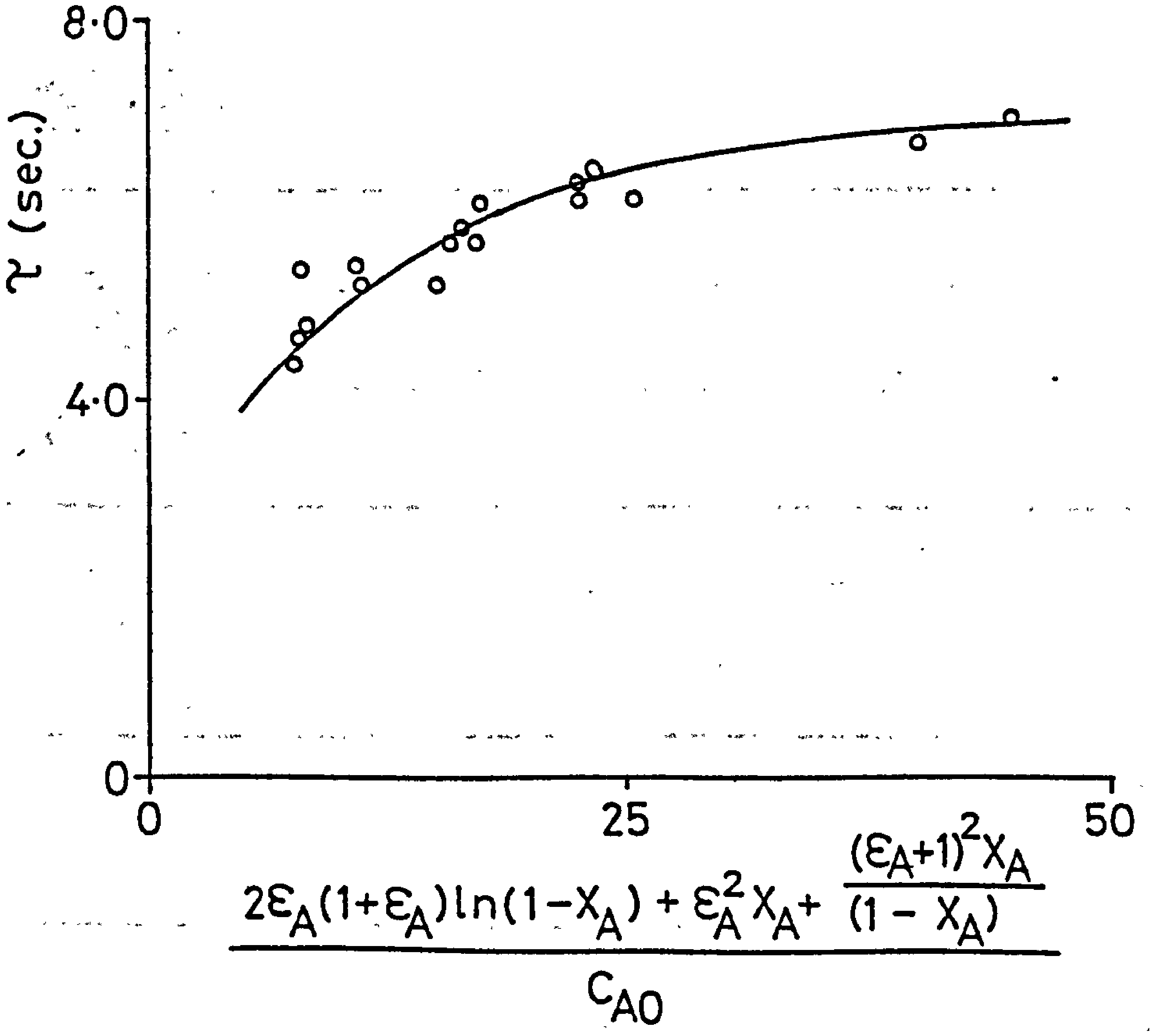


Fig. 14 Second order rate plot– carbonised tube

TABLE 25

Third order rate plot for the pyrolysis of chloroform (510°) in a carbonised tube

Run No.	X_A	$\frac{(1+\varepsilon_A X_A)}{(1-X_A)}$	$\left\{\frac{(1+\varepsilon_A X_A)}{(1-X_A)}\right\}^3$	$\int_0^{X_A}\left\{\frac{(1+\varepsilon_A X_A)}{(1-X_A)}\right\}^3 dX_A$	C_{A0}	$\frac{1}{C_{A0}^2}$	$\frac{1}{C_{A0}^2}$ x integral ($\times 10^{-3}$)	τ (sec.)
C.T.9	0.0504	1.0559	1.1772	0.0549	0.00616	26,354	1.45	5.41
C.T.10	0.0554	1.0624	1.1991	0.0609	0.00744	18,066	1.10	4.69
C.T.11	0.0453	1.0500	1.1576	0.0489	0.00617	26,268	1.28	5.41
C.T.13	0.0885	1.1018	1.3375	0.1034	0.00566	31,215	3.23	5.70
C.T.14	0.1099	1.1286	1.4375	0.1339	0.00488	41,991	5.62	6.14
C.T.15	0.0805	1.0916	1.3007	0.0926	0.00531	35,466	3.28	5.89
C.T.17	0.0807	1.0927	1.3047	0.0930	0.00648	23,815	2.21	5.24
C.T.19	0.0966	1.1110	1.3713	0.1145	0.00453	48,731	5.58	6.33
C.T.20	0.1286	1.1517	1.5276	0.1625	0.00329	92,386	15.02	7.03
C.T.21	0.1302	1.1545	1.5388	0.1653	0.00375	71,111	11.75	6.77
C.T.24	0.0821	1.0938	1.3086	0.0948	0.00565	31,326	2.97	5.70
C.T.25	0.0977	1.1128	1.3780	0.1162	0.00481	43,222	5.02	6.18
C.T.27	0.0664	1.0750	1.2423	0.0744	0.00638	24,567	1.83	5.29
C.T.28	0.0920	1.1051	1.3496	0.1081	0.00436	52,605	5.69	6.43
C.T.31	0.0571	1.0643	1.2056	0.0630	0.00721	19,237	1.21	4.82
C.T.32	0.0620	1.0695	1.2233	0.0689	0.00605	27,321	1.88	5.48
C.T.33	0.0797	1.0903	1.2961	0.0915	0.00496	40,648	3.72	6.09

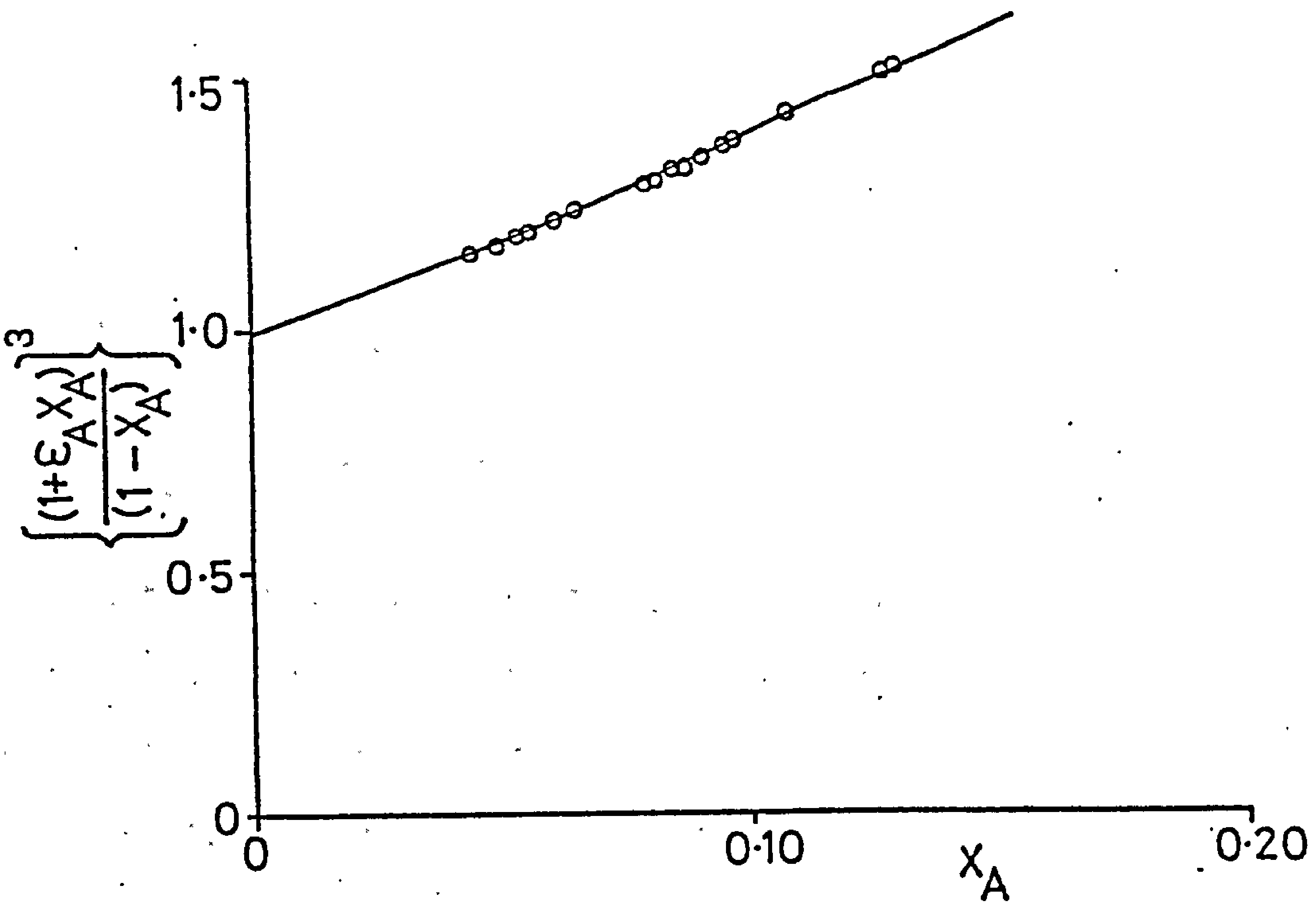


Fig. 15 Determination of $\int_0^{X_A} \left\{\frac{(1+\varepsilon_A X_A)}{(1-X_A)}\right\}^3 dX_A$

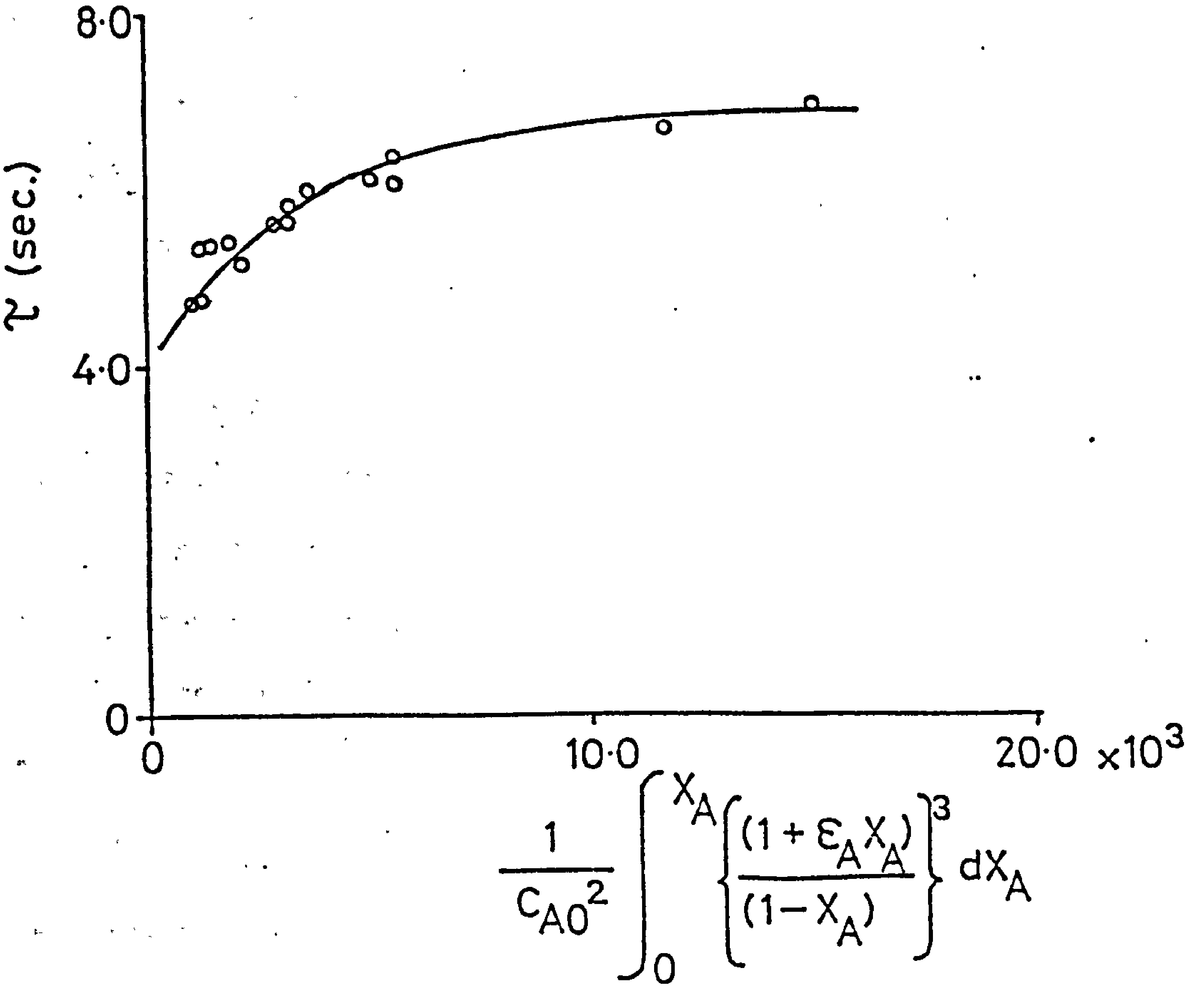


Fig. 16 Third order rate plot—carbonised tube

CHAPTER 7

THE ALKALINE HYDROLYSIS OF CHLOROFORM

7.I. GENERAL PROCEDURE FOR HYDROLYSIS EXPERIMENTS

A solution of aqueous sodium hydroxide in 1,4-dioxane was prepared, by measuring the required volumes of distilled water, standardised sodium hydroxide solution, (British Drug Houses Co. Ltd. avs., carbonate free solution) and 1,4-dioxane, (Aldrich Chemical Co. Ltd., analar or spectroscopic grade solvent), into a conical flask. A small amount of impurity (<0.1 %) was always present in the dioxane, even when spectroscopic grade solvent was used. This had to be removed before use since it gave a small peak on the chromatogram which interfered with the chloroform peak. The dioxane was therefore fractionated through a column (2.5 cm. i.d., 25 cm. in length) packed with glass rings, and each fraction analysed by g.l.c. to ensure its purity, prior to use. Where it was necessary to know the composition of the solution very accurately, it was made up by weight rather than by volume.

An aliquot of the solution (usually 100 ml.) was transferred to a conical flask (250 ml.), fitted with a drying tube containing soda-lime, to prevent absorption of carbon dioxide by the hydroxide solution. The conical flask was then clamped in a thermostatically controlled water bath ($\pm$ 0.1°C), so that the level of the solution was one inch below the surface of the water. The solution was allowed to equilibrate to the temperature of the water bath for at least 30 min.

At time zero, a known amount of chloroform was introduced into the solution and the reaction mixture swirled vigorously in the water bath to ensure complete dissolution. Samples of the solution (1.0 ml.) were removed at known time intervals using a Gilson Pipetman P1000 automatic pipette, and the reaction stopped, by neutralising with the minimum amount of hydrochloric acid (~ 3 M), in a glass sample tube. The acid was cooled in ice before, and during, addition of the alkaline solution, to prevent chloroform evaporation due to the heat of neutralisation. Swirling of the sample tube facilitated mixing, but at no time was the solution allowed to come into contact with sample tube caps, since it was shown that if these were made of polythene, they rapidly absorbed chloroform from the solution. Analysis of the neutralised sample was carried out by g.l.c. to determine the concentration of chloroform.

To follow the reaction with respect to the concentration of sodium hydroxide, samples (1.0 ml.) of the reaction mixture were removed at known time intervals, and diluted with ice-cooled, distilled water (approx. 10 ml.). The solution was then titrated against standardised hydrochloric acid, using phenolphthalein indicator. It had previously been shown that the acid-base titration was not affected by the presence of sodium formate if phenolphthalein indicator was used, but, with methyl orange, a clear end point could not be obtained. Although the reaction was not absolutely stopped before titration of the sodium hydroxide, it was found that by diluting and cooling the solution, the reaction was sufficiently slowed down, for the amount of reaction which occurred during the time taken to titrate the solution, (less than 1 min.), to be negligible.

Chromatographic analysis

The concentration of chloroform in each sample was determined by g.l.c. using a Pye Unicam G.C.D. chromatograph (flame ionisation detector), in conjunction with a Pye Unicam AR 55 linear recorder and a DP 88 computing integrator. Thus, a printout was obtained giving the retention time and integrated peak area of each component in the solution. The peak area could then be converted to concentration, using a calibration curve.

The column used for this work was Carbowax 20M (15 %) on Diatomite C (60-80 mesh), acid washed, and treated with dimethyldichlorosilane. Nitrogen carrier gas was used, at a flow rate of 30 ml. min.^{-1}

Retention time of chloroform (70°C) : 324 sec.

To determine the volume of solution after neutralisation

Samples withdrawn from the reaction mixture were neutralised in order to stop the reaction. This resulted in a change in chloroform concentration as a result of the increased volume due to the added acid. In order to make a correction for this change in chloroform concentration, the volume of the neutralised sample had to be determined, and a worked example of the way in which this was calculated is given below.

In run 71, 1.0 ml. aliquots of the alkaline reaction mixture were neutralised with 0.25 ml. of dilute hydrochloric acid. The average weight of a number of neutralised samples was determined by weighing the sample tubes before and after the solutions had been added.

The density of the neutralised reaction mixture was determined for one sample by taking known volumes of the solution and weighing them accurately. A plot of weight against volume could then be constructed, the slope of which gave the density of the mixture. This value could be applied to all samples from the same run, since the density change throughout the run would be negligible. The volume of the neutralised samples could now be determined since both its weight and density were known, and a correction for the change in chloroform concentration could be applied

Volume of neutralised mixture (ml.)	0.80	1.0	1.20	1.40	1.60
Wt. of tube + mixture (g.)	2.8452	3.2229	3.3139	3.5300	3.7204
Wt. of tube (g.)	2.0106	2.1743	2.0588	2.0836	2.0486
∴ Wt. of mixture (g.)	0.8346	1.0486	1.2551	1.4464	1.6718

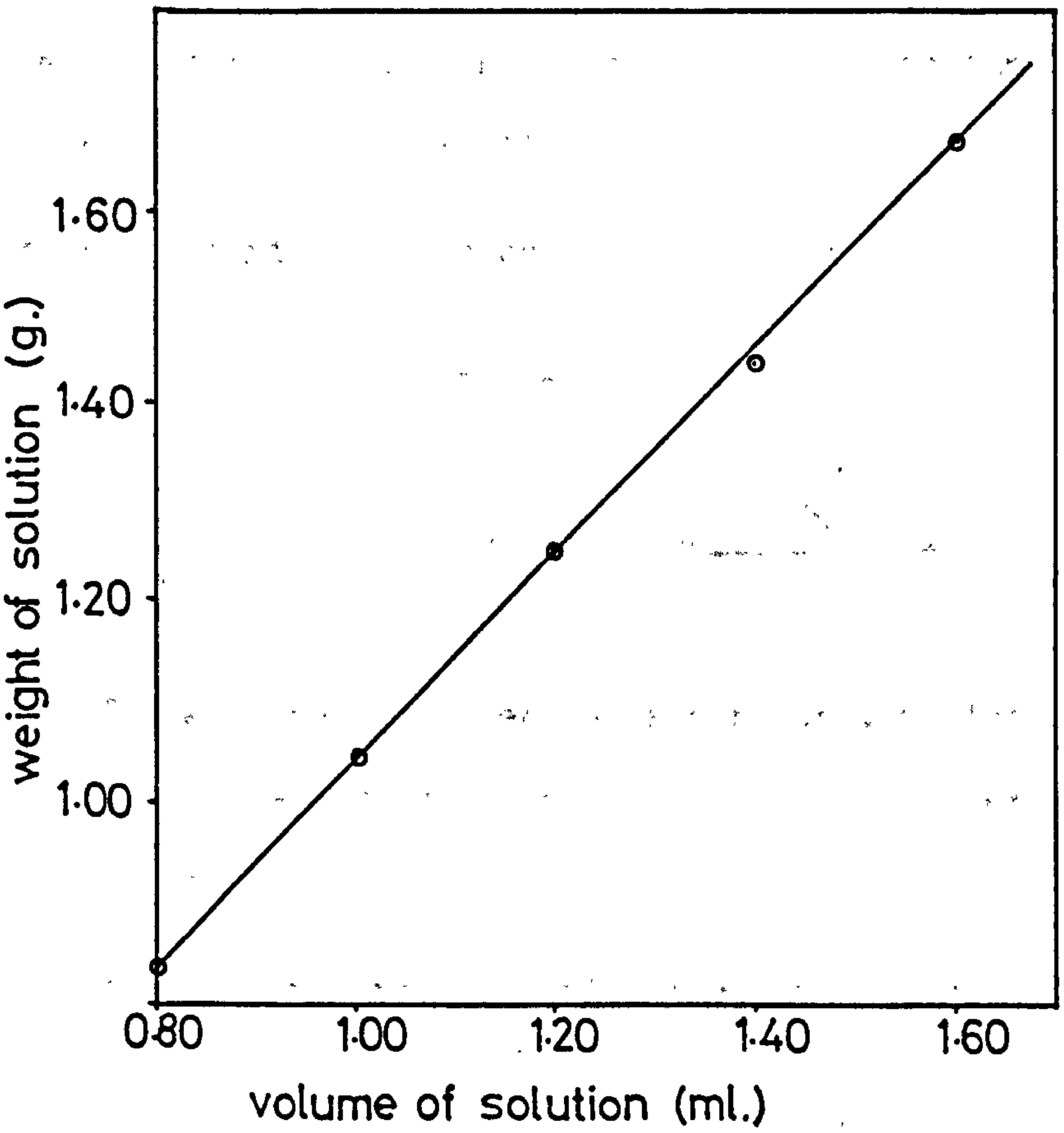
Wt. of tube + neutralised sample (g.)	3.3985	3.4302	3.4463	3.3924
Wt. of tube (g.)	2.0766	2.1087	2.1256	2.0727
∴ Wt. of sample (g.)	1.3219	1.3215	1.3207	1.3197

Average wt. of neutralised sample = 1.3210 g.

∴ Average vol. of neutralised sample = 1.2628 ml.

FIGURE 17

Graph to determine density of neutralised sample



The volume of the neutralised sample may be determined directly from the graph, the slope of which gives the solution density.

Volume of neutralised sample = 1.26 ml.

If concentration of chloroform in neutralised sample = x $mol.l.^{-1}$
concentration in reaction mixture = 1.26x $mol.l.^{-1}$

Determination of order and rate of reaction

Once the concentration of chloroform in each sample taken has been determined the order of the reaction may be determined.

For a first order reaction

$$k_1 t = \ln \frac{a}{(a-x)}$$

where a is the initial concentration of the reactant, and (a-x) is the concentration at time 't'.

On rearrangement this becomes

$$\ln (a-x) = -k_1 t + \ln a$$

or

$$\log_{10}(a-x) = \left(\frac{-k_1}{2.303}\right) t + \log_{10} a.$$

Since, for any one experiment a is constant, a plot of $\log_{10}(a-x)$ against t should yield a straight line in which the y intercept will be $\log_{10}a$ and the slope $(-k_1/2.303)$.

For a second order reaction the rate equation is given by the relationship

$$k_2 = \frac{1}{t(a-b)} . \ln \frac{b(a-x)}{a(b-x)}$$

When the two reactants are the same, this is simplified to give

$$k_2 = \frac{1}{at} . \frac{x}{(a-x)}$$

According to this equation a plot of $\frac{x}{a} . \frac{1}{(a-x)}$ should be linear with slope k_2 for a second order reaction. When one of the reactants is present in large excess, so that the change in its concentration during the reaction is negligible, the reaction becomes pseudo-unimolecular. Under these conditions $(b-x) = b$, and the rate equation becomes

$$\frac{dx}{dt} = k_2(a-x)b$$

On integration this leads to

$$k_1' = bk_2 = \frac{2.303}{t}.\log_{10}\frac{a}{(a-x)}$$

which is the equation for a first order reaction. The new constant k_1', is not independent of the concentration of b, as is the case with true first order constants, but may vary with b if the latter is changed appreciably. When this is the case, the true constant k_2 can be obtained from k_1' by dividing the latter by b.

A worked example of the determination of order and rate constant is given below.

Hydrolysis of chloroform - Run 74

Temperature of reaction: 36 ± 0.1°C (309 K)
Concentration of dioxane: 3.784 mol.l.^{-1}, (32 % v/v)
Initial concentration of sodium hydroxide: 0.2017 mol.l.^{-1}
Initial concentration of chloroform: 0.0103 mol.l.^{-1}
Volume of samples after neutralisation: 1.065 ml.

Since the reaction was carried out in the presence of excess sodium hydroxide, it appeared pseudo-unimolecular with respect to chloroform.

TABLE 26

Hydrolysis of chloroform, run 74

Time (sec)	Peak area	Conc^n.$CHCl_3$ $(mol.l.^{-1}) \times 10^3$ (a-x)	$(a-x) \times 10^3$ corrected * to 1 ml.	$-\log_{10}(a-x)$	Conc^n.$CHCl_3$ reacted (x) $(mol.l.^{-1}) \times 10^3$	$\frac{x}{a} \cdot \frac{1}{(a-x)}$
0	365100	9.67	10.30	1.9872	0.00	0.00
60	371719	9.83	10.47	1.9801	—	—
900	331819	8.76	9.33	2.0301	0.97	10.09
1680	312730	8.25	8.79	2.0560	1.51	16.68
2520	292447	7.71	8.21	2.0857	2.09	24.72
3420	275481	7.26	7.73	2.1118	2.57	32.28
4260	260359	6.88	7.33	2.1349	2.97	39.34
5070	232405	6.15	6.55	2.1838	3.75	55.58
5940	219314	5.81	6.19	2.2083	4.11	64.46
6750	205490	5.45	5.80	2.2366	4.50	75.33
7560	184055	4.88	5.20	2.2840	5.10	95.22
8610	178111	4.70	5.01	2.3002	5.29	102.51
9450	158209	4.18	4.45	2.3516	5.85	127.63

Contd....

TABLE 26 (Contd.)

Time (sec)	Peak area	Conc^n.CHCl$_3$ (mol.l.$^{-1}$) x 10^3 (a-x)	(a-x) x 10^3 corrected* to 1 ml.	- $\log_{10}$ (a-x)	Conc^n.CHCl$_3$ reacted (x) (mol.l.$^{-1}$) x 10^3	$\frac{x}{a} \cdot \frac{1}{(a-x)}$
10380	155246	4.10	4.37	2.3595	5.93	131.75
11910	137623	3.62	3.86	2.4134	6.44	161.98
12870	126970	3.36	3.58	2.4461	6.72	182.24
13650	118137	3.11	3.31	2.4802	6.99	205.03
14820	109086	2.86	3.05	2.5157	7.25	230.78
15570	102543	2.71	2.89	2.5391	7.41	248.93
16320	95383	2.51	2.67	2.5735	7.63	277.44
17160	89423	2.37	2.52	2.5986	7.78	299.74
17910	83839	2.20	2.34	2.6308	7.96	330.26
18810	77252	2.03	2.16	2.6655	8.14	365.88
19740	73112	1.83	1.95	2.7100	8.35	415.73

* Neutralisation of the samples prior to analysis resulted in dilution of the reaction mixture for which a correction had to be made. See Page 133

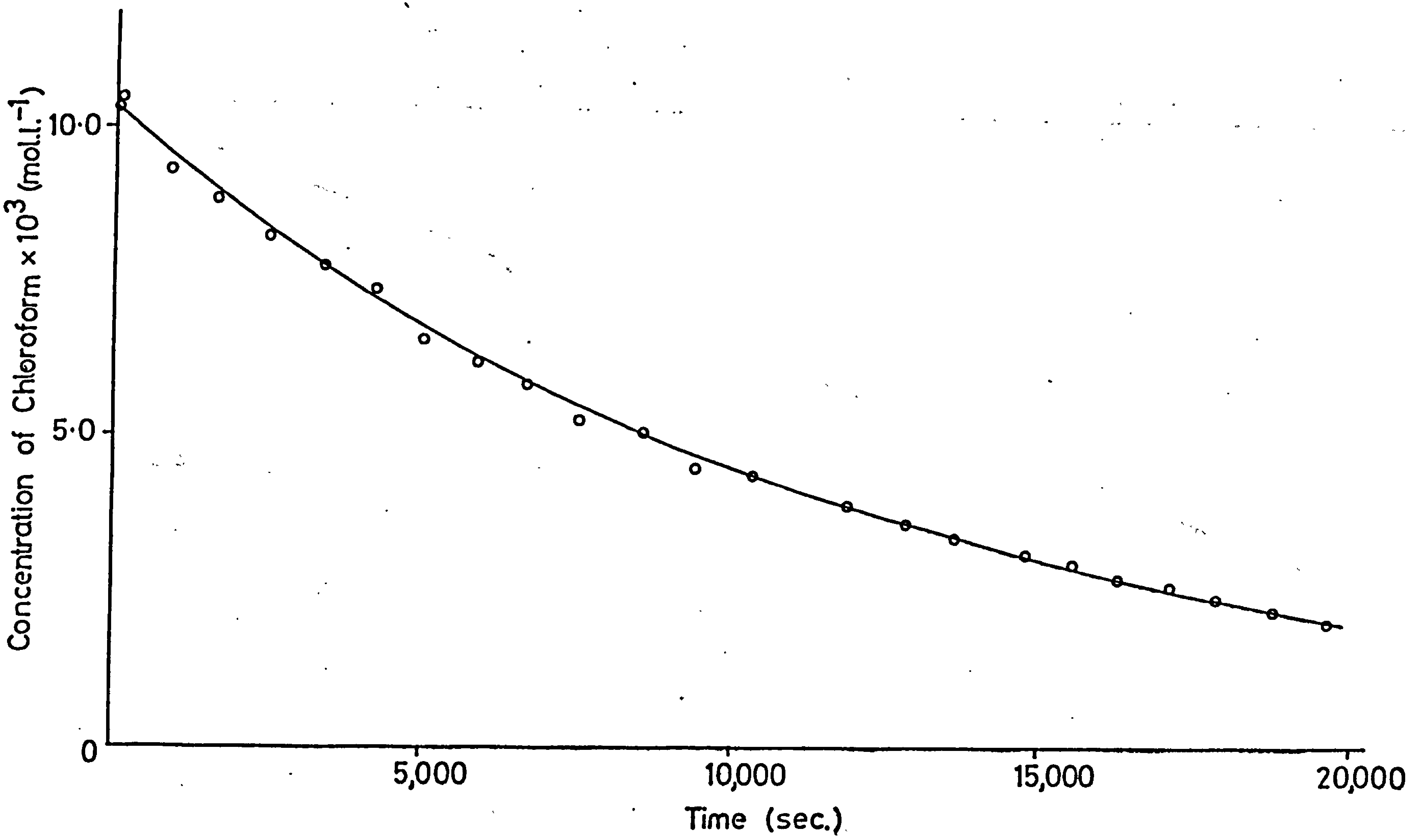


Fig. 18 Hydrolysis of Chloroform - Run 74

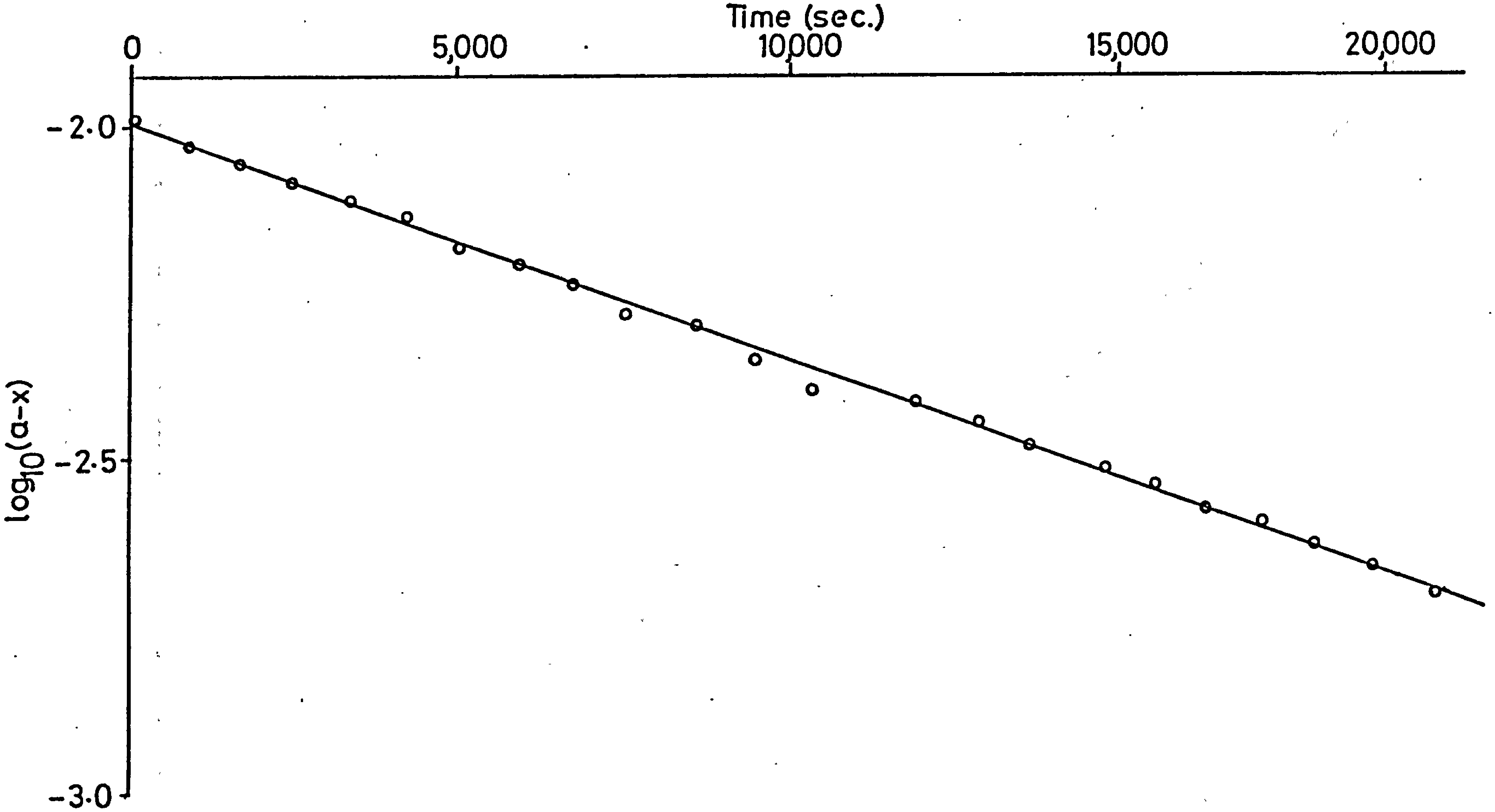


Fig. 19 First Order Rate Plot-Run 74

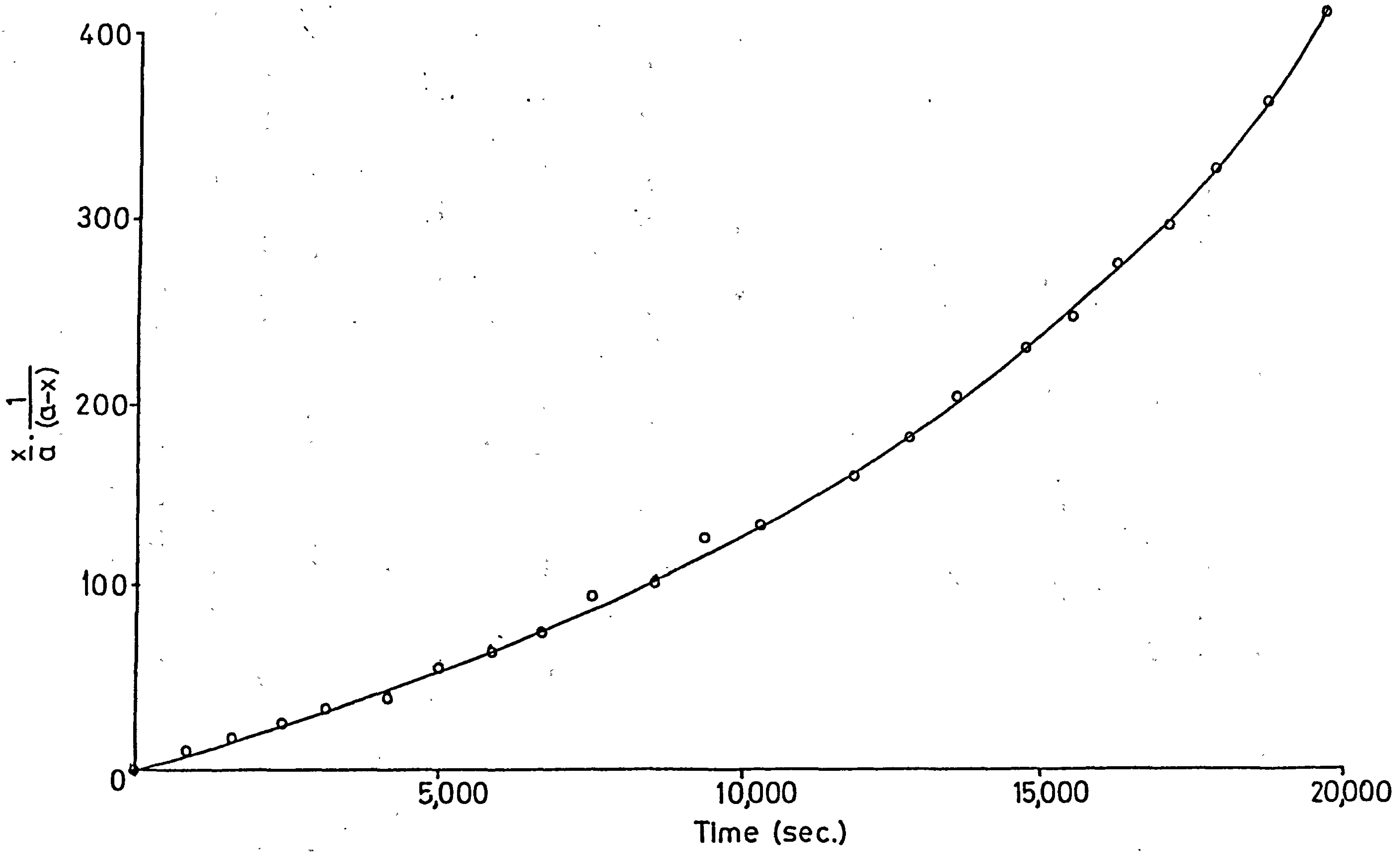


Fig. 20 Second Order Rate Plot-Run 74

From the first and second order rate plots it can be seen that the reaction is undoubtedly first order with respect to chloroform. The first order rate constant for the reaction is obtained from the slope of the graph.

$$\text{Slope} = \frac{k_1'}{2.303} = 3.576 \times 10^{-5} \text{ sec}^{-1}.$$

$$k_1 = 2.303 \times 3.576 \times 10^{-5} \text{ sec}^{-1}.$$

$$= 8.24 \times 10^{-5} \text{ sec}^{-1}.$$

Hydrolysis of chloroform - Run 29

Temperature of reaction: 36 ± 0.1°C (309 K)

Concentration of dioxane: 32 % v/v

Initial concentration of sodium hydroxide: 0.3403 mol.l.^{-1}

Initial concentration of chloroform: 0.1730 mol.l.^{-1}

Concentration of hydrochloric acid used - solution A: 0.0205 mol.l.^{-1}

solution B: 0.01025 mol.l.^{-1}

Two hydrochloric acid solutions were employed for titration of the sodium hydroxide solution, because of the difference in concentration between the beginning and the end of the run. Towards the end of the reaction the volume of acid required to titrate the sodium hydroxide became small resulting in a larger relative error. It was more satisfactory therefore to use a larger volume of a weaker acid.

The initial concentrations of chloroform and sodium hydroxide were comparable, so that the reaction could be followed with respect to both reactants.

TABLE 27

First and second order rate plots for the hydrolysis of chloroform with respect to sodium hydroxide, (run 29).

Time (sec)	Vol.HCl required for titration (ml.)	Conc^{n}.OH^{-} (a-x) (mol.l.$^{-1}$)	- log (a-x)	Conc^{n}.OH^{-} reacted (x) (mol.l.$^{-1}$)	$\frac{x}{a} \cdot \frac{1}{(a-x)}$
	Solution A				
0	16.60	0.3436	0.4639	0.0000	0.00
210	15.57	0.3223	0.4917	0.0213	0.19
630	15.20	0.3146	0.5023	0.0287	0.27
1290	13.37	0.2741	0.5620	0.0662	0.71
1830	13.15	0.2722	0.5651	0.0714	0.76
2400	12.58	0.2579	0.5886	0.0824	0.94
3150	11.90	0.2463	0.6068	0.0973	1.15
3720	11.25	0.2306	0.6372	0.1097	1.40
4560	10.60	0.3194	0.6588	0.1242	1.65
5280	10.05	0.2060	0.6861	0.1343	1.92
6060	9.45	0.1937	0.7128	0.1466	2.22
6900	8.90	0.1842	0.7347	0.1594	2.52
7740	8.35	0.1712	0.7665	0.1691	2.90
10080	7.10	0.1470	0.8327	0.1966	3.89
11160	6.60	0.1366	0.8646	0.2070	4.41
12120	6.23	0.1277	0.8938	0.2126	4.89
13680	5.83	0.1195	0.9226	0.2208	5.43
14880	5.20	0.1076	0.9681	0.2337	6.44
16290	4.88	0.1000	1.0000	0.2403	7.06
	Solution B				
17280	9.35	0.0958	1.0186	0.2445	7.50
18480	8.63	0.0885	1.0531	0.2518	8.36
19380	8.26	0.0846	1.0726	0.2557	8.88

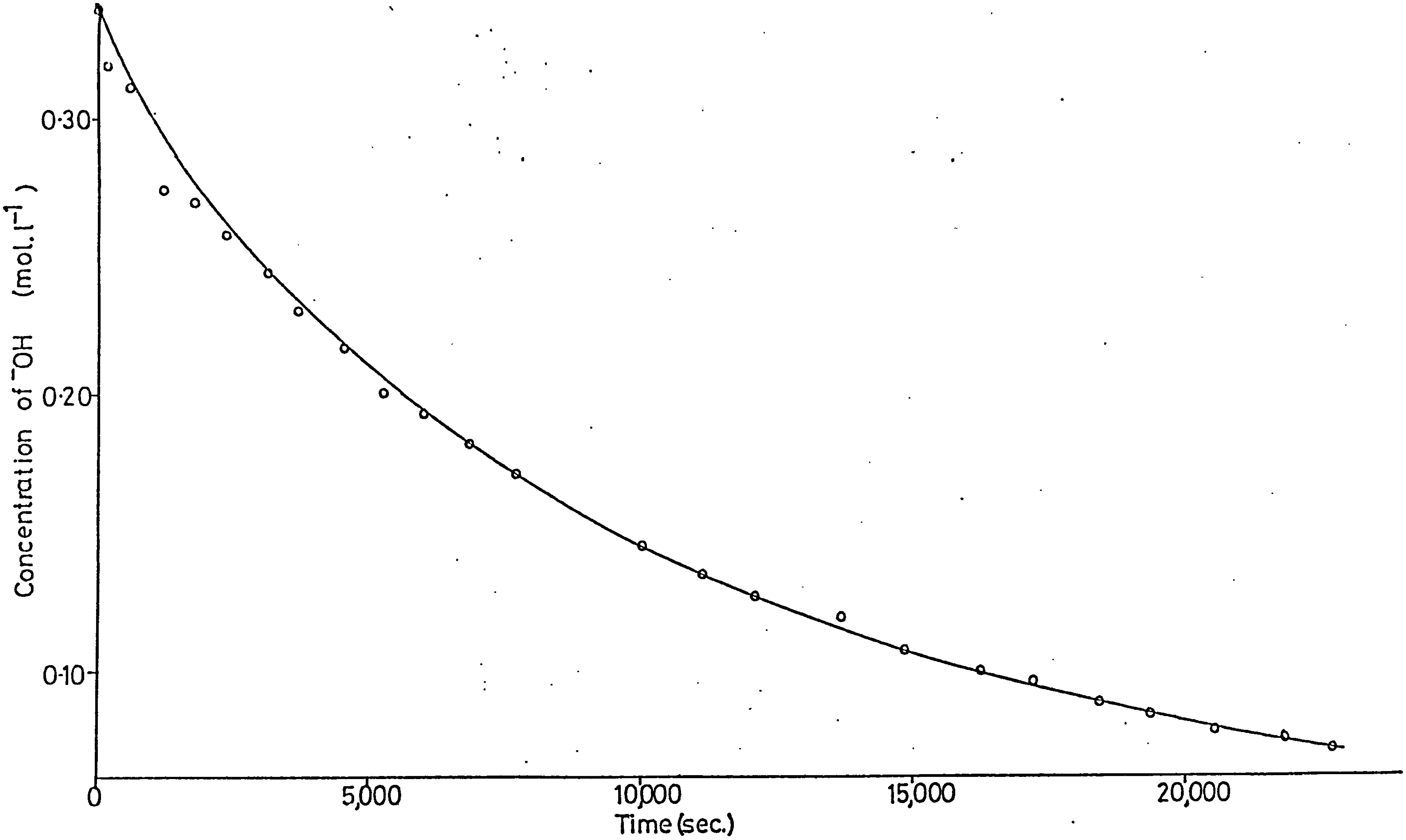


Fig. 21 Hydrolysis of Chloroform with respect to NaOH – Run 29

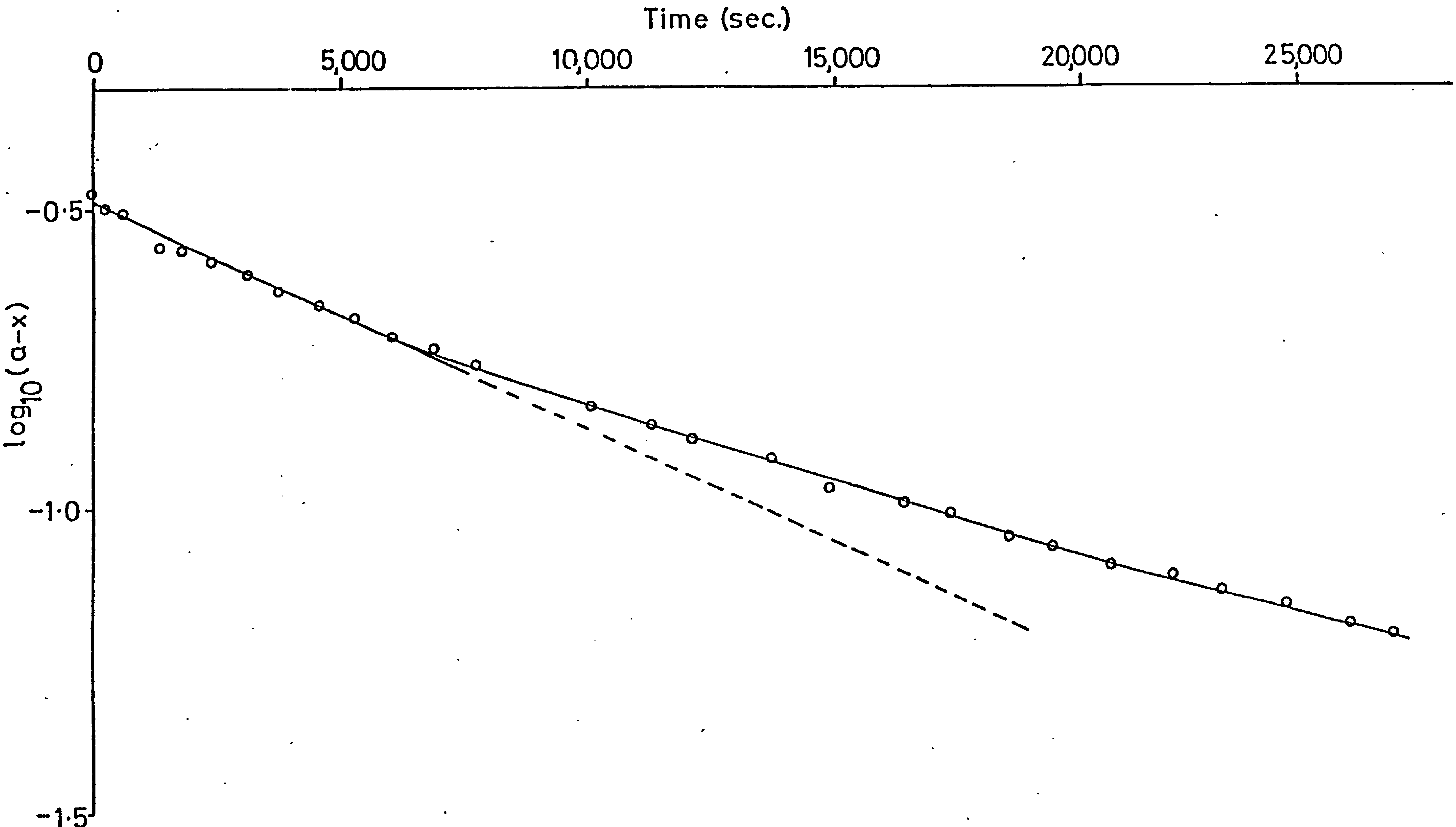


Fig. 22 First Order Rate Plot – Run 29

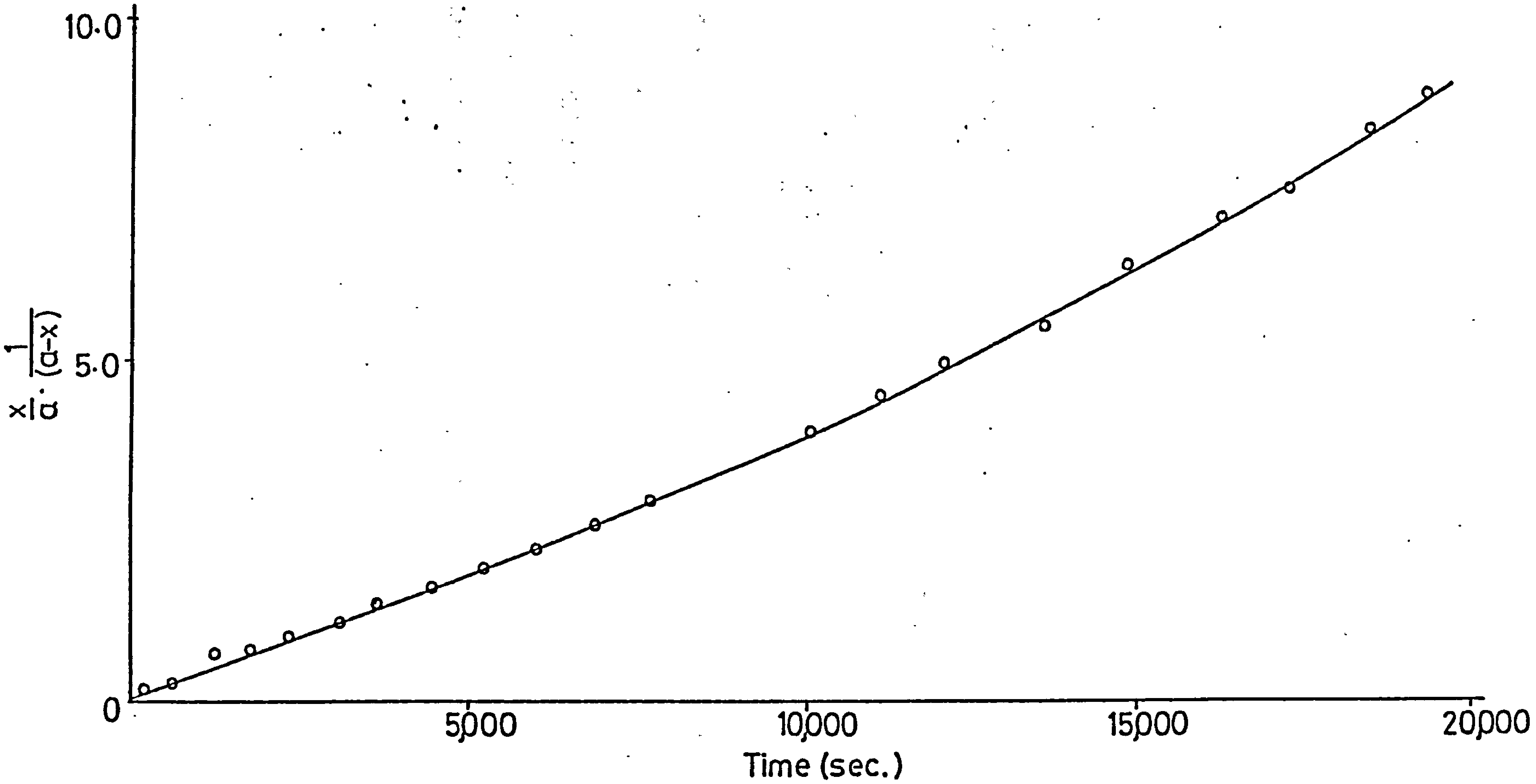


Fig. 23 Second Order Rate Plot-Run 29

To determine the overall order of the reaction the concentration of both reactants at the same time intervals must be known. An overall second order rate plot can then be constructed.

$$k_2t = \frac{1}{a_o-b_o} \ln \frac{b_o\ a_t}{a_o\ b_t}$$

where a_o = initial concentration of NaOH = 0.3436 mol.$1.^{-1}$

b_o = initial concentration of $CHCl_3$ = 0.1730 mol.$1.^{-1}$

a_t = concentration of NaOH at time t.

b_t = concentration of $CHCl_3$ at time t.

From the plot for the overall second order reaction, the second order rate constant, k_2 was calculated to be 2.176×10^{-4} mol.$^{-1}$ sec^{-1}.

The stoichiometry of the reaction was found to be 2.97 moles of OH^- to 1.00 moles of $CHCl_3$ when the amount of chloroform which had reacted at a given time was plotted against the amount of hydroxide that had reacted.

TABLE 28

Overall second order rate plot for the
hydrolysis of chloroform, (runs 12 and 29).

Time (sec.)	Concentration $CHCl_3$ b_t (mol.l.$^{-1}$)	Concentration NaOH a_t (mol.l.$^{-1}$)	$-\frac{1}{a_o-b_o}.\ln\frac{a_t\ b_o}{a_o\ b_t}$
60	0.170	0.336	0.2867
330	0.170	0.321	0.2963
600	0.168	0.308	0.4691
780	0.165	0.302	0.4788
1140	0.162	0.291	0.5888
1620	0.154	0.277	0.5809
2520	0.148	0.255	0.8331
2850	0.148	0.248	0.9962
3300	0.142	0.239	0.9703
4170	0.137	0.223	1.1664
4920	0.134	0.211	1.3608
5760	0.129	0.198	1.5107
6420	0.125	0.189	1.5987
7200	0.120	0.178	1.7109
7920	0.121	0.169	2.0636
10080	0.111	0.146	2.4156
10800	0.109	0.139	2.5970
11400	0.106	0.133	2.6920
12060	0.107	0.128	2.9717
12630	0.104	0.123	3.0386
13260	0.104	0.119	3.2324
14040	0.101	0.113	3.3640
15900	0.096	0.102	3.6789
17160	0.094	0.098	3.7528
17910	0.093	0.092	4.0602
18840	0.092	0.087	4.3433
19470	0.092	0.084	4.5490

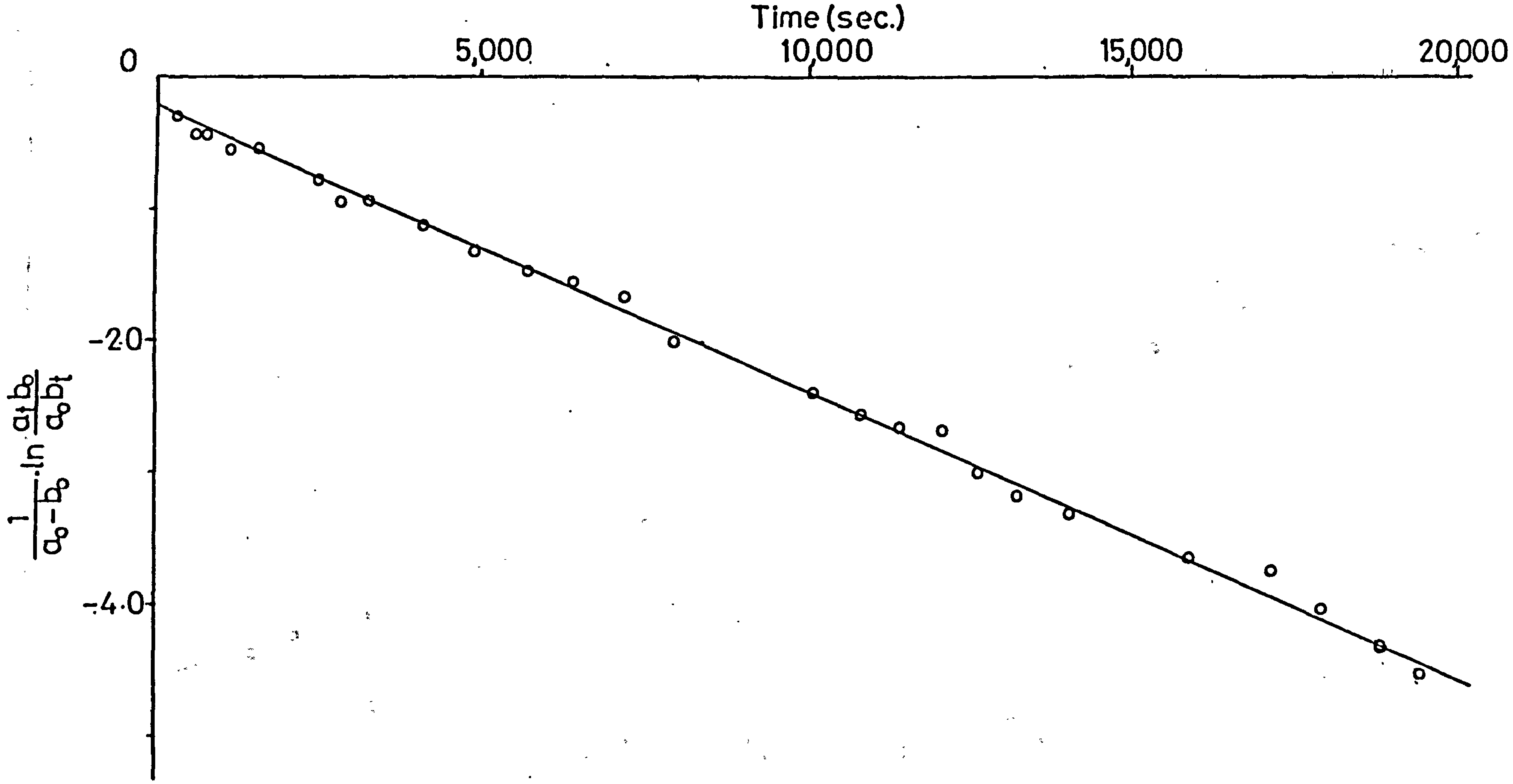


Fig. 24 Overall second-order rate plot - Runs 12 and 29

Fig. 25 Plot to determine the stoichiometry of the reaction between chloroform and sodium hydroxide – Runs 12 and 29

7.I.i. DETERMINATION OF THE ORDER OF REACTION USING THE "METHOD OF FRACTIONAL LIFE"

One means of testing the order of a reaction is known as the "fractional life method". In this method the time taken to decompose a definite fraction of the reactant, usually one-half, is determined for a number of different values of a. When one-half of the reactant has undergone decomposition, a-x = a/2, and the time, $t_{\frac{1}{2}}$, nececessary for this to occur follows from equation (55) as

$$t_{\frac{1}{2}} = \frac{1}{k_1} . \left(\ln \frac{a}{\frac{a}{2}} \right) \quad (54)$$

$$= \frac{\ln 2}{k_1} \quad (55)$$

According to this relationship $t_{\frac{1}{2}}$; the half-life period of the reaction is independent of the initial concentration of the reactant for a first order reaction.

In the case of a second order reaction the period of half-life is given by

$$t_{\frac{1}{2}} = \frac{1}{k_2} . \frac{(\frac{a}{2})}{a(\frac{a}{2})} \quad (56)$$

$$= \frac{1}{k_2 a} \quad (57)$$

Therefore, for a second order reaction the period of half-life is inversely proportional to the first power of the initial concentration of the reactant.

The order of the hydrolysis of chloroform with respect to chloroform was investigated using the method of fractional life. The reaction was carried out under the same conditions but with differing initial chloroform concentrations, and the time taken for one-half of the chloroform to react was determined.

Runs 97–100

Temperature of reaction: 36 ± 0.1°C (309 K)

Concentration of dioxane: 32% v/v

Initial concentration of sodium hydroxide: 0.40 mol.l.$^{-1}$

TABLE 29

Determination of order by the "method of fractional life".

Run No.	Initial conc^{n}. $CHCl_3$ (mol.l.$^{-1}$)	$t_{\frac{1}{2}}$ (sec)
99	5.54×10^{-3}	4580
100	9.00×10^{-3}	4580
97	13.30×10^{-3}	4530
98	18.12×10^{-3}	4560

The period of half-life was shown to be independent of the initial concentration of chloroform, and an average value of 4,563 sec. was obtained. This confirmed that the reaction was first order with

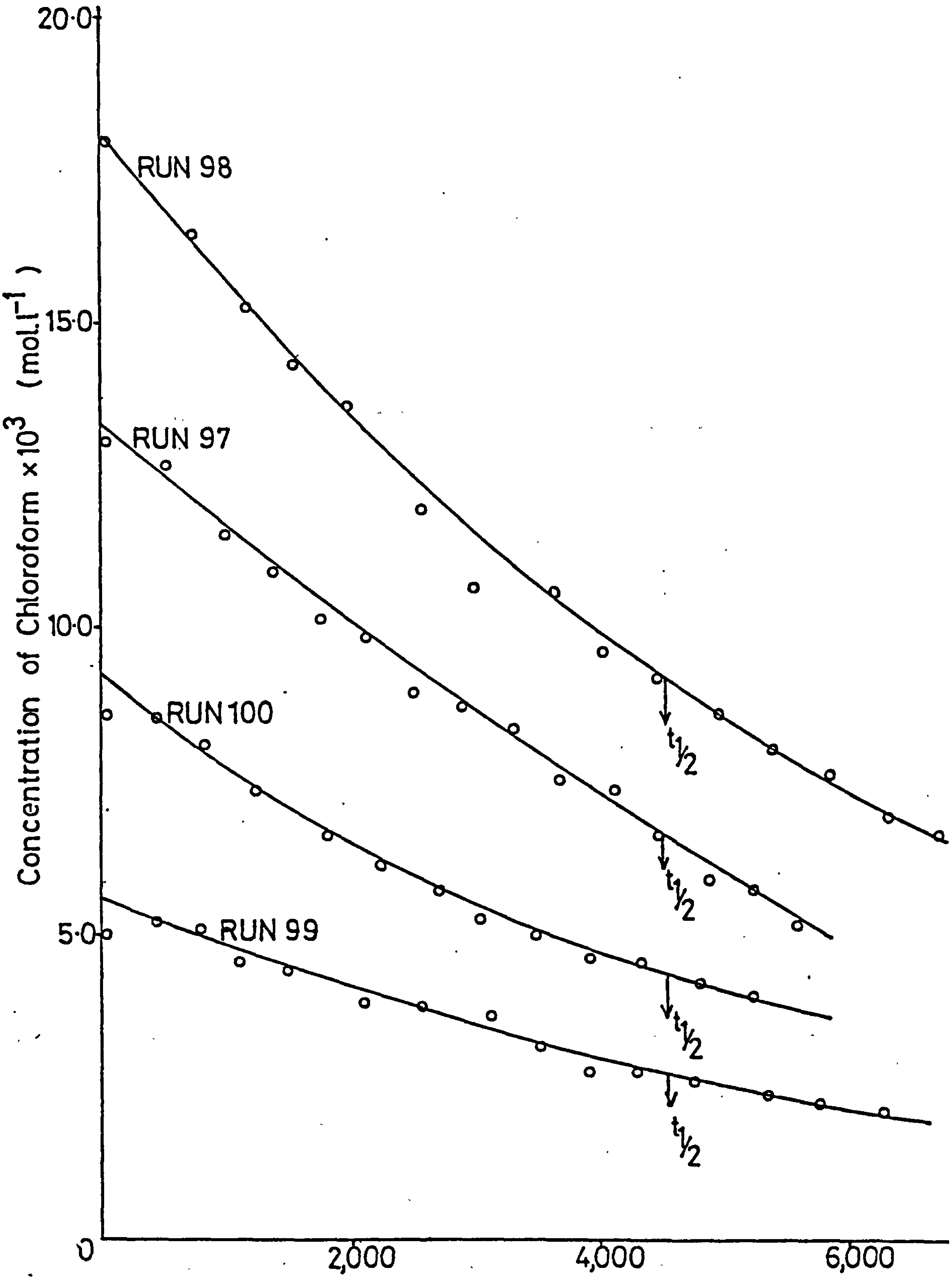


Fig. 26 Determination of order by method of "fractional-life"

respect to chloroform.

Substituting this value into equation (55)

$$4{,}563 = \frac{\ln 2}{k_1'}$$

$$k_1' = 1.52 \times 10^{-4} \text{ sec.}^{-1}$$

7.I.ii. TO DETERMINE THE EFFECT OF ADDED SALTS ON THE RATE OF HYDROLYSIS OF CHLOROFORM

Experiments were carried out to determine the effect of added inorganic salts on the reaction rate. Runs were carried out at 41 ± 0.1°C (314 K) with an initial concentration of 0.0375 mol.l.$^{-1}$ sodium hydroxide.

TABLE 30

The effects of added salts on the hydrolysis of chloroform

Run No.	Conc^{n}.dioxane (% v/v)	Salt added	Conc^{n}. salt (mol.l.$^{-1}$)	k_1' (sec^{-1})	Change in k_1' due to salt
101	32.0	—	—	7.16×10^{-5}	—
102	32.0	KNO_3	0.01	5.59×10^{-5}	-21.9 %
103	10.0	—	—	14.60×10^{-5}	—
104	10.0	NaCl	0.01	7.07×10^{-5}	-51.6 %

7.I.iii. TO SHOW THE EFFECT OF DIOXANE CONCENTRATION ON THE RATE OF REACTION

To determine the effect of changing the concentration of dioxane on the rate of reaction, a number of reactions were carried out in which the concentration of dioxane was slightly higher than that usually employed.

TABLE 31

To show the effect of dioxane concentration on reaction rate

Run No.	Conc^n. dioxane (mol.l.$^{-1}$)	Conc^n. NaOH (mol.l.$^{-1}$)	k_1' (sec.$^{-1}$) x 10^5
82	4.1067	0.9687	27.58
85	4.1220	1.1555	29.01
81	4.1160	1.2733	30.44
84	4.1168	1.3540	31.71
83	4.1380	1.4332	32.24
86	3.7945	0.8949	28.71
72	3.7910	0.9998	30.36
69	3.7877	1.2956	36.25
68	3.7799	1.4950	38.12

7.I.iv. REACTION OF DEUTEROCHLOROFORM WITH SODIUM DEUTEROXIDE

The hydrolysis of deuterochloroform by sodium deuteroxide was carried out in the same way as that of chloroform, except that deuterium oxide was used to make up the solutions instead of water. Deuterochloroform

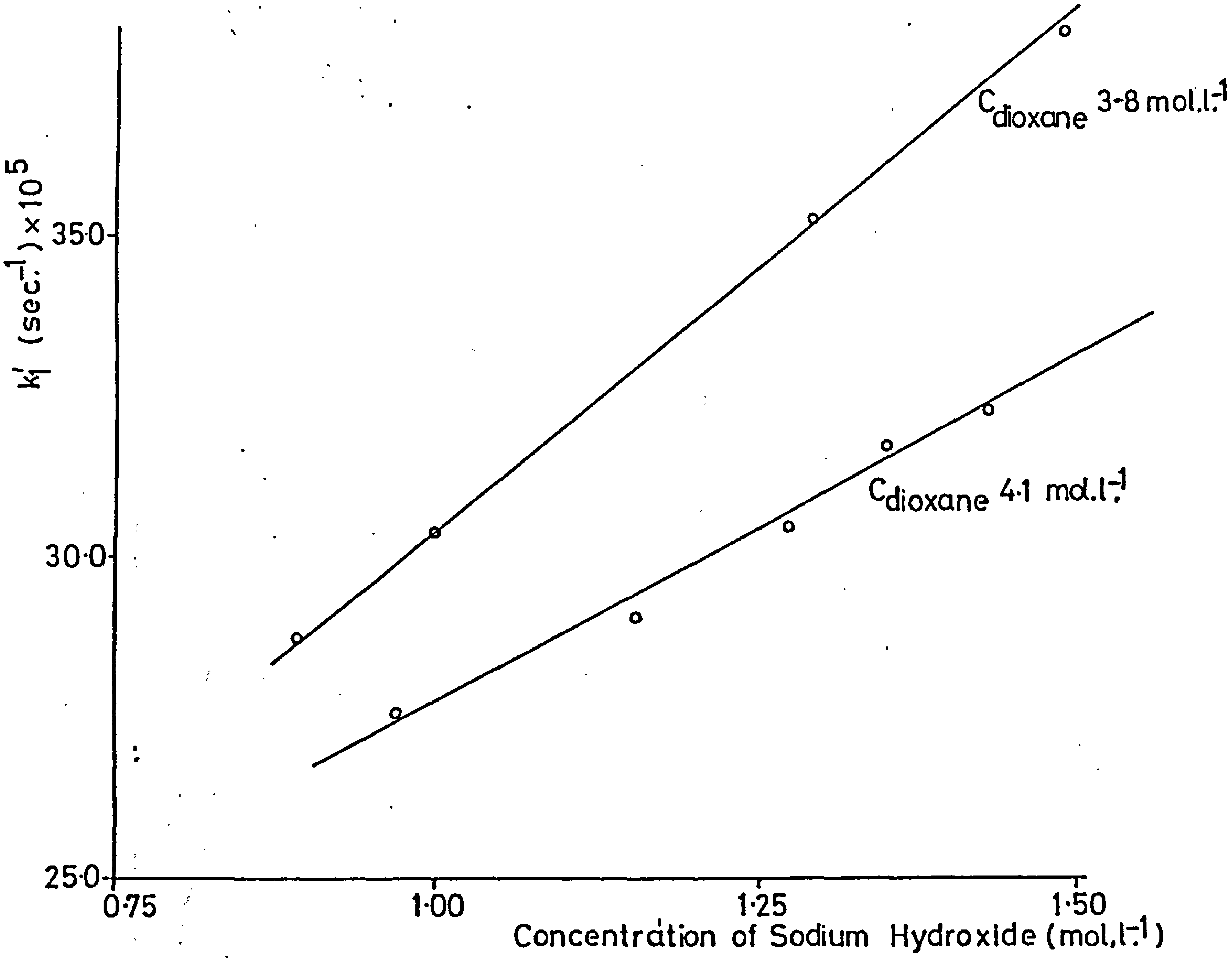


Fig. 27 Graph to show the effect of dioxane concentration on reaction rate

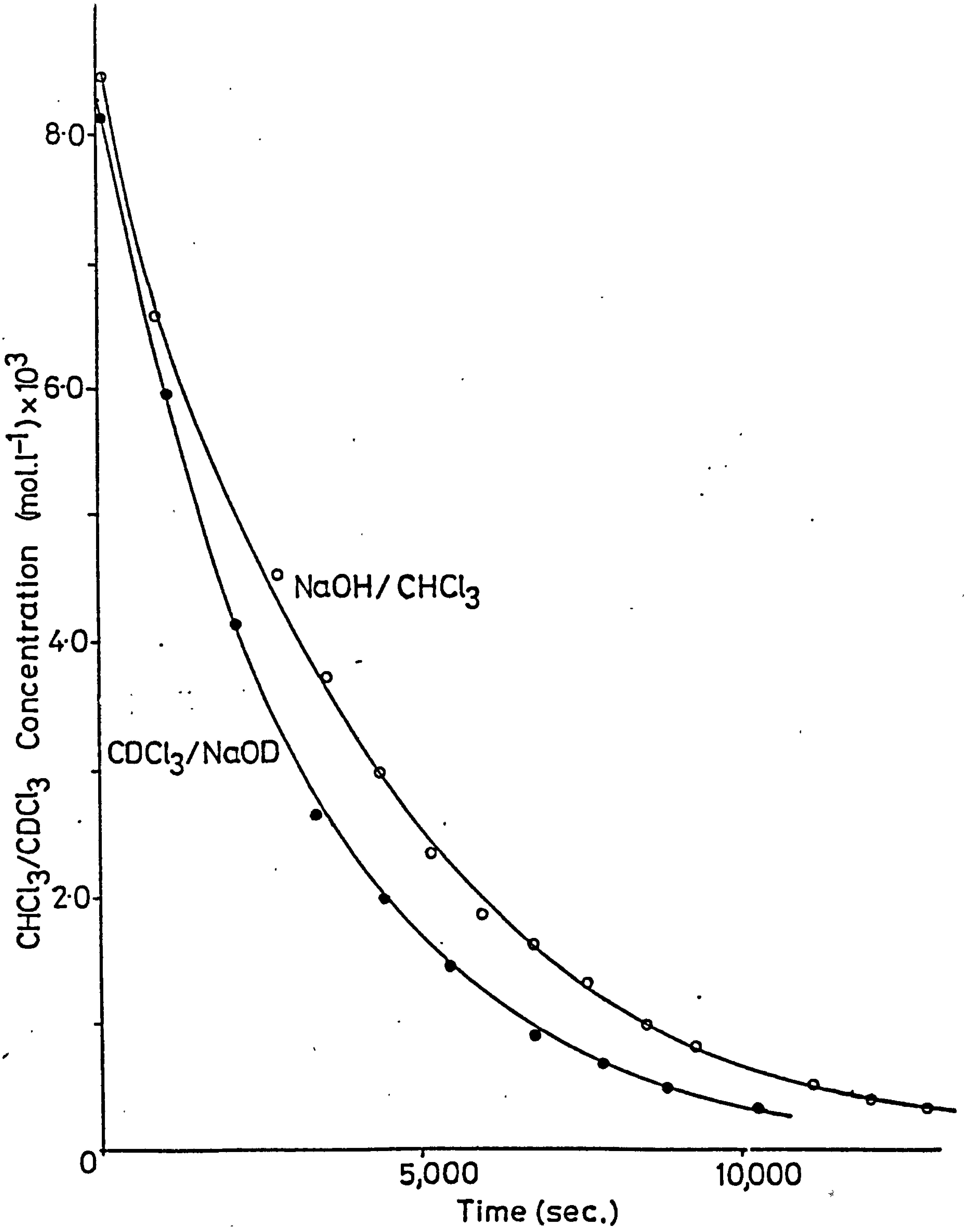


Fig. 28 The hydrolysis of deuterochloroform in sodium deuteroxide solution

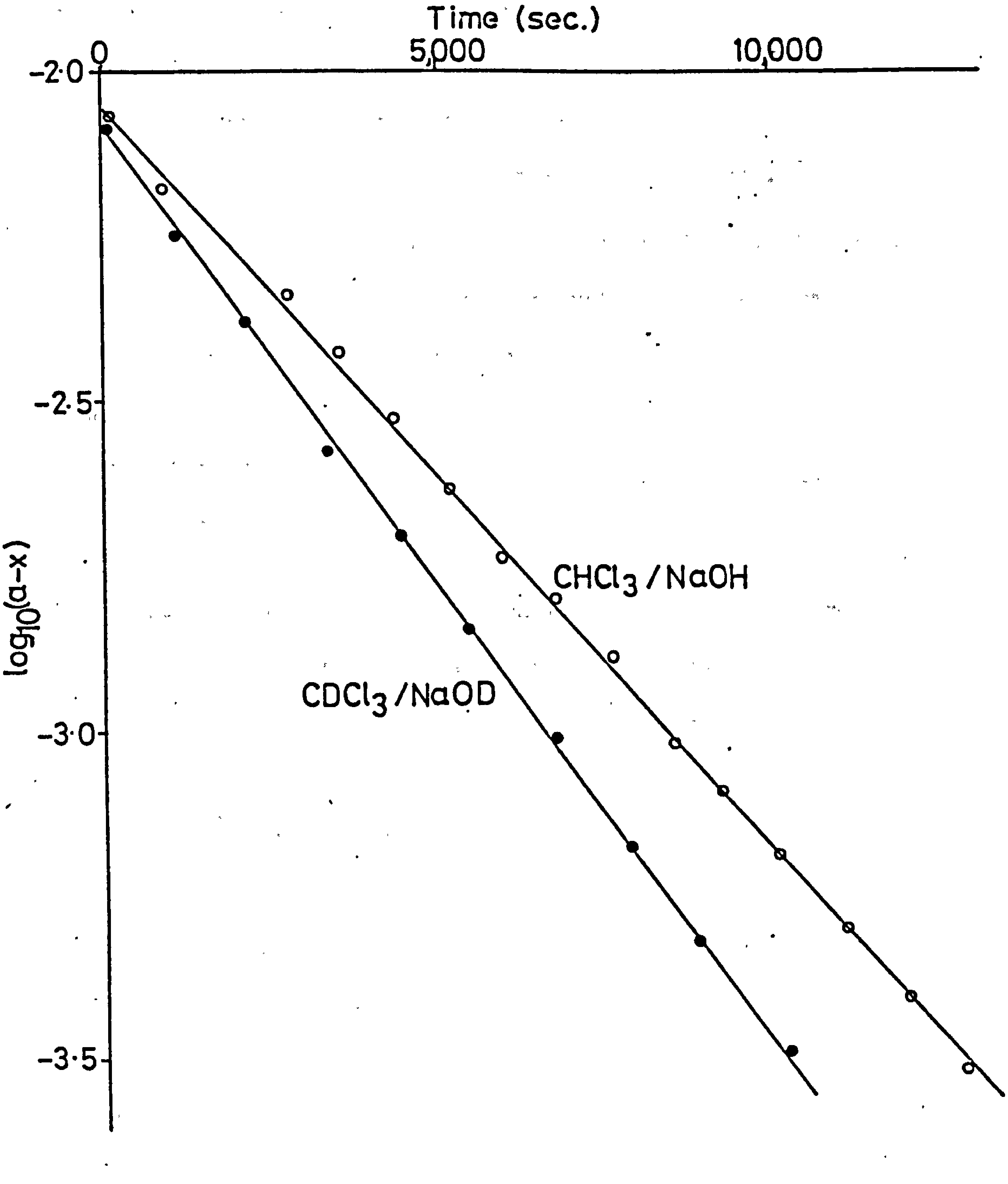


Fig. 29 First order rate plot for the hydrolysis of deuterochloroform in sodium deuteroxide

was used instead of chloroform in order to prevent exchange between the deuterium of the OD^- ion and protons released by dissociation of chloroform.

Run 96

Temperature of reaction: $36 \pm 0.1^\circ C$ (309 K)

Concentration of dioxane: 32 % v/v

Initial concentration of sodium deuteroxide: 0.80 $mol.l.^{-1}$

Initial concentration of deuterochloroform: 0.00822 $mol.l.^{-1}$

The first order rate constant was found to be 3.19×10^{-4} $sec.^{-1}$ compared to 2.57×10^{-4} $sec.^{-1}$ for the hydrolysis of chloroform in sodium hydroxide under the same conditions.

7.I.v. DETERMINATION OF ARRHENIUS ACTIVATION ENERGY AND ENTROPY OF ACTIVATION

Increasing the temperature of a reaction leads to an increase in reaction velocity and hence an increase in the rate constant. This variation may be represented by the Arrhenius equation

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

where k = The reaction rate constant

T = Absolute temperature

R = Gas constant

E_a = The energy of activation

If E_a is assumed to be constant, integration gives

$$\log_{10} k = \frac{-E_a}{2.303\ R} \cdot \frac{1}{T} + C \tag{58}$$

where C is a constant of integration. However if the equation is integrated between the limits $k=k_1$ at $T=T_1$, $k=k_2$ at $T=T_2$, then

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303\ R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \tag{59}$$

Hence if the energy of activation and a value of k at a particular temperature are known, k may be calculated at any other temperature.

From equation (58) it can be seen that a plot of $\log_{10}k$ against $\frac{1}{T}$ should be a straight line with slope equal to $-E_a/2.303R$, and y intercept equal to C.

Transition state theory has shown that the rate constant of any reaction may be given by the expression

$$k = \frac{RT}{Nh} K^{\ddagger} \tag{60}$$

where R = Gas constant: 1.9872 $\text{cal.mol}^{-1}\ \text{deg}^{-1}$

N = Avogadro's number: $6.0225 \times 10^{23}\ \text{mol.}^{-1}$

h = Planck's constant: 1.5836×10^{-34} cal.sec.

T = Absolute temperature

$K^{\ddagger}$ = Equilibrium constant for the formation of the activated complex from the reactants

$K^{\ddagger}$ may be written

$$\ln K^{\ddagger} = -\frac{\Delta G^{\ddagger}}{RT} \qquad (61)$$

$$= -\frac{(\Delta H^{\ddagger} - T\Delta S^{\ddagger})}{RT} \qquad (62)$$

where $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the free energy, enthalpy and entropy of activation respectively. Introducing this into equation (60), we obtain for k

$$k = \frac{RT}{Nh} e^{\frac{\Delta S^{\ddagger}}{R}} e^{-\frac{\Delta H^{\ddagger}}{RT}} \qquad (63)$$

or

$$\ln k = \ln\left(\frac{RT}{Nh}\right) + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} \qquad (64)$$

$$\therefore \ln k = \ln\left(\frac{R}{Nh}\right) + \ln T + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} \qquad (65)$$

$$\therefore \ln \frac{k}{T} = \ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} \qquad (66)$$

From the above relationship it may be seen that by plotting ln k/T against 1/T a straight line is obtained with slope $-\frac{\Delta H^{\ddagger}}{R}$ and intercept $(1/T = 0)$, $\ln (R/Nh) + \Delta S^{\ddagger}/R$. Since R, N and h are known constants $\Delta S^{\ddagger}$ may thus be determined. However, it is more usual to determine this value numerically.

In order to determine the Arrhenius activation energy and the entropy of activation the hydrolysis of chloroform was carried out at

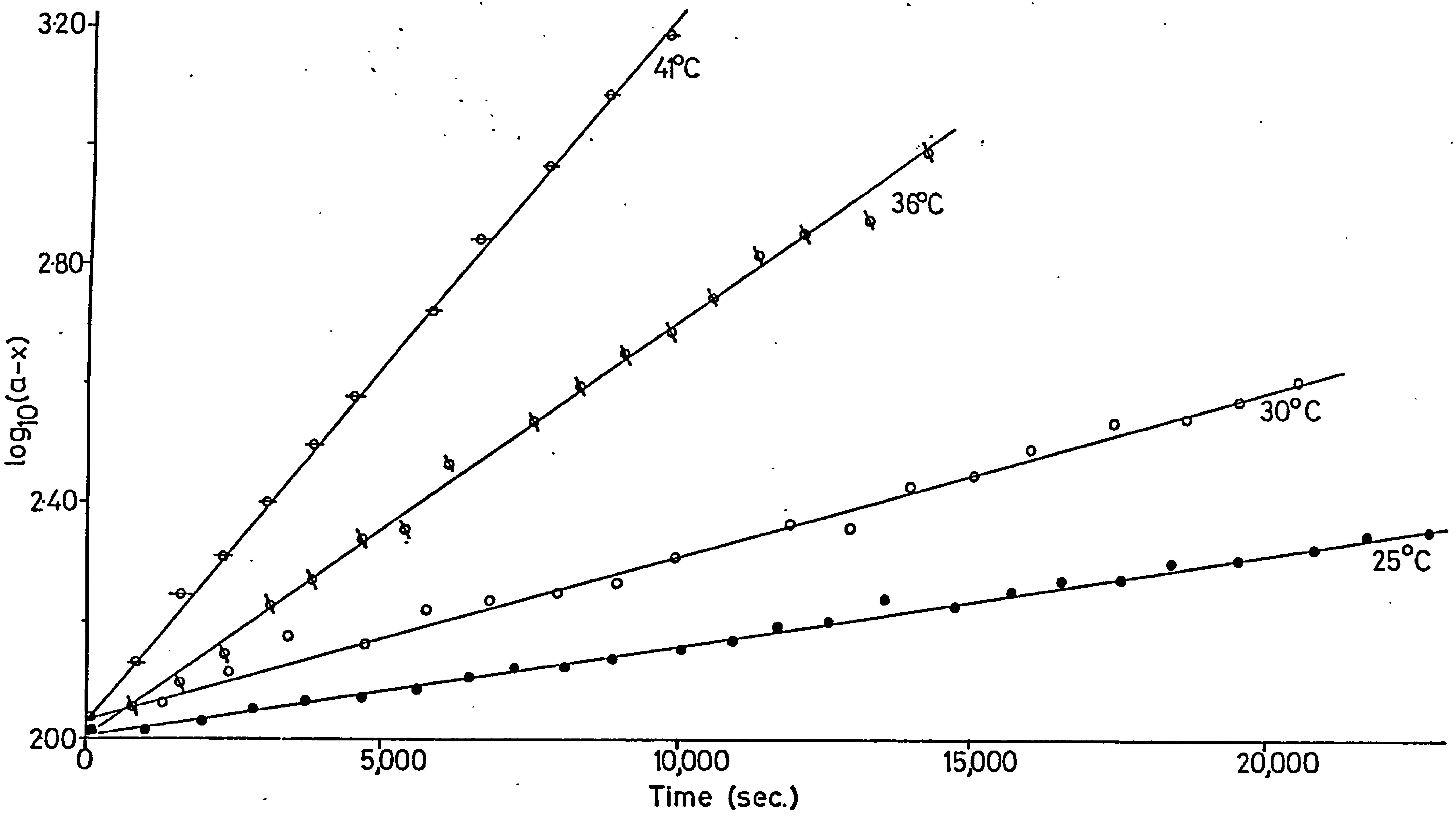


Fig.30 First order rate plots used to determine activation parameters–
0·40M Sodium, hydroxide

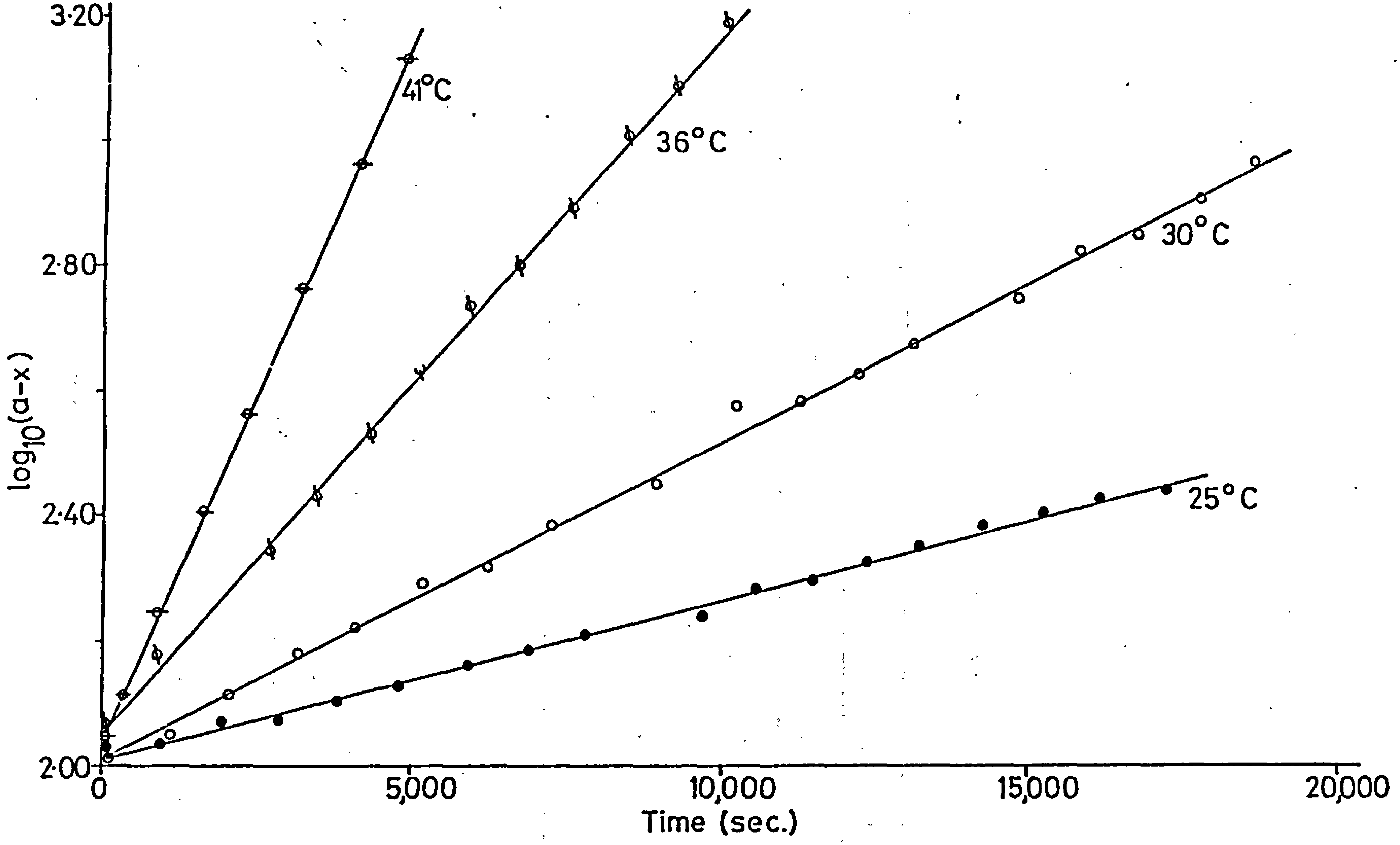


Fig. 30A First order rate plots used to determine activation parameters– 0·79 M Sodium hydroxide several temperatures and the first order rate constants for each reaction determined;

Runs 70, 76, 90-95

TABLE 32

Determination of Arrhenius activation energy

T(K)	$\frac{1}{T}$ (K^{-1})	0.40 M NaOH		0.79 M NaOH	
		k_1' ($sec.^{-1}$)	$\log_{10} k_1'$	k_1' ($sec.^{-1}$)	$\log_{10} k_1'$
314	3.185×10^{-3}	2.71×10^{-4}	-3.5670	5.17×10^{-4}	-3.2865
309	3.236×10^{-3}	1.60×10^{-4}	-3.7959	2.57×10^{-4}	-3.5901
303	3.300×10^{-3}	0.614×10^{-4}	-4.2118	1.16×10^{-4}	-3.9355
298	3.355×10^{-3}	0.355×10^{-4}	-4.4498	0.587×10^{-4}	-4.2336

The slope of the line was obtained from the plot using the 'method of least squares'.

0.40 M NaOH

$$\text{Slope} = -5.366 \times 10^3 = \frac{-E_a}{2.303\ R}$$

$$E_a = 5.366 \times 10^3 \times 2.303 \times 1.987 \ \text{cal.mol.}^{-1}$$

$$\underline{E_a = 24.6 \ \text{Kcal. mol.}^{-1}}, (102.8 \ \text{KJ. mol.}^{-1})$$

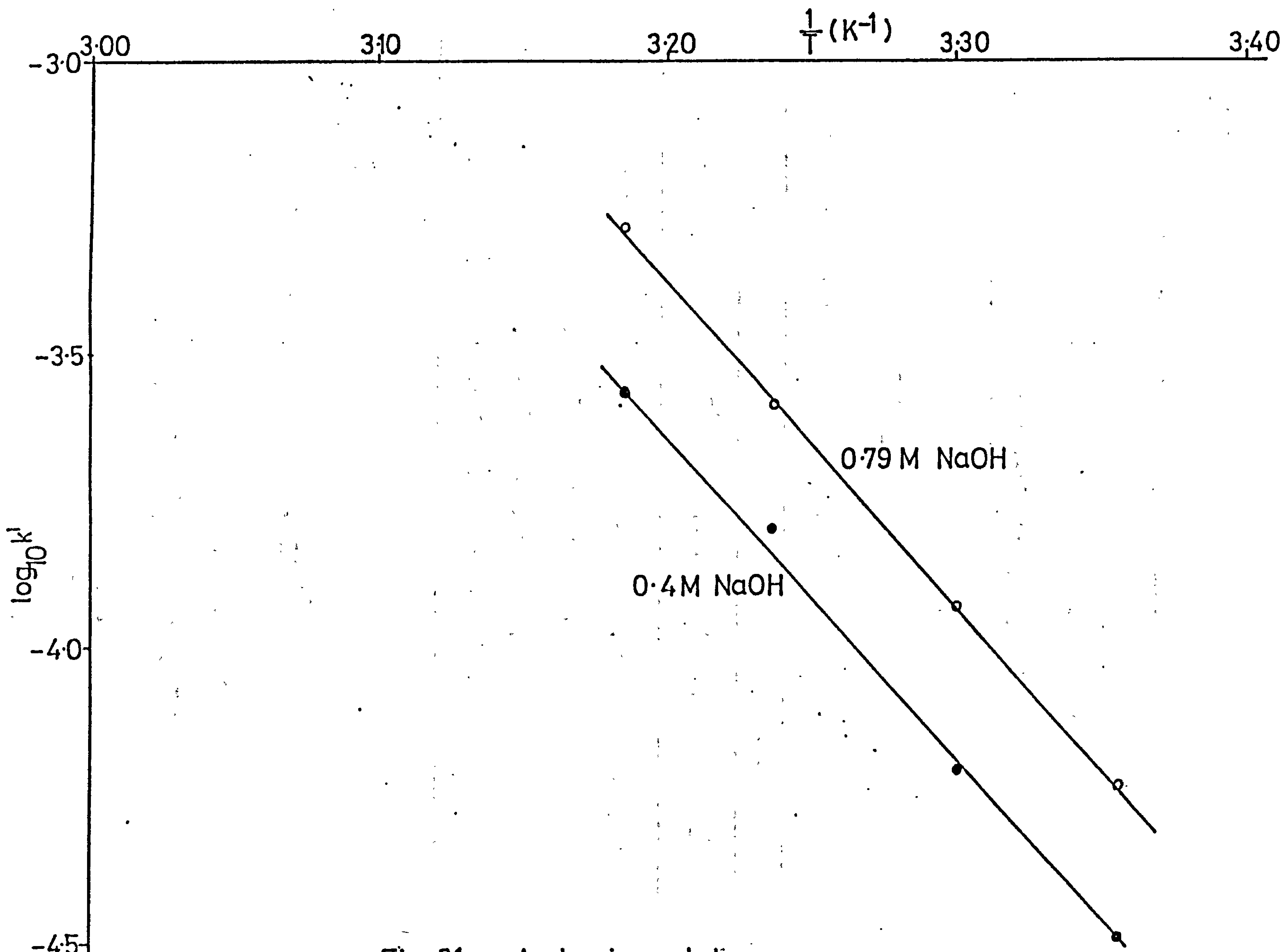


Fig. 31 Arrhenius plot

0.79 M NaOH

$$\text{Slope} = -5.561 \times 10^3 = \frac{-E_a}{2.303\ R}$$

$$E_a = 5.561 \times 10^3 \times 2.303 \times 1.987\ \text{cal.mol}^{-1}$$

$$\underline{E_a = 25.5\ \text{Kcal.mol}^{-1}}\ (106.5\text{KJ.mol}^{-1})$$

TABLE 33

Graphical determination of enthalpy and entropy of activation

T(K)	$\frac{1}{T}(K^{-1})$	0.40 M NaOH		0.79 M NaOH	
		$k_1'(\text{sec}^{-1})$	$\ln \frac{k_1'}{T}$	$k_1'(\text{sec}^{-1})$	$\ln \frac{k_1'}{T}$
314	3.185×10^{-3}	2.71×10^{-4}	-13.9628	5.17×10^{-4}	-13.3169
309	3.236×10^{-3}	1.60×10^{-4}	-14.4737	2.57×10^{-4}	-13.9998
303	3.300×10^{-3}	0.614×10^{-4}	-15.4118	1.16×10^{-4}	-14.7757
298	3.355×10^{-3}	0.355×10^{-4}	-15.9431	0.587×10^{-4}	-15.4402

0.40 M NaOH

$$\text{Slope} = -12.051 \times 10^3 = \frac{-\Delta H^*}{R}$$

$$\therefore \Delta H^* = 12.051 \times 10^3 \times 1.987\ \text{cal.mol}^{-1}$$

$$\underline{\Delta H^* = 24.0\ \text{Kcal.mol}^{-1}}\ (100.2\ \text{KJ.mol}^{-1})$$

$$\text{Intercept}\ \left(\frac{1}{T} = 0\right) = 24.4471 = \ln \frac{R}{Nh} + \frac{\Delta S^*}{R}$$

$$= 23.7599 + \frac{\Delta S^*}{1.987}$$

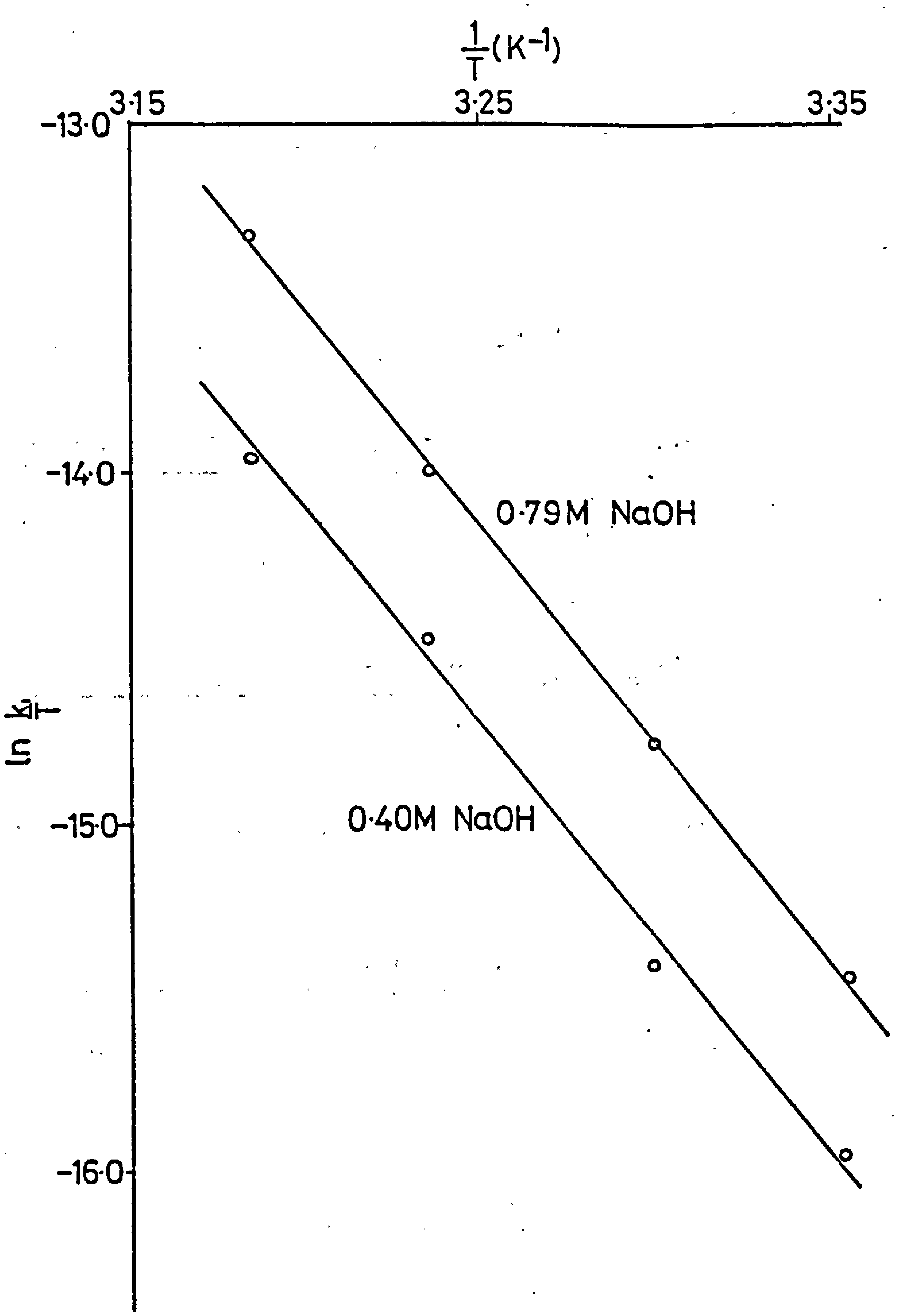


Fig. 32 Determination of entropy of activation

$$\Delta S^{*} = (24.4471 - 23.7566)1.987 \text{ cal.mol.}^{-1} \text{ deg.}^{-1}$$

$$\underline{\Delta S^{*} = 1.4 \text{ cal.mol.}^{-1} \text{ deg.}^{-1}} \ (5.9 \text{ J.mol.}^{-1} \text{ deg.}^{-1})$$

0.79 M NaOH

$$\text{Slope} = -12.475 \times 10^{3} = \frac{-\Delta H^{*}}{R}$$

$$\underline{\Delta H^{*} = 24.8 \text{ Kcal.mol.}^{-1}} \ (103.7 \text{ KJ.mol.}^{-1})$$

$$\text{Intercept} \quad (\tfrac{1}{T} = 0) = 26.38596 = \frac{\ln R}{Nh} + \frac{\Delta S^{*}}{R}$$

$$\underline{\Delta S^{*} = 5.2 \text{ cal.mol.}^{-1} \text{ deg.}^{-1}} \ (21.8 \text{ J.mol.}^{-1} \text{ deg.}^{-1})$$

The entropy of activation may also be determined numerically from eq. (64).

$$\ln \frac{k}{T} = \ln \frac{RT}{Nh} + \frac{\Delta S^{*}}{R} - \frac{\Delta H^{*}}{RT} \qquad (64)$$

0.40 M, 298K

$$-10.2460 = 29.4571 - 40.5447 + \frac{\Delta S^{*}}{R}$$

$$\underline{\Delta S^{*} = 1.7 \text{ cal.mol.}^{-1} \text{ deg.}^{-1}} \ (7.1 \text{ J.mol.}^{-1} \text{ deg.}^{-1})$$

This may be repeated for each temperature, and the average value taken.

TABLE 34

Numerical determination of entropy of activation

T(K)	0.40 M NaOH		0.79 M NaOH	
	$\Delta S^{\ddagger}$(cal.mol.$^{-1}$deg.$^{-1}$)	$\Delta S^{\ddagger}$(J.mol.$^{-1}$deg.$^{-1}$)	$\Delta S^{\ddagger}$(cal.mol.$^{-1}$deg.$^{-1}$)	$\Delta S^{\ddagger}$(J.mol.$^{-1}$deg.$^{-1}$)
298	1.7	7.1	5.7	23.8
303	1.4	5.9	5.6	23.4
309	1.7	7.1	5.6	23.4
314	1.4	5.9	5.6	23.4
Average	1.5	6.3	5.6	23.4

TABLE 35

Summary of activation parameters

	0.40 M NaOH	0.79 M NaOH
E_a(Kcal.mol.$^{-1}$)	24.6	25.5
(KJ.mol.$^{-1}$)	102.8	106.5
$\Delta H^{\ddagger}$(Kcal.mol.$^{-1}$)	24.0	24.8
KJ.mol.$^{-1}$)	100.2	103.7
$\Delta S^{\ddagger}$graphical		
(cal.mol.$^{-1}$deg.$^{-1}$)	1.4	5.2
(J.mol.$^{-1}$deg.$^{-1}$)	5.9	21.8
$\Delta S^{\ddagger}$numerical		
(cal.mol.$^{-1}$deg.$^{-1}$)	1.5	5.6
(J.mol.$^{-1}$deg.$^{-1}$)	6.3	23.4

7.II. CONSTRUCTION OF YAGIL PLOT

To determine the number of water molecules involved in the transition state of the reaction a Yagil Plot was constructed. This required accurate determinations of rate constants at different initial concentrations of sodium hydroxide solution. Calculation of the unbound water concentration required accurate values of sodium hydroxide and dioxane concentrations, and the densities of the solutions at the temperature of the reactions. By measuring the weight of each constituent in the reaction mixture precise values of concentration could be obtained as shown below.

To ensure that the sodium hydroxide solution remained carbonate-free double distilled water was used and this was reboiled and then allowed to cool with a stream of nitrogen bubbling through it. Commercially obtained carbonate-free volumetric sodium hydroxide solution was used. This was standardised by titration, at frequent intervals, and stored under nitrogen. Dioxane was also stored under nitrogen.

When the reaction mixture had been made up a portion of it (~ 50 ml.) was stored under nitrogen in a stoppered flask, for density determination the following day.

Run 70

Weight of flask = 107.59 g.

Weight of flask + water = 271.18 g.

Weight of flask + water + NaOH solution = 152.14 g.

Weight of flask + water + NaOH solution + dioxane = 205.84 g.

Density of reaction mixture at 36 ± 0.01°C = 1.0486 g. ml.$^{-1}$

Weight of NaOH solution in mixture = 44.55 g.

By titration it was shown that 11.15 g. of original NaOH solution contained 3.195×10^{-2} mol. NaOH

$$\therefore \quad 44.55 \text{ g. contains } \frac{3.195 \times 10^{-2} \times 44.55}{11.15} \text{ mol. NaOH}$$

$$= 0.1277 \text{ mol.}$$

168.59 g. or $\frac{168.59}{1.0486}$ ml. reaction soln. contains 0.1277 mol.

$$\therefore \quad 1 \text{ l. contains } 0.1277 \times \frac{1.0486}{168.59} \times 10^{3} \text{ mol.}$$

Concentration NaOH (C_{OH^-}) = 0.7942 M

Weight of dioxane in mixture = 53.70 g.

No. of moles dioxane in mixture = $\frac{53.70}{88.11}$ mol.

$$\therefore \text{ No. of moles of dioxane in 1 l.} = \frac{53.70}{88.11} \times \frac{1.0486}{168.59} \times 10^{3} \text{ mol.}$$

Concentration dioxane ($C_{Dioxane}$) = 3.7907 M

First order rate constants determined at a number of different hydroxide concentrations are summarized below.

TABLE 36

First order rate constants for the hydrolysis of chloroform at different concentrations of sodium hydroxide

Run No.	$C_{Dioxane}$ $(mol.l.^{-1})$	C_{OH^-} $(mol.l.^{-1})$	$\log_{10} C_{OH^-}$	k_1' $(sec.^{-1})x10^5$	$\log_{10} k_1'$
79	3.7810	0.0511	-1.2920	3.32	-4.4789
78	3.7730	0.1020	-0.9914	4.72	-4.3261
77	3.7700	0.1527	-0.8162	7.46	-4.1273
74	3.7841	0.2017	-0.6953	8.21	-4.0857
75	3.7719	0.3047	-0.5161	11.92	-3.9237
76	3.7801	0.4026	-0.3951	16.00	-3.7959
67	3.7895	0.5057	-0.2961	18.72	-3.7277
88	3.7867	0.5975	-0.2237	20.86	-3.6807
73	3.7870	0.6952	-0.1579	23.97	-3.6203
70	3.7907	0.7942	-0.1001	25.71	-3.5899
86	3.7945	0.8949	-0.0482	28.71	-3.5420
72	3.7910	0.9998	-0.0001	30.36	-3.5177
89	3.7811	1.0894	0.0372	31.58	-3.5006
87	3.7902	1.1996	0.0790	33.66	-3.4729
69	3.7877	1.2956	0.1125	36.25	-3.4407
68	3.7810	1.4950	0.1746	38.12	-3.4188

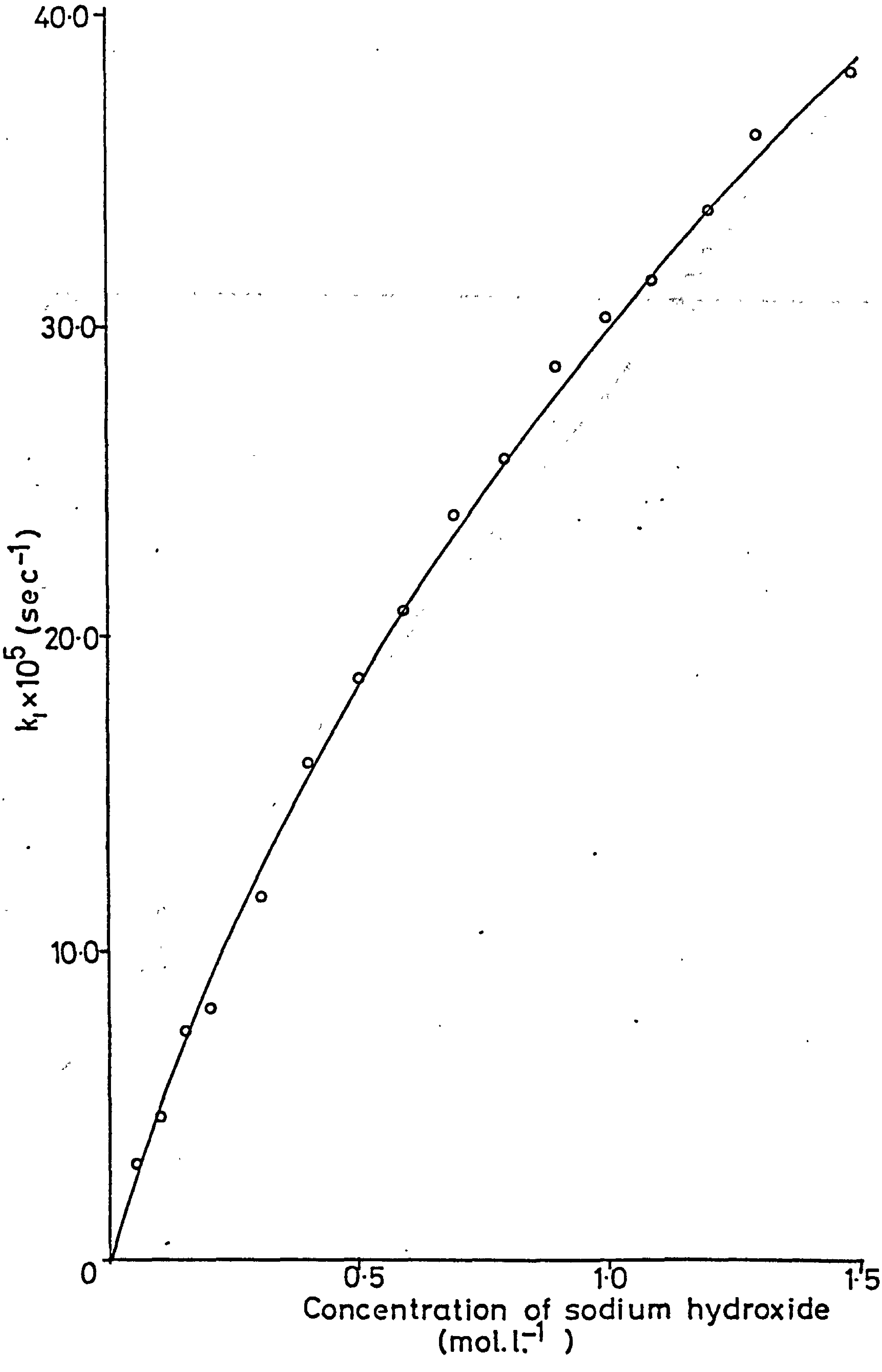


Fig. 33 Graph to show the effect of sodium hydroxide concentration on the first order rate constant

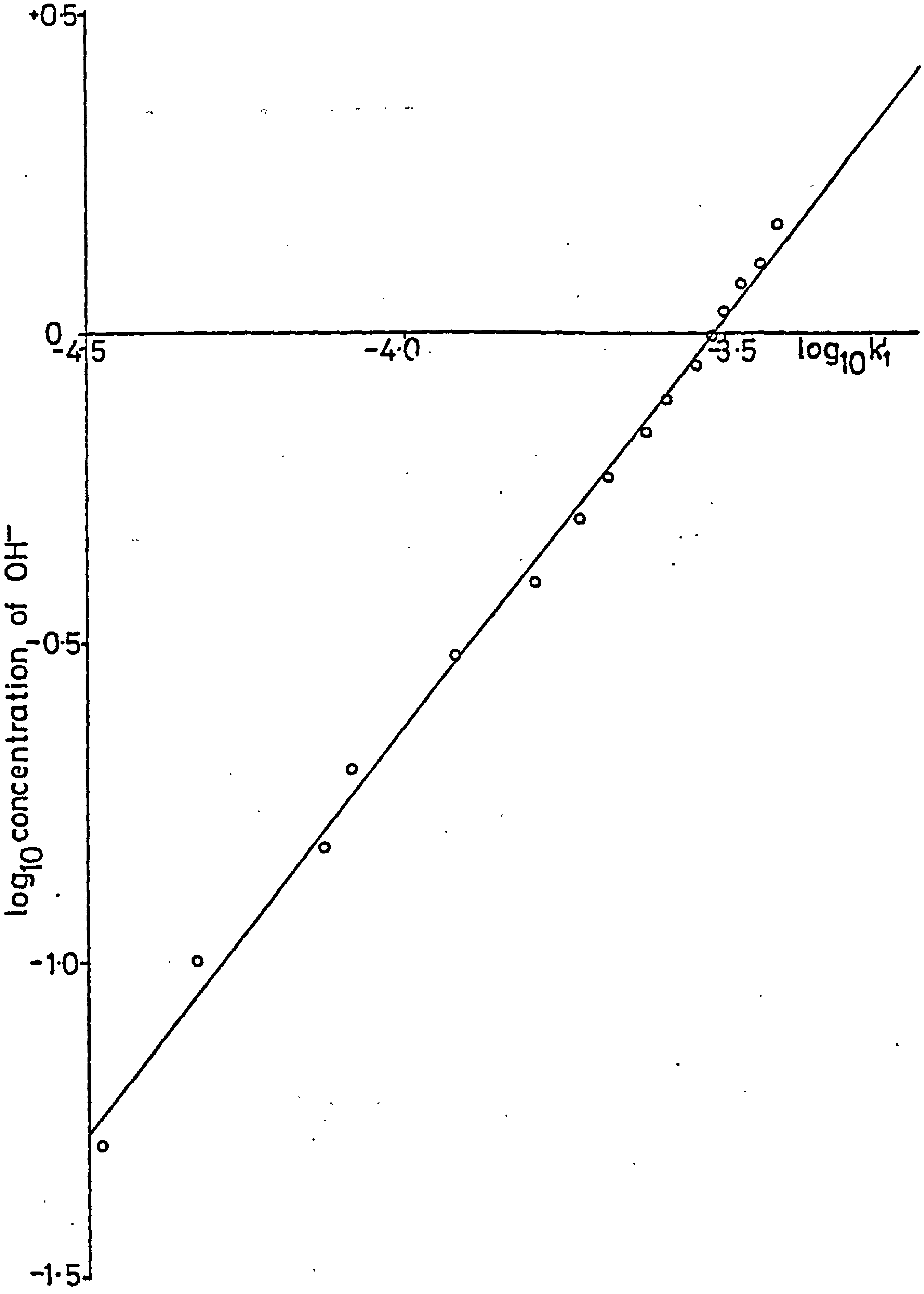
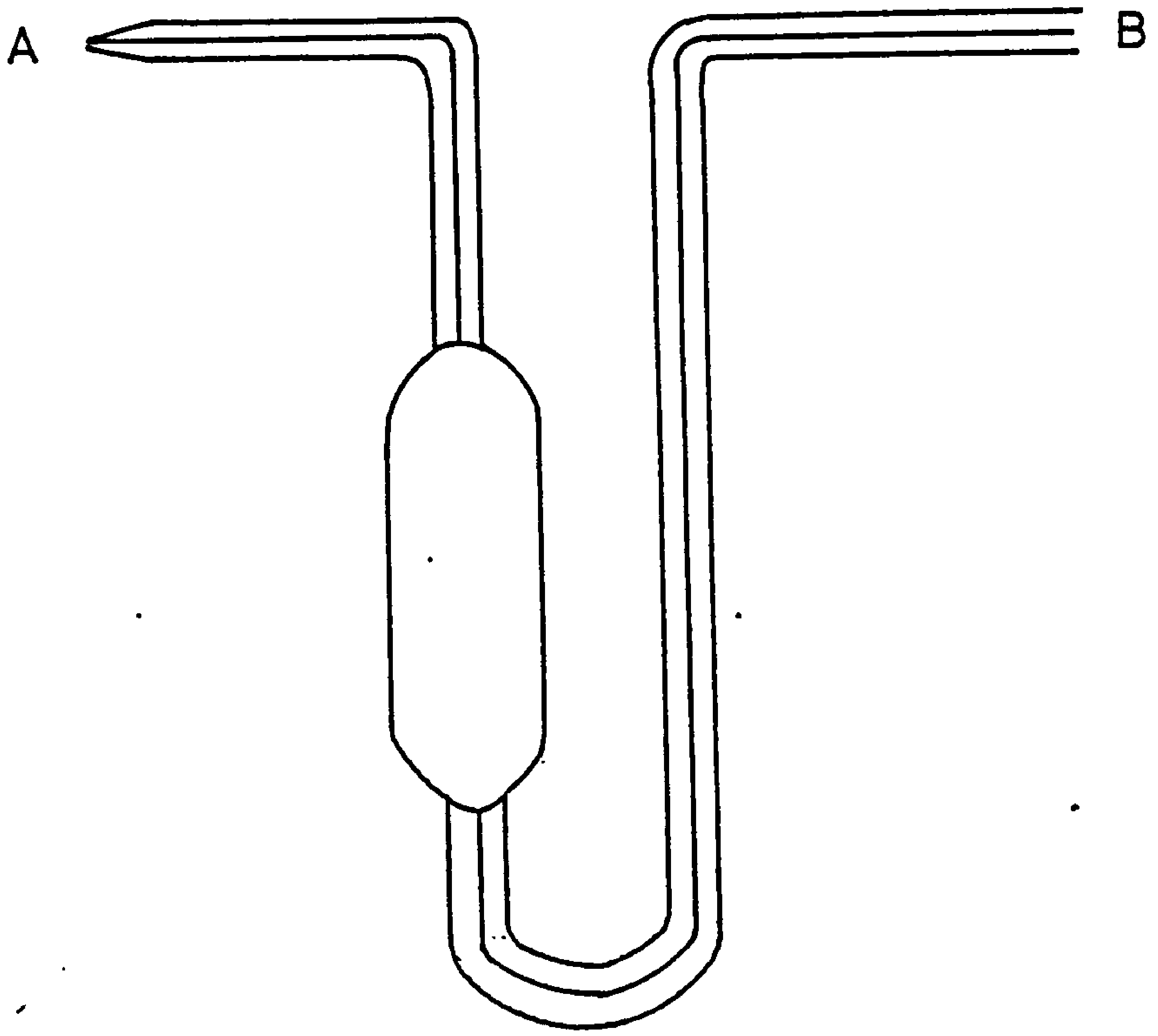


Fig. 34 Graph of $\log_{10}$ concentration OH$^-$ against $\log_{10}k_1'$

7.II.i. DETERMINATION OF SOLUTION DENSITIES

Solution densities were determined by pyknometry. This involves the calculation of the volume of a suitable vessel, called a pyknometer, by weighing it first empty and then filled with water. The pyknometer is then weighed when filled with the solution of interest.

FIGURE 35. Pyknometer



A thermostat was set up at 36 ± 0.01°C. Since the density of solutions varies considerably with a small change in temperature, the latter must be controlled to ± 0.01°C. For this reason a Beckmann thermometer was used to record the temperature of the water bath. The thermometer was set to 36°C using the thermometer which had been used to set the temperature for the kinetic runs.

The pyknometer was washed successively with chromic acid, distilled water, ethanol and a little ether. It was then dried by drawing a current of air, first filtered through a cotton-wool plug, through the vessel. A thin piece of nickel wire was attached to the vessel so that it could be hung on the balance.

To ensure that the outer glass surface was always in the same state of dryness, the pyknometer was dipped (not the capillary ends) into the thermostat water and dried carefully with a dry cloth. The vessel was allowed to hang in the balance case for 15 min. and weighed. This operation was repeated until the weight was constant to 0.25 mg.

The pyknometer was filled with air-free distilled water by dipping the end B into the water and sucking through a plastic tube attached to A. The pyknometer was suspended in the water bath for 15-20 min, and the volume of water adjusted. It was found that better reproducibility was obtained if the pyknometer was filled to the ends of both arms, rather than trying to align the meniscus with the mark on the arm B. The pyknometer was checked to see that there were no air bubbles in the solution. When the adjustment was complete, the pyknometer was removed from the thermostat, wiped, and weighed, after allowing it to hang in the balance case for 15 min. This was repeated until the variations in weight were within 0.25 mg.

The pyknometer was emptied, dried and filled with the solution under investigation. This was done by attaching B to a Dreschel bottle containing the solution and drawing the solution into the pyknometer under suction. When the pyknometer was full the tubing between the

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pyknometer and the Dreschel bottle was clamped before disconnecting it. The other arm of the Dreschel bottle was attached to a soda-lime tube. It was hoped that by doing this the amount of carbon dioxide reacting with the sodium hydroxide in the solution could be minimized.

The solution was allowed to equilibrate to the temperature of the thermostat (15-20 min.), adjusted, dried, and weighed as before. The process was repeated until a concordant result was obtained.

Correction of weights to vacuo

Correction must be made for the weight of air displaced by the pyknometer and the contents during weighing. On weighing the pyknometer empty, the volume of air displaced is equal to the volume of the glass.

Weight of pyknometer = 28.1218 g.

Density of glass = 2.23 g. ml.^{-1}

$\therefore$ Volume of glass $= \dfrac{28.1218}{2.23} = 12.61$ ml.

Density of air under the conditions of weighing = 0.0012 g.ml.^{-1}

$\therefore$ Weight of air displaced by glass = 12.61 x 0.0012 g. = $\underline{0.0151}$ g.

$$\text{Approximate volume of pyknometer} = \frac{(\text{wt. of pyknometer + water}) - \text{wt.of pyknomete}}{\text{density of water at } 36^\circ\text{C}}$$

$$= \frac{43.6890 - 28.7524}{0.99371} \text{ ml.} = 15.0311 \text{ ml.}$$

$\therefore$ Weight of air displaced by solution = 15.0311 x 0.0012 g. = $\underline{0.0180}$ g.

Total weight of air displaced = $\underline{0.0331}$ g. (corrected to vacuo).

Results

Temperature of determination : 36 ± 0.01°C.

Run 61

Wt. of pyknometer (g)	Wt. of pyknometer + distilled water (g)	Wt. of pyknometer + solution (g)
28.7524	43.6895	44.6406
28.7524	43.6890	44.6405
	43.6890	44.6407
average: 28.7524	average: 43.6890	average: 44.6406

Weight of pyknometer + distilled water = 43.6890 + 0.0331 g.

= 43.7221 g.

Weight of pyknometer empty = 28.7524 + 0.0151 g.

= 28.7675 g.

∴ Weight of distilled water = 14.9546 g.

Density of distilled water at 36°C = 0.99371 g. ml^{-1}

∴ Volume of pyknometer = 15.0493 ml.

Weight of pyknometer + solution = 44.6406 + 0.0331 g.

= 44.6737 g.

∴ Weight of solution = 15.9062 g.

∴ Density of solution = 1.0569 g. ml^{-1}

All weights quoted here have been corrected to vacuo.

When a number of solution densities had been determined a calibration curve of density against concentration of sodium hydroxide was constructed. Since the solution density must be known in order to calculate the concentration in moles per litre, the units moles per gram were employed.

Run 61

Weight of NaOH solution in mixture = 113.80 g.

11.15 g. NaOH solution contains 3.195×10^{-2} mol.

$$\therefore \; 113.80 \text{ g. contains } \frac{3.195 \times 10^{2}}{11.15} \times 113.80 \text{ mol.}$$

$$= 0.3261 \text{ mol.}$$

Weight of reaction mixture = 340.47 g.

$$\underline{\text{Concentration NaOH} = 0.9577 \times 10^{-3}} \text{ mol. g}^{-1}$$

Once the solution densities were known the concentration of sodium hydroxide and dioxane in moles per litre could be calculated.

340.47 g. of reaction mixture contains 0.3261 mol.

Density of solution = 1.0569 g. ml.$^{-1}$

$$\therefore \; \frac{340.47}{1.0569} \text{ ml. reaction mixture contains } 0.3261 \text{ mol.}$$

$$\therefore \; 1 \text{ l. reaction mixture contains } 0.3261 \times \frac{1.0569}{340.47} \times 10^{3} \text{ mol.}$$

$$\underline{C_{OH^-} = 1.0122 \text{ mol.l.}^{-1}}$$

TABLE 37

Determination of solution densities

Run No.	Wt. of pyknometer + solution (g)	Average value (g)	Density (g. ml.$^{-1}$)	Conc^{n}.NaOH (mol.g.$^{-1}$) x 10^{3}
60	44.7843 44.7851 44.7868	44.7854	1.0666	1.1975
61	44.6406 44.6405 44.6407	44.6406	1.0569	0.9577
62	47.5711 47.5677 47.5678	47.5678	1.0457	0.6832
63	47.3833 47.3828 47.3829	47.3829	1.0335	0.3893
67	47.4460 47.4460	47.4460	1.0377	0.4874
	47.5138 47.5136 47.5135	47.5136	1.0421	0.6252
Dioxane/H_2O mixture	47.1348 47.1311 47.1310	47.1311	1.0167	0.0000

Fig. 36 Plot of density aginst concentration of sodium hydroxide

Weight of dioxane in mixture $= 107.62$ g.

$\therefore$ No. of moles in 340.47 g. mixture $= \dfrac{107.62}{88.11}$ mol.

$\therefore$ No. of moles dioxane in 1 l. $= \dfrac{107.62}{88.11} \times \dfrac{1.0569}{340.47} \times 10^3$ mol.

$$\underline{C}_{\text{Dioxane}} = \underline{3.7916 \text{ mol.l.}^{-1}}$$

Determination of "free water" concentration

The concentration of "free water" C_w, is given by the formula

$$C_w = \frac{1000[M_D(d-w_D)-M_{H_2O}Nw_D] - M_D C_{OH^-}[M_{NaOH} + 3M_{H_2O}]}{1000[(d_o-w^o_D)M_D-Nw^o_D M_{H_2O}]}$$

where:

d = density of the solution (g.ml.$^{-1}$)

d_o = density of solution when the concentration of NaOH is zero = 1.0167 g. ml.$^{-1}$

M_{H_2O} = molecular weight of water (18.0)

M_D = molecular weight of dioxane (88.11)

M_{NaOH} = molecular weight of sodium hydroxide (40.0)

C_{OH^-} = concentration of NaOH (mol.l.$^{-1}$)

w_D = weight of dioxane in 1 ml. of solution (g. ml.$^{-1}$)

w^o_D = weight of dioxane in 1 ml. of solution when concentration of NaOH is zero (g. ml.$^{-1}$) = 0.33342 g. ml.$^{-1}$

N = number of water molecules associated with one dioxane molecule. The value taken is 2.25, and the determination of this value will be given in the following section.

Run 67

$d = 1.0373\ \text{g. ml.}^{-1}$

$d_o = 1.0167\ \text{g. ml.}^{-1}$

$C_{OH^-} = 0.5057\ \text{mol.l.}^{-1}$

$w_D = 0.33385\ \text{g. ml.}^{-1}$

$w_{oD} = 0.33342\ \text{g. ml.}^{-1}$

$$C_w = \frac{1000\,[88.11(1.0373-0.33385)-(18 \times 2.25 \times 0.33385)]-(88.11 \times 0.5057)[40+54]}{1000[(1.0167-0.33342)88.11-(2.25 \times 18 \times 0.33342)]}$$

$$= \frac{48460.05-4188.38}{46700.29}$$

$\underline{C_w = 0.9480}$

Construction of Yagil Plot

The Yagil plot was constructed by plotting $\log_{10} C_w$ against $\log_{10} k'_1/C_{OH^-}$, giving a straight line with a positive slope of 3.14 (method of least squares).

TABLE 38

Determination of C_w

Run No.	C_{OH^-} (mol. $l.^{-1}$)	Density (g. $ml.^{-1}$)	w_D (g. $ml.^{-1}$)	C_w
79	0.0511	1.0195	0.33311	0.9971
78	0.1020	1.0215	0.33248	0.9936
77	0.1527	1.0235	0.33218	0.9892
74	0.2017	1.0254	0.33342	0.9806
75	0.3047	1.0295	0.33213	0.9737
76	0.4026	1.0334	0.33306	0.9611
67	0.5057	1.0373	0.33385	0.9480
88	0.5975	1.0409	0.33365	0.9391
73	0.6952	1.0446	0.33472	0.9257
70	0.7942	1.0486	0.33400	0.9177
86	0.8949	1.0523	0.33434	0.9059
72	0.9998	1.0567	0.33403	0.8953
89	1.0894	1.0592	0.33380	0.8790
87	1.1996	1.0636	0.33396	0.8742
69	1.2956	1.0673	0.33374	0.8648
68	1.4950	1.0744	0.33305	0.8448

TABLE 39

Data required for Yagil Plot

Run No.	C_w	$\log_{10} C_w$	C_{OH^-} (mol.l.$^{-1}$)	$k_1' \times 10^5$ (sec.$^{-1}$)	$k_1'/C_{OH^-} \times 10^4$	$\log_{10} \frac{k_1'}{C_{OH^-}}$
79	0.9971	-0.0013	0.0511	3.32	6.503	-3.1862
78	0.9936	-0.0028	0.1020	4.72	4.627	-3.3347
77	0.9892	-0.0047	0.1527	7.46	4.883	-3.3112
74	0.9806	-0.0085	0.2017	8.21	4.070	-3.3904
75	0.9737	-0.0116	0.3047	11.92	3.912	-3.4076
76	0.9611	-0.0172	0.4026	16.00	3.974	-3.4008
67	0.9480	-0.0232	0.5057	18.72	3.701	-3.4317
88	0.9391	-0.0273	0.5975	20.86	3.491	-3.4571
73	0.9257	-0.0335	0.6952	23.97	3.448	-3.4624
70	0.9177	-0.0373	0.7942	25.71	3.237	-3.4899
86	0.9059	-0.0429	0.8949	28.71	3.208	-3.4938
72	0.8953	-0.0480	0.9998	30.36	3.037	-3.5176
89	0.8790	-0.0560	1.0894	31.58	2.899	-3.5377
87	0.8742	-0.0584	1.1996	33.66	2.806	-3.5519
69	0.8648	-0.0631	1.2956	36.25	2.798	-3.5531
68	0.8448	-0.0732	1.4950	38.12	2.550	-3.5935

Fig.37 Yagil plot

7.III. DETERMINATION OF THE HYDRATION NUMBER OF DIOXANE

To determine the number of water molecules associated with a dioxane molecule in an aqueous solution, the ionisation ratio of a weak acid in the dioxane-water mixture must be compared with that in pure water. This may be determined spectrophotometrically provided there is a pronounced difference between the absorption of the molecular and ionic forms of the substance.

If A_{HA}, A_{A^-} and A are the measured absorbances (at the same wavelength) of the neutral solution, the solution in which complete dissociation has occurred, and a solution of intermediate basicity respectively, and if α is the degree of dissociation, then:

$$\frac{C_{A^-}}{C_{HA}} = \frac{\alpha}{1-\alpha} \tag{67}$$

and

$$A = (1-\alpha)A_{HA} + \alpha A_{A^-} \tag{68}$$

or

$$\alpha = \frac{A_{HA} - A}{A_{HA} - A_{A^-}} \tag{69}$$

Combining equations (67) and (69)

$$\frac{C_{A^-}}{C_{HA}} = \frac{A_{HA} - A}{A - A_{A^-}} \tag{70}$$

since

$$K_a = \frac{a_{HA}\ a_{OH^-}}{a_{A^-}\ a_{H_2O}} \tag{71}$$

if activity coefficients are ignored, this may be combined with equation (70) to give

$$K_a = \frac{A_{A^-} - A}{A - A_{HA}} C_{OH^-} \qquad (72)$$

or, on rearranging,

$$\frac{A - A_{HA^-}}{C_{OH^-}} = \frac{A_{A^-}}{K_a} - \frac{A}{K_a} \qquad (73)$$

Since A_{A^-} cannot be measured experimentally, it must be determined from the intercept $(A-A_{HA}/C_{OH^-} = 0)$ of a plot of A against $(A-A_{HA})/C_{OH^-}$. The value obtained can then be substituted into equation (70) to give the ionisation ratio.

The acid indicator used for this work was 6-bromo-2,4-dinitroaniline which ionises in the basicity range of interest. The compound was obtained commercially (Aldrich Chemical Co. Ltd.,) and recrystallised from ethanol, m.pt 153.5°C. Two clear absorption bands were obtained due to the neutral molecule ($\lambda_{max.}$ 276 nm, $\varepsilon_{max.}$ 9,210; $\lambda_{max.}$ 350 nm, $\varepsilon_{max.}$ 12,600), whilst the anion formed on addition of sodium hydroxide solution, gave rise to two bands ($\lambda_{max.}$ 395 nm and λ_{max} 510 nm, ε_{max} 12,500).

All spectroscopic measurements were carried out using a Perkin Elmer model 402, ultraviolet and visible spectrophotometer, equipped with a heated cell block which was thermostatically maintained at 36 ± 0.1°C.

To determine the stability of the 6-bromo-2,4-dinitroaniline anion in a basic solution.

6-Bromo-2,4-dinitroaniline (0.0131 g.) was dissolved in acetone and the solution transferred to a volumetric flask (250 ml.). The acetone was removed by evaporation under reduced pressure (~ 80 mmHg, 20 min.), leaving a film of the compound on the bottom of the flask. After addition of distilled water, the solution was warmed and stirred continuously to aid dissolution. All water used was double distilled, then reboiled prior to use, and allowed to cool under a stream of nitrogen. On cooling, the indicator solution was diluted to the required volume giving a concentration of 2.00×10^{-4} mol.l.$^{-1}$.

The 6-bromo-2,4-dinitroaniline solution was added to a solution of sodium hydroxide (2.0 mol.l.$^{-1}$, 5 ml.) in a 10 ml. volumetric flask. The resulting solution was 1.0 mol.l.$^{-1}$ in sodium hydroxide and 1.00×10^{-4} mol.l.$^{-1}$ with respect to the indicator. The u.v. and visible spectrum was recorded at known time intervals.

TABLE 40

Change in absorbance of 6-bromo-2,4-dinitroaniline anion with time

Time (min.)	Absorbance (510 nm.)
2.0	5.5
3.5	5.6
4.5	5.7
6.5	5.7
15.0	5.7
25.0	5.7
30.0	5.65

The tabulated results show that the concentration of the anion formed by abstraction of a proton from the acid by the hydroxide, reached a maximum concentration (as measured by its absorbance at 510 nm), after 4.5 min.. There was a decrease (0.09 %) in absorbance after 30 min., but up until this time the anion appeared to be quite stable under the given conditions.

Determination of the ionisation ratios of 6-bromo-2,4-dinitroaniline in water, and a dioxane-water mixture

A solution of 6-bromo-2,4-dinitroaniline in water (2.00×10^{-4} mol.l.$^{-1}$, 5 ml.) was placed in a 10 ml. volumetric flask which was sealed with a rubber cap. The solution was purged with nitrogen, which was passed through inlet and outlet syringe needles. Sodium hydroxide solution (4.0 mol.l.$^{-1}$, 0.25 ml.) was added to the indicator solution by means of a volumetric syringe, and the solution diluted to 10 ml. with distilled water. The flask was then placed in the water bath which supplied the water to heat the cell block, and allowed to equilibrate at $36 \pm 0.1^{\circ}$C. The u.v. and visible spectra of the solution were recorded against distilled water, in silica cells (1 cm. path length) fitted with ground glass stoppers.

The procedure was repeated, different amounts of sodium hydroxide solution being added according to the final concentration required.

Ionisation ratios were determined from the absorbance at 510 nm, since, at this wavelength the undissociated species does not absorb, thus, $A_{HA} = 0$.

The procedure was repeated for a mixture of dioxane (32 % v/v) and water. 6-Bromo-2,4-dinitroaniline in dioxane (2.00 x 10^{-4} mol.l^{-1} 3.20 ml.) was placed in a 10 ml. volumetric flask and nitrogen bubbled through it as before. The experiment was continued as for the aqueous solutions, except that spectrophotometric measurements were made against a blank containing 32 % v/v dioxane in water as opposed to pure water.

TABLE 41

Determination of ionisation ratios in pure water

C_{OH^-} (mol.l^{-1})	A(510 nm)	$\frac{A-A_{HA}}{C_{OH^-}}$	$A_{A^-}-A$	$\frac{A-A_{HA}}{A_{A^-}-A}$ (r)
0.10	0.090	0.900	0.940	0.0957
0.20	0.165	0.825	0.865	0.1908
0.30	0.230	0.766	0.800	0.2875
0.40	0.280	0.700	0.750	0.3733
0.60	0.390	0.650	0.640	0.6094
0.70	0.420	0.600	0.610	0.6885
0.80	0.445	0.556	0.556	0.8004
0.90	0.470	0.522	0.560	0.8393
1.00	0.490	0.490	0.540	0.9074

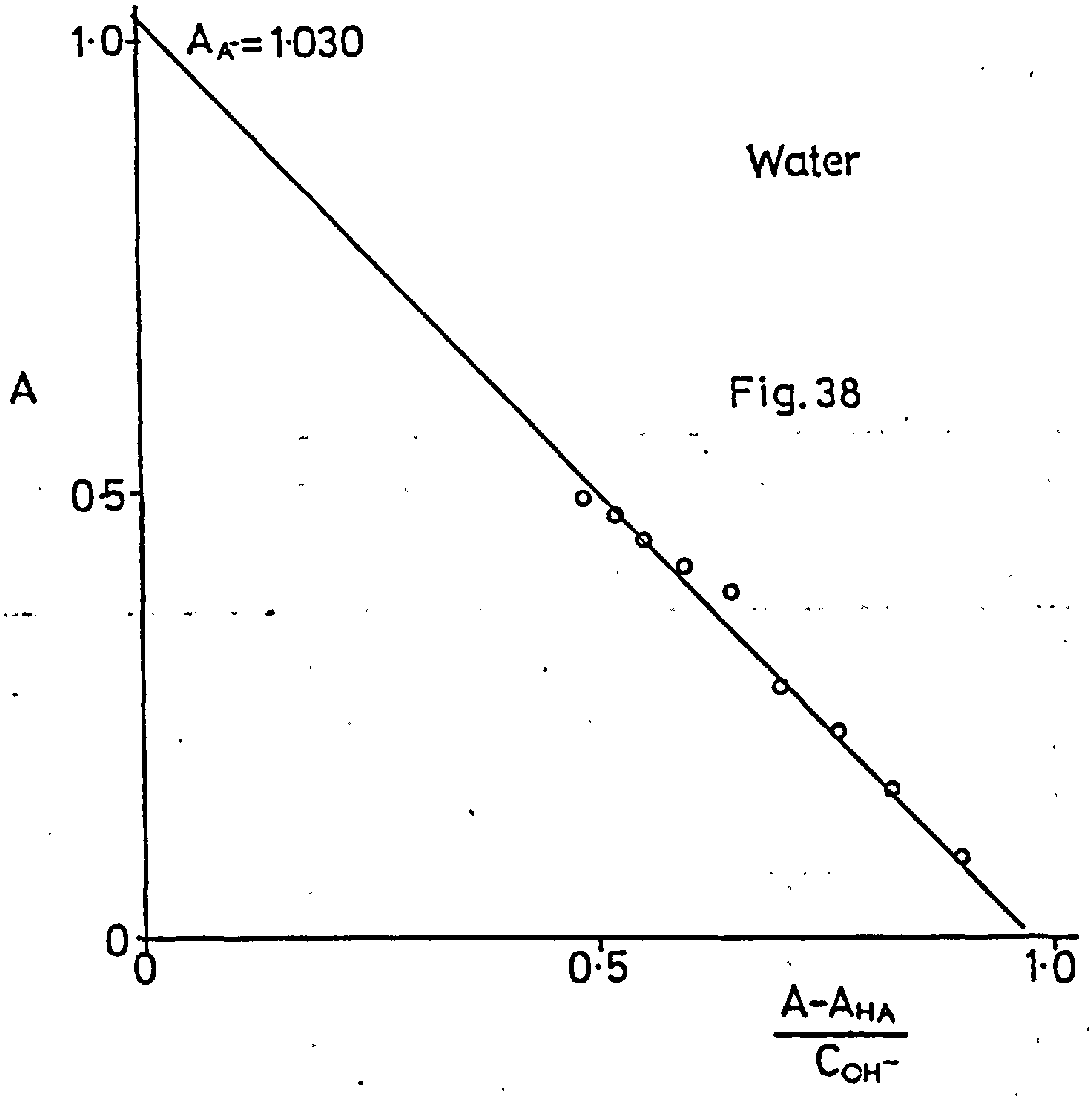


Fig. 38

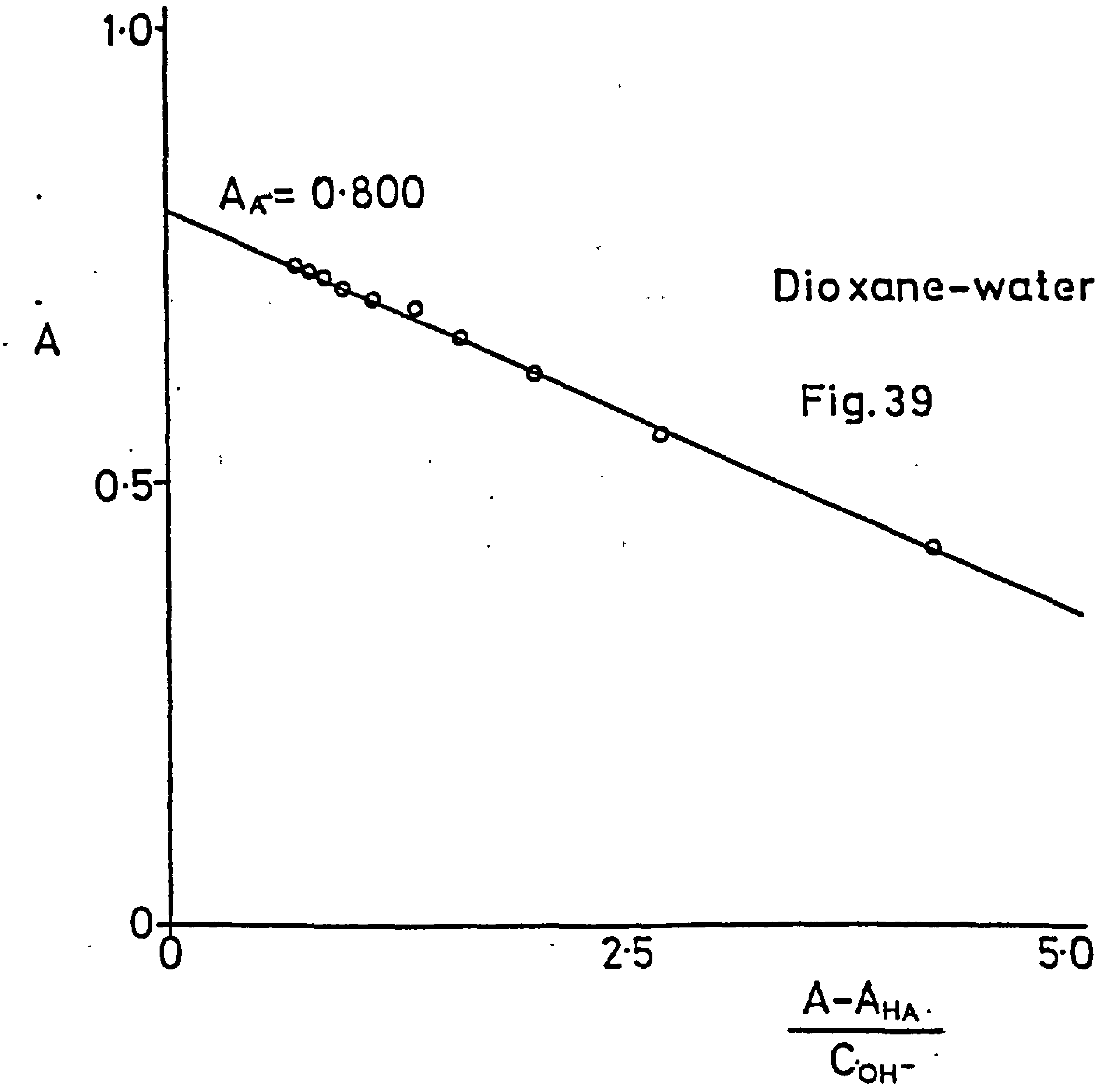


Fig. 39

Graphs to determine A_{A^-}

TABLE 42

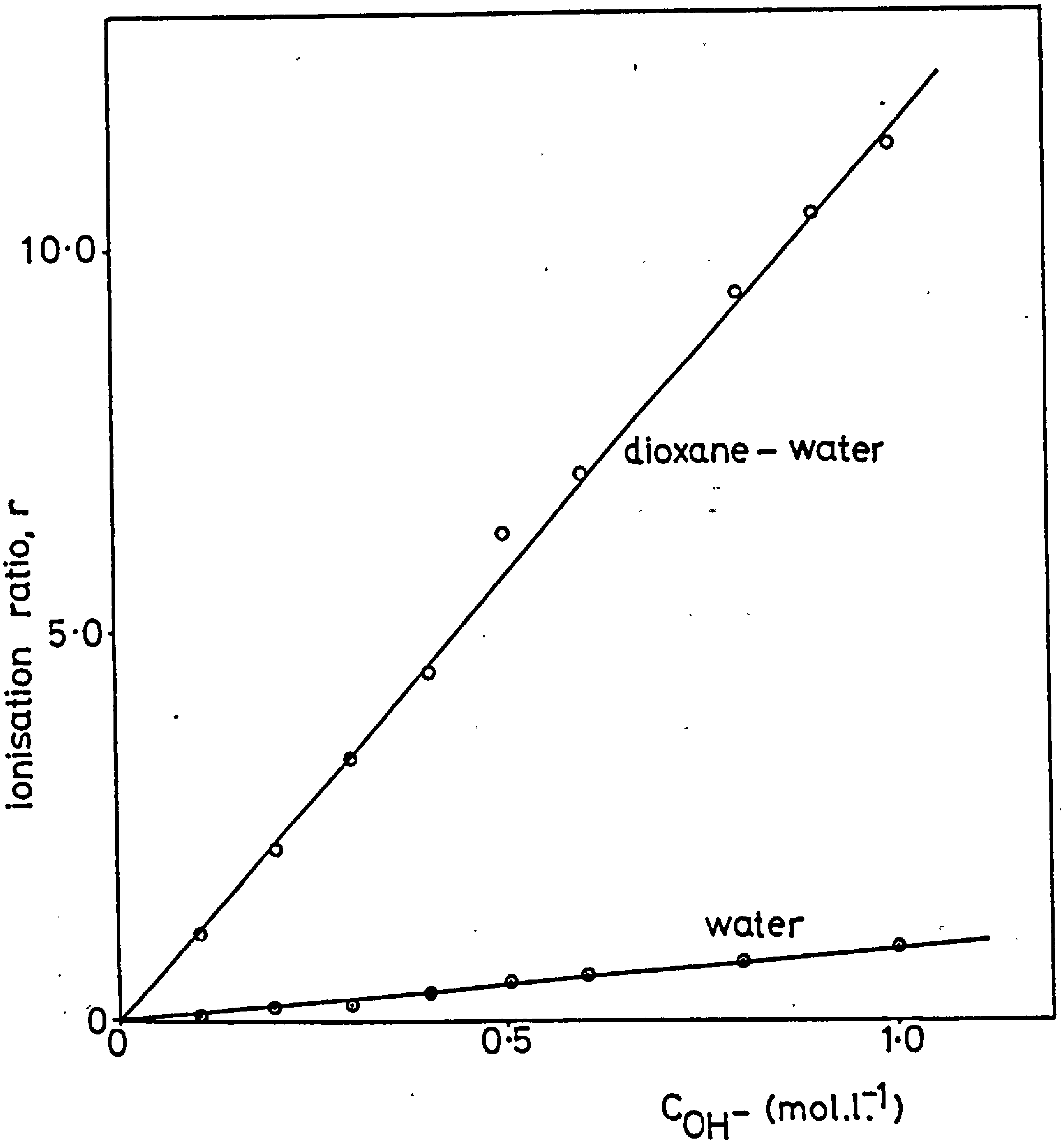
Determination of ionisation ratios
in dioxane and water

C_{OH^-} (mol.l.$^{-1}$)	A(510 nm)	$\frac{A-A_{HA}}{C_{OH^-}}$	$A_{A^-}-A$	$\frac{A-A_{HA}}{A_{A^-}-A}$ (r)
0.10	0.425	4.250	0.375	1.133
0.20	0.550	2.750	0.250	2.200
0.30	0.618	2.060	0.182	3.396
0.40	0.655	1.638	0.145	4.517
0.50	0.690	1.380	0.110	6.273
0.60	0.700	1.167	0.100	7.000
0.70	0.708	1.011	0.092	7.696
0.80	0.723	0.904	0.077	9.390
0.90	0.730	0.811	0.070	10.430
1.00	0.735	0.735	0.065	11.310

From the plots of A against $(A-A_{HA})/C_{OH^-}$, A_{A^-} was found to be 1.03 and 0.80 for water, and dioxane and water, respectively.

FIGURE 40

Comparison of ionisation ratios in water and dioxane water mixture



The number of water molecules bound by dioxane (h), is given by the equation[206].

$$h = \frac{(n_1 - n_w)}{n_2}$$

where, n_1 = total number of moles of water present in 1 l. = 37.98 mol.l.$^{-1}$

n_2 = number of moles of dioxane present in 1 l. = 3.79 mol.l.$^{-1}$

n_w = number of moles of bulk water present in 1 l., assuming that the partial molal volume of bulk water remains 18.05 ml. at all compositions, and is calculated from

$$n_w = 55.40\ V_w$$

V_w ; the volume fraction of bulk water is obtained from

ΔH_- ; the difference in the basicity between the dioxane-water mixture and pure water.

$$V_w = \text{antilog} - \frac{\Delta H_-}{4}$$

$$H_- = pK_a + \log_{10} r$$

However, since pK_a is the same for both water and aqueous dioxane, any difference in $H\_$ is really a difference in the ionisation ratio, r.

$$\Delta H_- = \left[pK_{a(\text{water})} + \log_{10} r_{(\text{water})}\right] - \left[pK_{a(\text{dioxane/water})} + \log_{10} r_{(\text{dioxane/water})}\right]$$

$$pK_a(\text{water}) = pK_a(\text{dioxane/water})$$

$$\therefore \Delta H_- = \log_{10} r_{(\text{water})} - \log_{10}\ (\text{dioxane/water}) = \Delta \log_{10} r$$

$$\therefore V_w = \text{antilog} - \frac{\Delta \log_{10} r}{4}$$

TABLE 43

Determination of the hydration number of dioxane

C_{OH^-} (mol.l.$^{-1}$)	$\log_{10} r^*$ water	$\log_{10} r$ dioxane-water	$\Delta \log_{10} r$	V_w	n_w	h
0.10	-1.0721	0.0542	1.12	0.525	29.09	2.36
0.20	-0.7300	0.3424	1.07	0.540	29.92	2.12
0.30	-0.5599	0.5310	1.09	0.534	29.58	2.23
0.40	-0.4279	0.6549	1.08	0.537	29.75	2.18
0.50	-0.3170	0.7975	1.12	0.525	29.09	2.40
0.60	-0.2415	0.8451	1.09	0.534	29.58	2.20
0.70	-0.1695	0.8862	1.06	0.543	30.08	2.07
0.80	-0.1387	0.9727	1.11	0.528	29.25	2.29
0.90	-0.1018	1.0182	1.12	0.525	29.09	2.32
1.00	-0.0396	1.0535	1.12	0.525	29.09	2.32

* Average value from three determinations.

The average number of water molecules associated with a dioxane molecule was found to be 2.25.

PART THREE

DISCUSSION AND CONCLUSIONS

CHAPTER 8

DISCUSSION OF THE PYROLYSIS OF CHLOROFORM

The mechanism by which the thermal decomposition of chloroform takes place is still open to debate, and the main reason for undertaking this study was to try to distinguish between the existing mechanisms. Semeluk and Bernstein[4,5] have studied the reaction in a flow system, and interpreted their results on the basis of a radical mechanism. On the other hand, Shilov and Sabirova[7-9], investigated the reaction under similar conditions, and postulated the formation of dichlorocarbene as an intermediate. However, they also had to invoke the formation of trichloromethyl radicals in order to explain the formation of hexachloroethane. In both cases hydrogen chloride and tetrachloroethylene were reported as the main reaction products.

Under the experimental conditions used in the present work (783K), pentachloroethane was found to be the major product ($\sim$24 mol. %), excluding hydrogen chloride, followed by hexachloroethane ($\sim$20 mol. %) and tetrachloroethylene ($\sim$18 mol. %). This is somewhat different to the results of Semeluk and coworkers, who reported that tetrachloroethylene constituted about 55 % of all the products (excluding HCl), together with smaller amounts of hexachloroethane ($\sim$27 %) and pentachloroethane ($\sim$7.5 %)[4]. However, since these results were obtained at considerably longer space times (0.4 min.), than we have used, and tetrachloroethylene is thought to be formed by loss of hydrogen chloride from pentachloroethane, one would expect the yields of tetrachloroethylene to increase and pentachloroethane to decrease, with increasing space time.

Small amounts of dichloromethane, carbon tetrachloride and trichloroethylene were formed, together with symmetrical-tetrachloroethane, which was detected, but not determined quantitatively. At longer space times, pentachlorobutadiene and hexachlorobutadiene were formed in similar small amounts. All the products obtained were identified from their mass spectra, which were in close agreement with those given in the literature[210]. Mass spectra are particularly useful in the identification of chlorinated hydrocarbons because of the characteristic isotopic chlorine clusters obtained.

The fraction of chloroform which had reacted, was estimated from the amount of products formed since it was not possible to measure this directly with a reasonable degree of accuracy. This was thought to be justified, since the extent of carbonisation was very low even at relatively long space times. The amount of chloroform lost via processes other than product formation would therefore be very small.

8.I.i. ANALYSIS OF THE EFFLUENT GAS FOR THE PRESENCE OF HYDROGEN AND CHLORINE

The effluent gas was analysed for chlorine by a chemical method, and for both hydrogen and chlorine by g.l.c., but neither of the gases were detected. This is in agreement with results reported elsewhere[4]. The chemical method had the advantage of being more sensitive, and also any chlorine present in the gas would have become concentrated (as potassium chloride), in the potassium iodide solution.

It was important to know whether chlorine and hydrogen were formed in the reaction, because of the information this provides about the mechanism of the reaction. Although it is not possible to say that they are definitely not formed, if they are present, their concentrations must be extremely low. On this basis, the following reactions may be rejected as major reaction pathways.

$$2CHCl_3 \xrightarrow{-H_2} CCl_3CCl_3 \xrightarrow{-Cl_2} Cl_2C{=}CCl_2$$

$$2CHCl_3 \xrightarrow{-Cl_2} CHCl_2CHCl_2 \xrightarrow{-H_2} Cl_2C{=}CCl_2$$

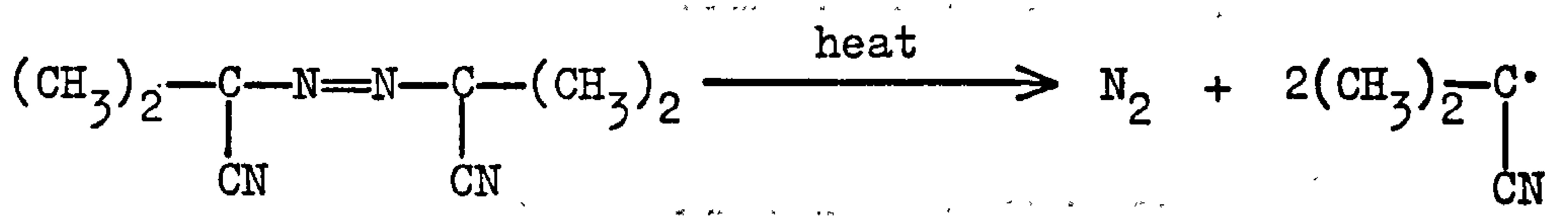
$$CHCl_3 + CCl_4 \xrightarrow{-Cl_2} CHCl_2CCl_3 \xrightarrow{-Cl_2} CHCl{=}CCl_2$$

$$CHCl_3 + CH_2Cl_2 \xrightarrow{-H_2} CHCl_2CCl_3$$

8.I.ii. THE EFFECT OF A RADICAL INITIATOR ON THE PYROLYSIS OF CHLOROFORM

To determine whether or not radicals were involved in the thermal decomposition of chloroform, the reaction was carried out in the presence of a radical initiator. Radical initiators are compounds which readily break down by a radical mechanism. The radicals thus formed, can then initiate radical formation in the main reaction, resulting in an increase in the reaction rate, compared to the case where no initiator is added.

The initiator chosen was azobisisobutyronitrile (AIBN), which decomposes readily at relatively low temperatures (60-90°C). The high heat of formation of nitrogen provides the driving force for the reaction.



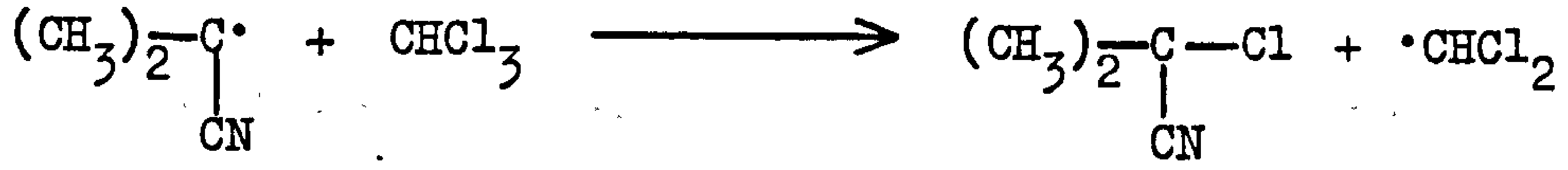
$$(CH_3)_2-\underset{\substack{|\\ CN}}{C}-N{=}N-\underset{\substack{|\\ CN}}{C}-(CH_3)_2 \xrightarrow{\text{heat}} N_2 + 2(CH_3)_2-\underset{\substack{|\\ CN}}{C}\cdot$$

The addition of catalytic amounts of AIBN increased the amount of chloroform which reacted by 7.4 % (see Table 9), considerably less than would be expected if the main reaction mechanism involved radicals. It is of particular interest to note that the yield of hexachloroethane was actually reduced (-4.8 %), when the initiator was added, whereas it is this compound which is most likely to be formed by a radical mechanism.

$$(CH_3)_2-\underset{\substack{|\\ CN}}{C}\cdot + CHCl_3 \longrightarrow (CH_3)_2-\underset{\substack{|\\ CN}}{C}-H + \cdot CCl_3$$

$$2\cdot CCl_3 \longrightarrow C_2Cl_6$$

The small increase in the amount of reaction when AIBN was present may have been due to the initiation of an alternative reaction. The main increases observed were in the formation of trichloroethylene, tetrachloroethylene and pentachloroethane, suggesting that AIBN may have initiated the formation of $\cdot CHCl_2$ radicals rather than $\cdot CCl_3$.



$$(CH_3)_2-\underset{\substack{|\\ CN}}{C}\cdot + CHCl_3 \longrightarrow (CH_3)_2-\underset{\substack{|\\ CN}}{C}-Cl + \cdot CHCl_2$$

$$\cdot\mathrm{CHCl_2} + \mathrm{CHCl_3} \longrightarrow \mathrm{CH_2Cl_2} + \cdot\mathrm{CCl_3}$$

$$2\cdot\mathrm{CHCl_2} \longrightarrow \mathrm{CHCl_2CHCl_2} \xrightarrow{-\mathrm{HCl}} \mathrm{HClC{=}CCl_2}$$

$$\cdot\mathrm{CHCl_2} + \cdot\mathrm{CCl_3} \longrightarrow \mathrm{CHCl_2CCl_3} \xrightarrow{-\mathrm{HCl}} \mathrm{Cl_2C{=}CCl_2}$$

Another effect resulting from the addition of the initiator, was an increase in the amount of carbonisation as has been reported elsewhere[211]. This could be seen by the change in the appearance of the reaction products, which were orange in colour, compared to the pale yellow solution obtained in its absence.

When the same initiator was added to the reaction of chloroform with 2,5-dimethylpyrrole in the gas phase, the overall recovery of material was reduced, probably due to an increase in the amount of carbonisation, polymerisation, fragmentation etc.[30]. Again, a small increase in the amount of products was observed, but this could not be held as conclusive evidence for a radical mechanism.

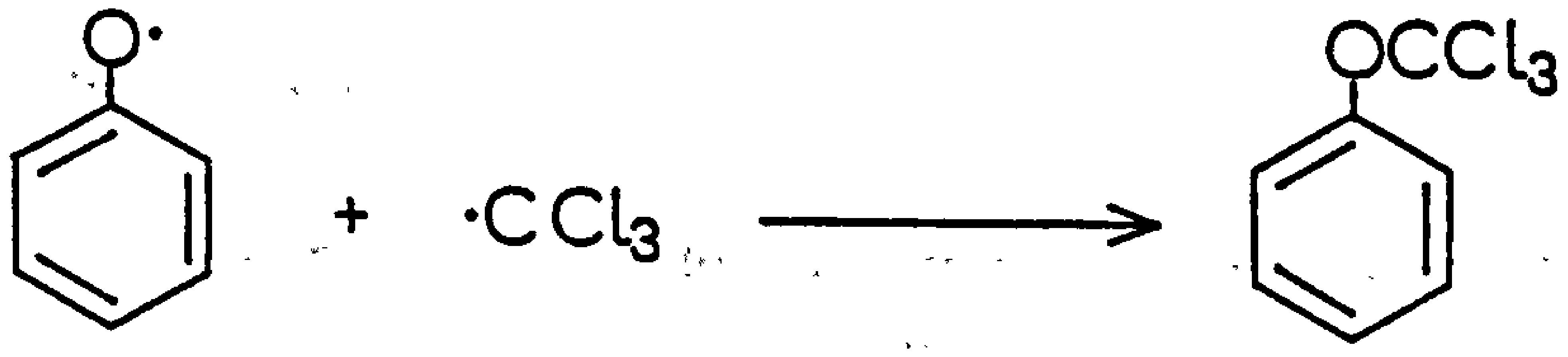
Similarly, Shilov and Sabirova[9] have found the decomposition of chloroform was not initiated by chlorine atoms, unlike other radical reactions[70].

8.I.iii. THE EFFECT OF A RADICAL INHIBITOR ON THE PYROLYSIS OF CHLOROFORM

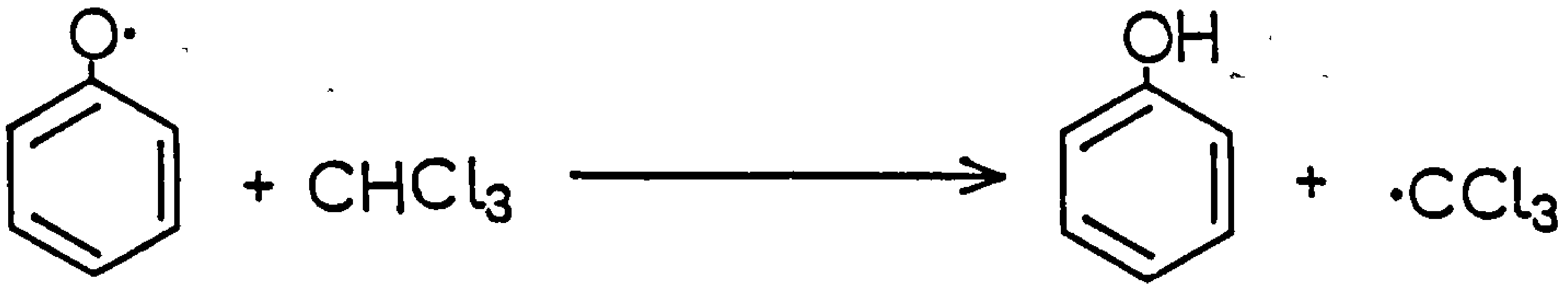
The rate of a radical reaction depends upon the lifetime of the radicals involved, and hence the addition of a foreign substance which reacts with the radicals is likely to cause a reduction in the rate. If the added molecules are intrinsically much more reactive towards the radicals than the reactant molecules the effect may be very large, since virtually every radical produced will be captured by an inhibitor before it can initiate the propagating cycle.

Phenol breaks down readily to give phenoxide radicals which will recombine with any other radicals present. However, the addition of phenol did not inhibit the pyrolytic breakdown of chloroform, but caused a slight increase in the amount of products formed. Again, this suggested that the main reaction does not involve radicals, but that a secondary reaction was initiated by the phenol radicals. The amount of carbon tetrachloride formed was consistently higher, but the yields of other products fluctuated, depending on the amount of phenol added.

Three new products were obtained as a result of interaction between phenol and chloroform, and/or the products of chloroform breakdown. One of these products was identified as trichloromethylphenyl ether, which could have been formed by the recombination of trichloromethyl radicals and phenol radicals.



The formation of $\cdot CCl_3$ radicals may have been initiated by phenol radicals, thus accounting for the small increase in the reaction rate.



This could also account for the increase in the amount of carbon tetrachloride formed, although an increase in the formation of hexachloroethane would also be expected, and this was not observed. However, if the radicals were only formed in low concentrations, reaction by extraction of a chlorine atom, to give carbon tetrachloride, may have occurred before two of them could come together to form hexachloroethane. It would, therefore, appear that instead of inhibiting the reaction, the addition of phenol has in fact had an initiating effect. The magnitude of this effect suggests that it is a secondary mechanism which has been effected, rather than the main mechanism. This would support the idea that the pyrolytic breakdown of chloroform does not involve free radicals.

Inhibitors have been used to show the radical nature of the thermal breakdown of certain chlorinated ethanes[68,77,86]. In these cases propylene was added to the reaction, the rate of which was suppressed by the presence of catalytic amounts of the inhibitor. Toluene has been added to chloroform, but this did not inhibit the rate of pyrolytic breakdown[9].

8.I.iv. THE EFFECT OF THE SURFACE ON THE PYROLYSIS OF CHLOROFORM

One of the most conclusive results obtained during our study of the thermal breakdown of chloroform, was obtained when the surface area of the reaction tube was increased, by the addition of small silica rings. The fraction of chloroform which reacted was found to increase linearly with the surface area, showing that the reaction takes place on the surface of the tube, rather than in the bulk of the gas. If two reactions were taking place, one in the bulk of the gas, and another on the surface, only the latter would be effected by changing the surface area, so that the extent by which the reaction would be increased would be small.

Although the formation of all products was favoured by increasing the surface area, it was the formation of the unsaturated compounds which showed the greatest increase. Since trichloroethylene and tetrachloroethylene are thought to be formed by the elimination of hydrogen chloride from *sym*-tetrachloroethane and pentachloroethane respectively, this is in keeping with the idea that dehydrohalogenation occurs readily at a surface[46].

The extent to which the surface area was increased was limited, in order to maintain plug flow conditions. In this way, the amount of turbulence caused by the rings was kept to a minimum, so that we could be sure that the increases in reaction observed resulted from the increased surface area, and not as a result of backmixing.

Treating the tube in various ways had little effect on the reaction, suggesting that either the treatments had little effect on the surface, or, that the nature of the surface is unimportant. The tube was steamed, and soaked in water, to try to increase the number of hydroxyl groups on the surface of the silica, as it was originally thought that such groups might be involved in direct hydrogen bonding with adsorbed chloroform molecules. Ballczo and Kosak[212] have reported that the catalytic activity of silicon dioxide on the pyrolysis of chloroform, was lost on ignition, but could be restored by moistening with water, and drying at 250°C. This result was explained by the participation of weakly acidic hydroxyl groups.

The adsorption of organic gases on silica surfaces has been studied by infrared spectroscopy[213]. Molecules such as chloroform were found to be hydrogen bonded to the surface, interaction occurring preferentially with surface hydroxyl groups. The heat of adsorption of chloroform with freely vibrating hydroxyl groups was determined as 5.6 ± 0.3 Kcal.mol.$^{-1}$ [213].

Fresh glass surfaces showed enhanced reactivity in the decomposition of chlorinated hydrocarbons[214]. Such surfaces almost certainly contain larger quantities of chemisorbed water than those which have been in use for some time. Treating the surface with hydrogen chloride also increased its activity[214]. Both of these results support the idea that surface protons may be assisting the formation of an activated complex.

Since we have carried out our experiments at a higher temperature than Ballczo and coworkers[212], it is possible that any increased activity due to surface hydroxyl groups resulting from soaking the tube in water, was subsequently lost on heating the tube to the reaction temperature. This would explain why we did not observe the increase in reaction reported elsewhere[212]. The concentration of hydroxyl groups on the surface of silica has been studied by many authors. The mean concentration of hydroxyl groups was determined for silica which had been ignited at different temperatures, and was found to decrease as the temperature increased[215].

The possibility of the reaction being catalysed by impurities in the silica was also considered. This would mean that such sites would have to be extremely active, since the impurities are only present in low concentrations. However, changing to a reaction tube made from high-purity synthetic silica (see Table 14), in which the concentration of impurities was considerably lower, resulted in a slight increase in the amount of reaction, compared to the case in which a new tube made from the more impure silica was used.

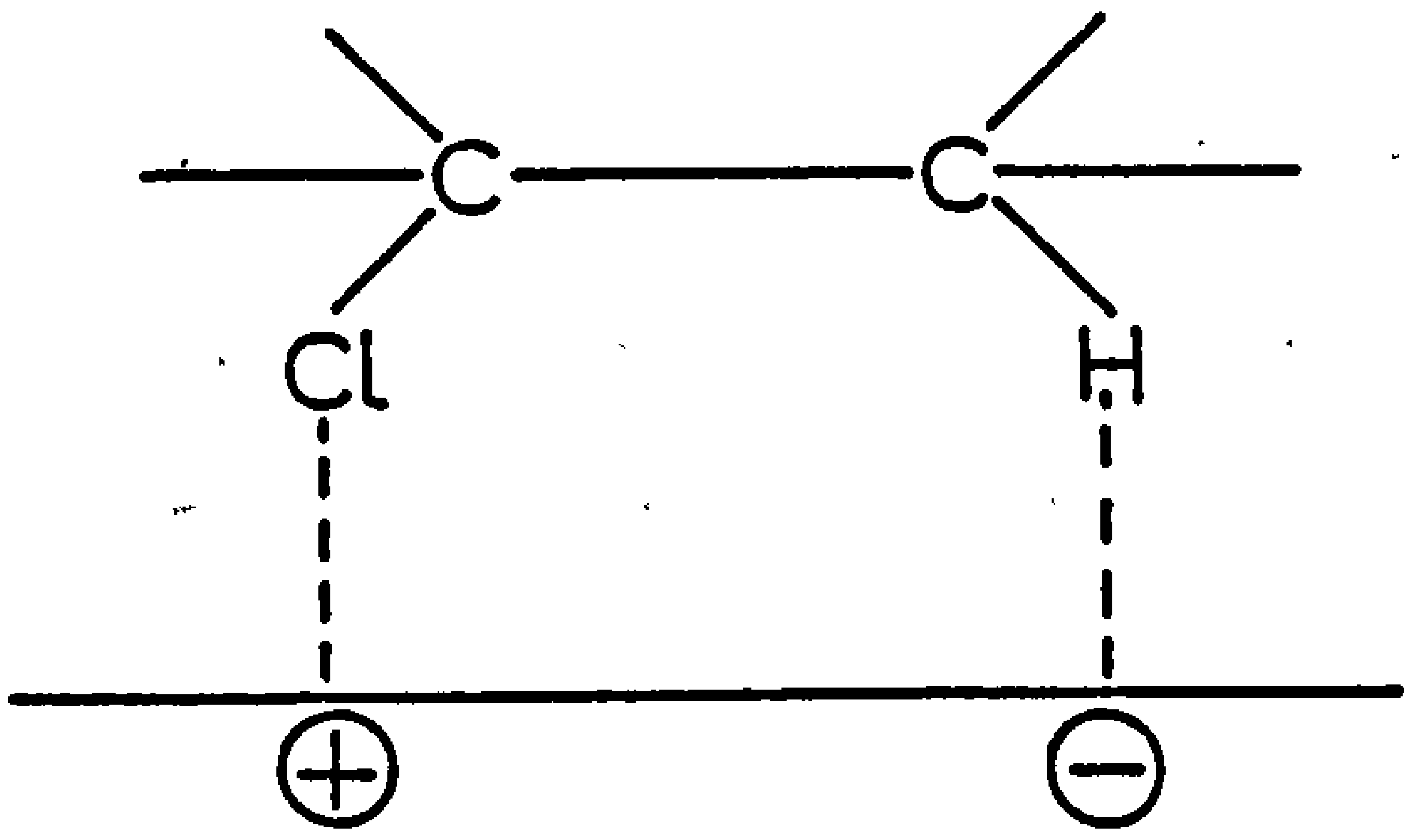
Soaking the tube in a solution of ethylenediaminetetra-acetic acid (EDTA), prior to use, also had very little effect on the reaction. The slight increase observed was probably due to the variation in the space time. It has been reported that the catalytic activity of porous vycor glass in the isomerisation of butenes, was eliminated by washing the glass with a solution of EDTA[216]. It was suggested that aluminium and zirconium atoms on the surface of the glass contributed to the formation of active sites, which could be removed by washing with EDTA.

Metal surfaces have been shown to catalyse the thermal breakdown of dichloromethane[45] and other chlorinated hydrocarbons[46]. Schwab, Nöller and coworkers[217-219] have made an extensive study of the decomposition of alkyl chlorides on a number of solid catalysts. They found that the most active catalysts were those with a high electrostatic field strength associated with a surface interatomic distance of about 2.6 Å. Campbell and Kemball[220] have studied the effect of metals on the decomposition of ethyl chloride, and found that the nature of the surface influenced whether rupture occurred at the carbon-hydrogen or carbon-halogen bond. It is evident, therefore, that metal surfaces can play an important role in the decomposition of chlorinated hydrocarbons.

Ageing appeared to reduce the catalytic activity of the tube. The reaction was 16.8 % greater in a new tube compared to one which had been used many times. This could be due to the harsh conditions used to clean the tube, which may gradually modify the surface in some way.

When the reactions were carried out in a carbonised tube which had been allowed to cool and then reheated, the extent of reaction increased by 53 %. This was thought to be due to the formation of a highly active carbon surface. On cooling, the carbon film which had been deposited on the surface became cracked and uneven. It is unlikely that the increase was due to an increase in the surface area, as this would have to have increased by approximately 40 % to account for the increase in reaction.

Surface catalysis in the pyrolysis of chlorinated hydrocarbons is not a novel idea. Many of the chlorinated ethanes or ethylenes have been shown to react on a surface at high temperatures[59,70,77,86], as has dichloromethane[44,45]. The dechlorination of hexachloroethane, either directly, or formed in the pyrolysis of carbon tetrachloride, is also thought to take place on the surface[59]. In the majority of these reactions, free radical mechanisms have been proposed, which is not thought to be the case with chloroform. Nöller and Ostermeier[219] have proposed an activated complex in the decomposition of alkyl chlorides, in which there is two-centred adsorption of the chlorinated hydrocarbon.



According to their mechanism, radicals are not formed at any stage.

In most radical mechanisms, surface catalysis occurs during chain initiation, and/or, chain termination. The effect of increasing the surface area will therefore depend on which of these two processes is most strongly effected. In the pyrolysis of 1,2-dichloroethane[70] and 1,1,1-trichloroethane[77], increasing the surface area decreased the rate of reaction, since the rate of chain termination was greatly increased. The rate of breakdown of dichloromethane increased linearly as the surface to volume ratio increased, as a result of the increased rate of initiation. But, the fraction of dichloromethane which reacted decreased, because of an increase in the rate of termination[44].

Changing the surface area of a reaction vessel has also been shown to effect the induction period of a reaction[44]. Since induction periods are thought to be the time required to build up a steady state concentration of the chain carrying species[68], increasing the surface area would be expected to reduce the induction period for a truly heterogeneous reaction. In the pyrolysis of sym-tetrachloroethane however, packing the reactor did not alter the induction period, supporting the idea that this reaction takes place in the bulk of the gas, rather than on a surface.

Many pyrolytic reactions depend on the extent to which the surface has been carbonised. Most have been found to be faster on a clean silica surface where chain initiation is thought to be easier[44,60,70]. As a carbon layer is built up, the reaction becomes slower and more reproducible, and for this reason several authors[5,60,69,76,214] have carbonised their reaction vessels by the equivalent of between ten and one hundred runs, before studying the reaction. In doing this they have assumed that any heterogeneous reaction is suppressed, so that the reactions studied are purely homogeneous[214].

In the decomposition of dichloromethane the formation of a stable graphitic type structure was thought to terminate the reaction, since it cannot supply new radicals for chain branching[44].

Very little information has been published on the role of surfaces in the pyrolysis of chloroform. Shilov and Sabirova[7] found that packing the reaction vessel did not cause any noticeable change in the reaction rate, when the surface to volume ratio was changed. However, their reactions were carried out in vessels which had been previously carbonised to improve the reproducibility, suggesting that surface effects were important when clean silica reaction vessels were used.

Ballczo and Kosak[212] have studied the catalytic action of silica and silicates on the decomposition of chloroform at 250°C, and they found that only silica was active. At this low temperature however, very little reaction would be expected to occur. Their results, as described earlier, were explained on the basis of interaction between chloroform and surface hydroxyl groups.

From their results on the application of very low pressure conditions to this reaction, Benson and Spokes have also suggested surface participation[78]. They found that the extent of chloroform decomposition was time dependent, and have suggested that surface catalysis may proceed via the interaction between a reaction product, such as C_2Cl_4 or HCl and the surface (SiO_2 or carbon). Since it has been shown that hydrogen chloride inhibits the decomposition, whilst tetrachloroethylene accelerates the reaction[5], interaction is more likely to occur via the latter. Further speculations on the mechanism of the reaction were withheld until further work had been carried out. At temperatures above 750°C, silicon tetrachloride was identified, by mass spectrometry[78], supporting the idea that there is interaction between chloroform and the surface of the silica reactor.

In the reaction of chloroform with pyrrole in the vapour phase[221], a series of reactions were carried out under standard plug-flow conditions but without removal of carbon from the silica reaction tube between each run. The yield of chloropyridines reached a maximum at about the fifth reaction, and by the twelfth reaction the yield was down to 77 % of the optimum. This also suggests that the surface of the reactor is involved.

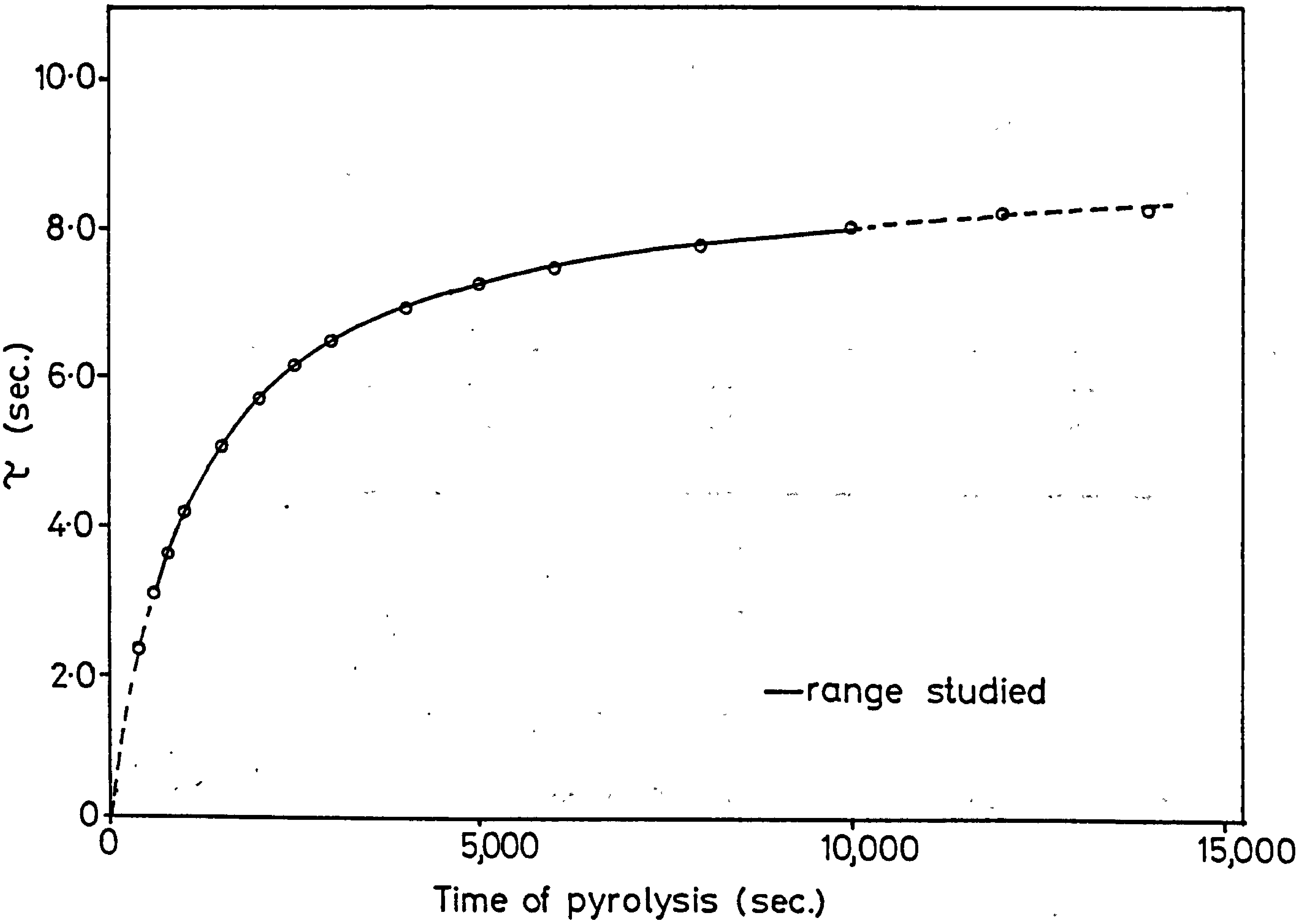
8.II. THE KINETICS OF THE PYROLYSIS OF CHLOROFORM AT 510°C

The kinetics of the pyrolysis of chloroform were investigated under plug-flow conditions at 510°C. The aim of this was to determine the order of the reaction with respect to chloroform. The rate of reaction was found to be relatively slow, the amount of chloroform which reacted was only 15 % at the highest space time.

The range of space time which could be studied had practical limitations. Below values of three seconds the rate of chloroform addition was too fast to be accurately controllable. It is also possible that at such rates vapourisation, prior to entering the reaction zone, would be incomplete. At space times greater than eight seconds the time of pyrolysis would have to be considerably increased in order to increase the space time by a small amount. At very long space times the rate of addition was extremely slow, and again this makes the accurate control of the input difficult.

FIGURE 41

Change in space time (τ) with time of pyrolysis
for 0.25 mol. of chloroform at 510°C, 770 mm.Hg
and a flow rate of nitrogen of
19.30 l. hr^{-1} (23°C, 760 mmHg)



Under the experimental conditions used, the extent of carbonisation was low, so that this did not introduce a large error in determining the amount of chloroform which had reacted. The carbon was deposited (less than 0.05 mg.), as a fine layer on the surface of the silica tube, but did not form the shiny graphitized film found in the pyrolysis of chloroform with heterocyclic substrates. The amount of carbon deposited could not be easily determined since it was difficult to recover it from the surface of the tube.

The experimental results obtained fitted a first order rate plot better than zero, second or third order plots. The rate constant determined from the reciprocal of the slope of the first order plot was 3.14×10^{-2} sec.^{-1}, which is slightly higher than values reported elsewhere.

TABLE 44

Comparison of first order rate constants for the pyrolysis of chloroform

Temperature (K)	k_1 $(\text{sec.}^{-1}) \times 10^2$	Ref.
783	3.14	This work
785	2.52	5
783	1.70 - 2.29 *	9

* depending on the initial pressure of chloroform

The first order rate plots showed an induction period of 2.63 sec. Induction periods have not been reported elsewhere for the pyrolysis of chloroform, although they are known to occur with other chlorinated hydrocarbons.

The results obtained with the carbonised tube showed considerably more scatter than those obtained with a clean silica tube, making the determination of order more difficult. However, the first order rate plot seemed to give a better straight line than the other orders. The rate constant was higher in the case of the carbonised tube; 4.98×10^{-2} $sec.^{-1}$, although this could not be determined as accurately, because of the greater degree of scatter. The induction period (4.05 sec.) was also higher when the reaction was carried out in a carbonised tube, but again there was more error in its determination, than in the clean tube.

Carrying out the pyrolysis in a carbonised tube did not have the desired effect of increasing the reproducibility of the reaction. This is understandable since it has been shown that the reaction is surface catalysed, and carbonising the tube as we have done would not give the reproducible surface desired, as the rate of carbonisation from the pyrolysis of chloroform is slow. In order to obtain a reproducible surface it would be necessary to form a much thicker carbon layer, so that a graphitic structure was established, and the nature of the surface would not be effected by further carbonisation. It has been reported elsewhere[69], that the equivalent of up to 100 runs were necessary, before reproducibility was obtained. Unfortunately, there was not sufficient time available to investigate this.

The fact that the reaction was faster in a carbonised tube, is in keeping with the observation that when the carbon layer broke up to form a highly irregular surface, the extent of reaction was considerably increased. It is evident, therefore, that a carbon surface can be extremely active under certain conditions. This is the opposite to effects observed in the pyrolysis of other chlorinated hydrocarbons, where carbonising the surface gave rise to a slower rate of reaction. However, in these cases the reaction was thought to involve free radicals, and the observed slowing down of the reaction, was thought to be due to the fact that radicals were less easily generated from a carbonised surface[44.60,70]. Furthermore, the rates of carbonisation were very much faster compared to the present case.

8.III. DISCUSSION OF THE MECHANISM OF THE VAPOUR PHASE PYROLYSIS OF CHLOROFORM

At present there are two existing mechanisms which have been postulated for the thermal decomposition of chloroform[4,5,9]. The experiments carried out by Semeluk and Bernstein[4,5] using a flow apparatus, were interpreted on the basis of the following radical mechanism.

$$\mathrm{CHCl_3} \longrightarrow \cdot\mathrm{CHCl_2} + \cdot\mathrm{Cl}$$

$$\cdot\mathrm{Cl} + \mathrm{CHCl_3} \rightleftharpoons \mathrm{HCl} + \cdot\mathrm{CCl_3}$$

$$\cdot\mathrm{CCl_3} + \cdot\mathrm{Cl} \longrightarrow \mathrm{CCl_4}$$

$$\cdot\mathrm{CCl_3} \longrightarrow :\mathrm{CCl_2} + \cdot\mathrm{Cl}$$

$$:\mathrm{CCl_2} + \mathrm{CHCl_3} \longrightarrow \mathrm{C_2Cl_4} + \mathrm{HCl}$$

Their argument in support of this mechanism has been outlined in Chapter 1.

Shilov and Sabirova[9], on the other hand have postulated the formation of dichlorocarbene by dehydrochlorination of chloroform, as the rate-determining step.

$$CHCl_3 \longrightarrow HCl + :CCl_2$$

Subsequent reactions explain the formation of the observed products

$$:CCl_2 + CHCl_3 \longrightarrow HCl + C_2Cl_4$$
$$:CCl_2 + CHCl_3 \longrightarrow \cdot CCl_3 + \cdot CHCl_2$$
$$2{:}CCl_2 \longrightarrow \cdot CCl_3 + \cdot CCl$$
$$2\cdot CCl_3 \longrightarrow C_2Cl_6$$

However, both mechanisms involve free radicals, and it is difficult to explain why, if free radicals are formed, products containing an odd number of carbon atoms (other than one), are not observed. Under the experimental conditions we have used, one, two and four-carbon species are observed, but no propane derivatives (three-carbon species), have been detected. Steudal[14] has reported the species C_3Cl_4 amongst the products from the pyrolysis of chloroform in the range 700-900°C, but the evidence for its existence is poor. At higher space times hexachlorobenzene has also been shown to be a product[222], but again no five-carbon compounds have been reported.

If chloroform decomposed by a free radical mechanism $\cdot CHCl_2$ radicals would be expected to be formed in the initial step, and this in turn might be expected to give rise to large amounts of 1,1,2,2-tetrachloroethane by dimerisation. However, neither this compound, nor its dehydrohalogenation product; trichloroethylene, are major products.

Experiments carried out in the course of this investigation have shown that the addition of a radical initiator had only a very small effect on the rate of the reaction. Similarly, the addition of both phenol and toluene[9] failed to inhibit the breakdown of chloroform. Also, other workers have found that carbonisation of the reactor surface reduces the rate of a radical reaction, whereas in our experiments, an increase in rate was observed. It is felt, therefore, that the pyrolysis of chloroform is unlikely to proceed by a radical mechanism, and an alternate explanation has been sought.

The formation of dichlorocarbene as the rate determining step of the reaction is one possible explanation. However, since we have shown that the reaction appears to be surface catalysed, modification of the existing mechanism is necessary. The mechanism postulated must also provide a feasible explanation for the observed induction period. Induction periods are usually described as the time required to build up a steady state concentration of some intermediate[223]. Such effects have been observed in the thermal decomposition of dichloromethane[40] and some chlorinated ethanes[68,76,87], where the intermediates concerned were chain carrying radicals. Most induction periods were temperature dependent[68,76]. Initiating the reaction reduced the induction period in the case of dichloromethane[40], since the rate of formation of the chain carrying species was increased. Conversely, in the decomposition of both isomers of tetrachloroethane, the addition of an inhibitor such as propylene prolonged the induction period[68]. Since the latter was unaffected by packing the reaction vessel, the reaction was thought to occur in the bulk of the gas, rather than on the surface. In the decomposition of trichloroethylene the induction period was pressure dependent, which supports the idea that chain initiation is bimolecular in this reaction[87].

The induction period observed in the pyrolysis of chloroform was not tested for temperature dependency, effect of surface area, etc., although it was found to increase when a carbonised reaction tube was used instead of a clean silica tube. An induction period has been observed in the gas phase reaction of chloroform with 2,5-dimethylpyrrole[30,31], and this was found to increase with increasing temperature. By plotting ln 1/induction period against 1/temperature, an activation energy of -3.8 Kcal.mol.$^{-1}$ was calculated for the induction reaction[30]. Although other, perhaps more feasible explanations may be given for this phenomenon, one possible explanation is that dichlorocarbene formed from the breakdown of chloroform may be generated in an excited singlet state, which must then give up energy, to produce either a triplet carbene, or a singlet carbene in the ground state, before reaction can take place[30].

The induction periods we have observed (2.63-4.05 sec.) are greater than those observed in the reaction with 2,5-dimethylpyrrole (1.72-1.86 sec.)[30], as might be expected, since the reaction is considerably slower. Since the observed induction periods are fairly large, it is thought unlikely that they are due to the build up of a steady state concentration of some intermediate such as dichlorocarbene or a radical.

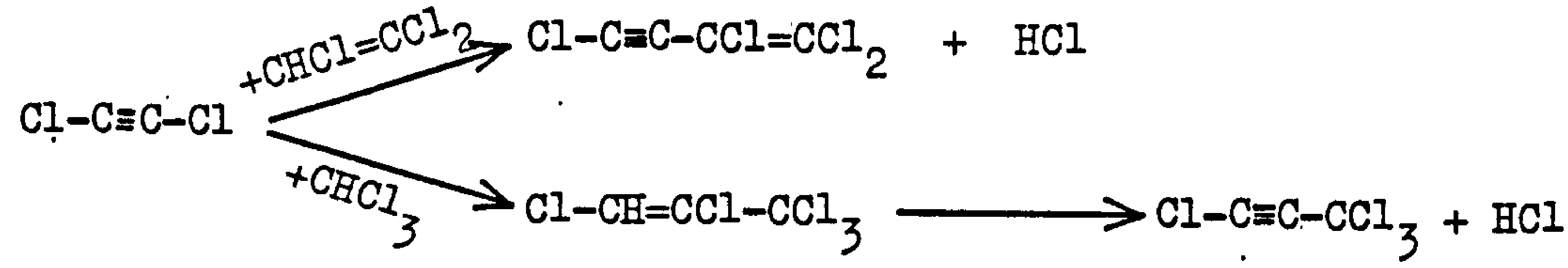
As an alternative possibility, it is suggested that the induction period is the time required for the build up of some sort of carbon polymer type intermediate on the surface of the reaction vessel. The following scheme has been suggested by Dr. R.E. Busby.

$$2CHCl_3 \longrightarrow C + CCl_4 + 2HCl$$

or some other carbon-producing reaction.

$$C + CHCl_3 \longrightarrow CHCl{=}CCl_2$$

$$CHCl{=}CCl_2 \longrightarrow HCl + Cl{-}C{\equiv}C{-}Cl$$

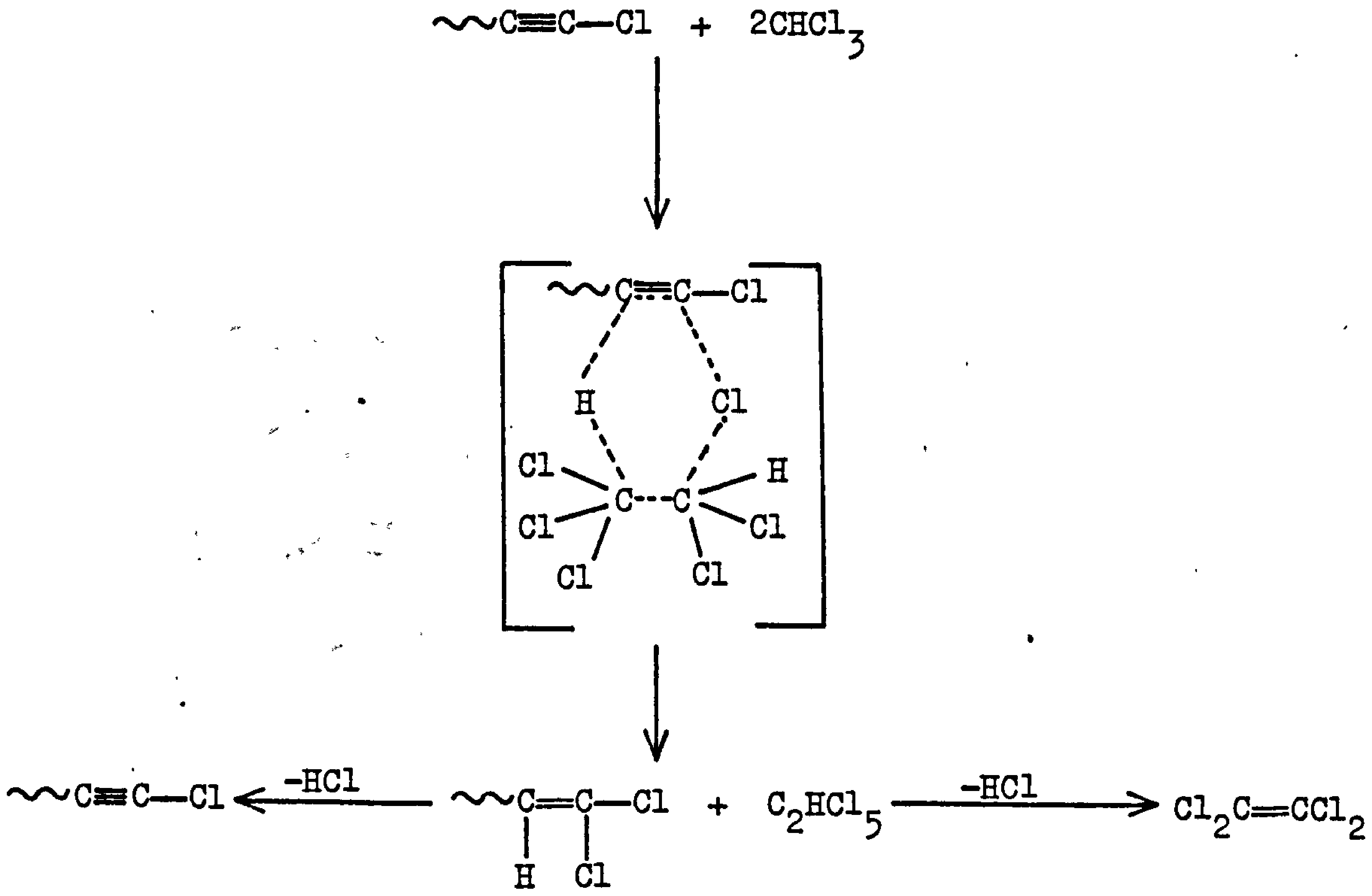


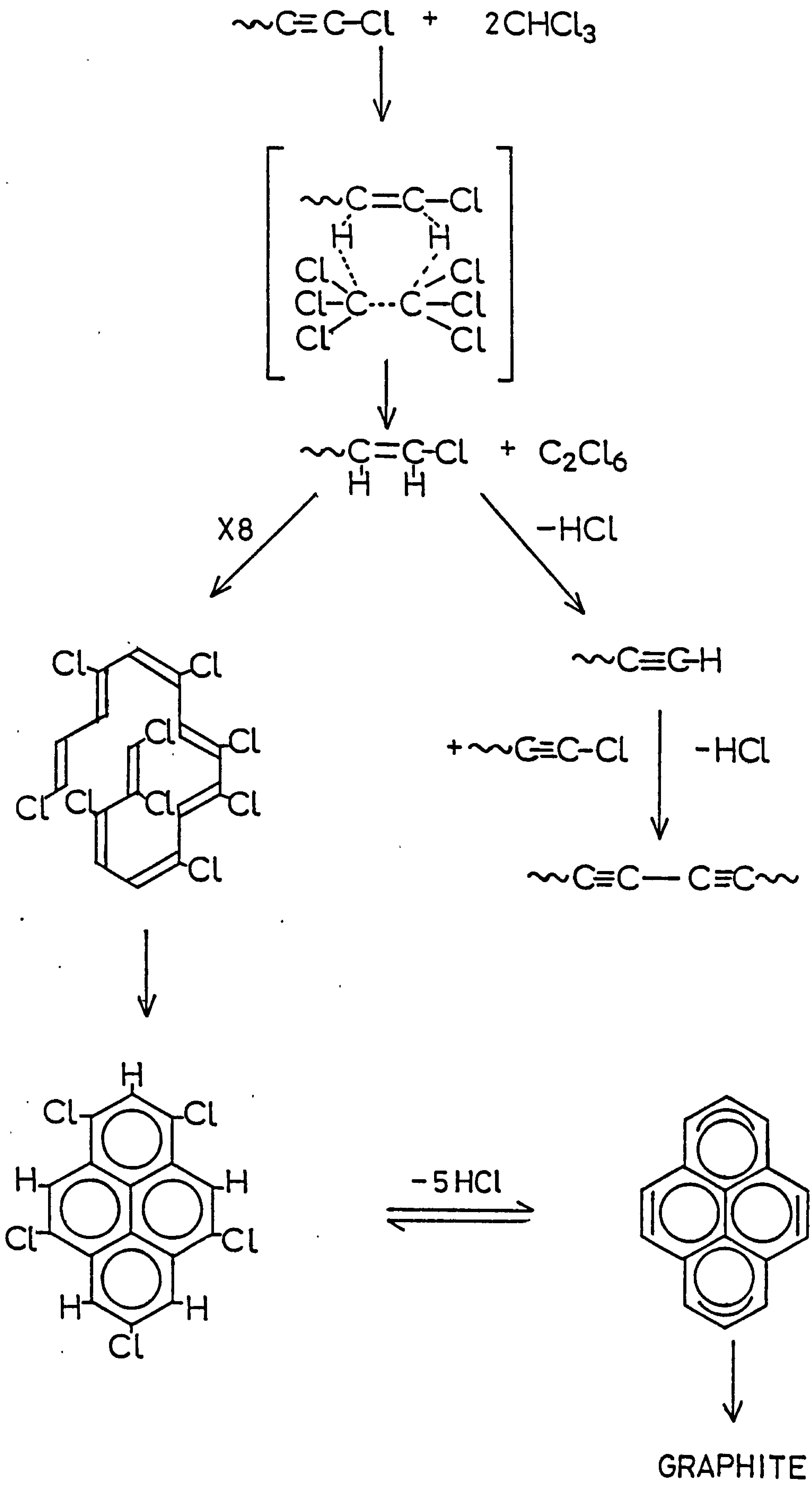
$$\begin{tikzcd}
 & Cl{-}C{\equiv}C{-}CCl{=}CCl_2 + HCl & \\
Cl{-}C{\equiv}C{-}Cl \arrow[ur, "+CHCl{=}CCl_2"] \arrow[dr, "+CHCl_3"'] & & \\
 & Cl{-}CH{=}CCl{-}CCl_3 \arrow[r] & Cl{-}C{\equiv}C{-}CCl_3 + HCl
\end{tikzcd}$$

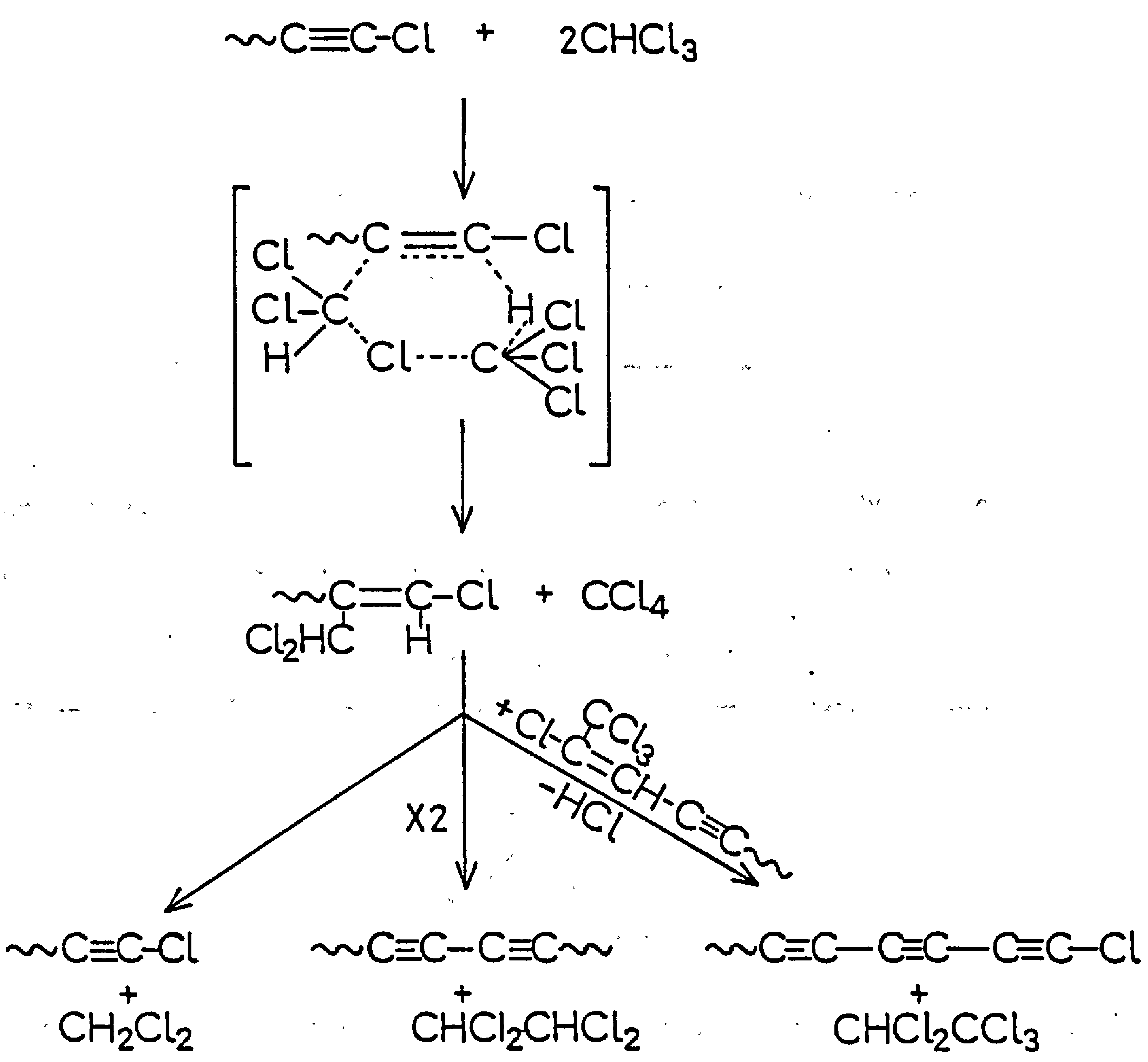
$$2Cl{-}C{\equiv}C{-}CCl_3 \longrightarrow Cl{-}C{\equiv}C{-}C{\equiv}C{-}Cl + C_2Cl_6$$

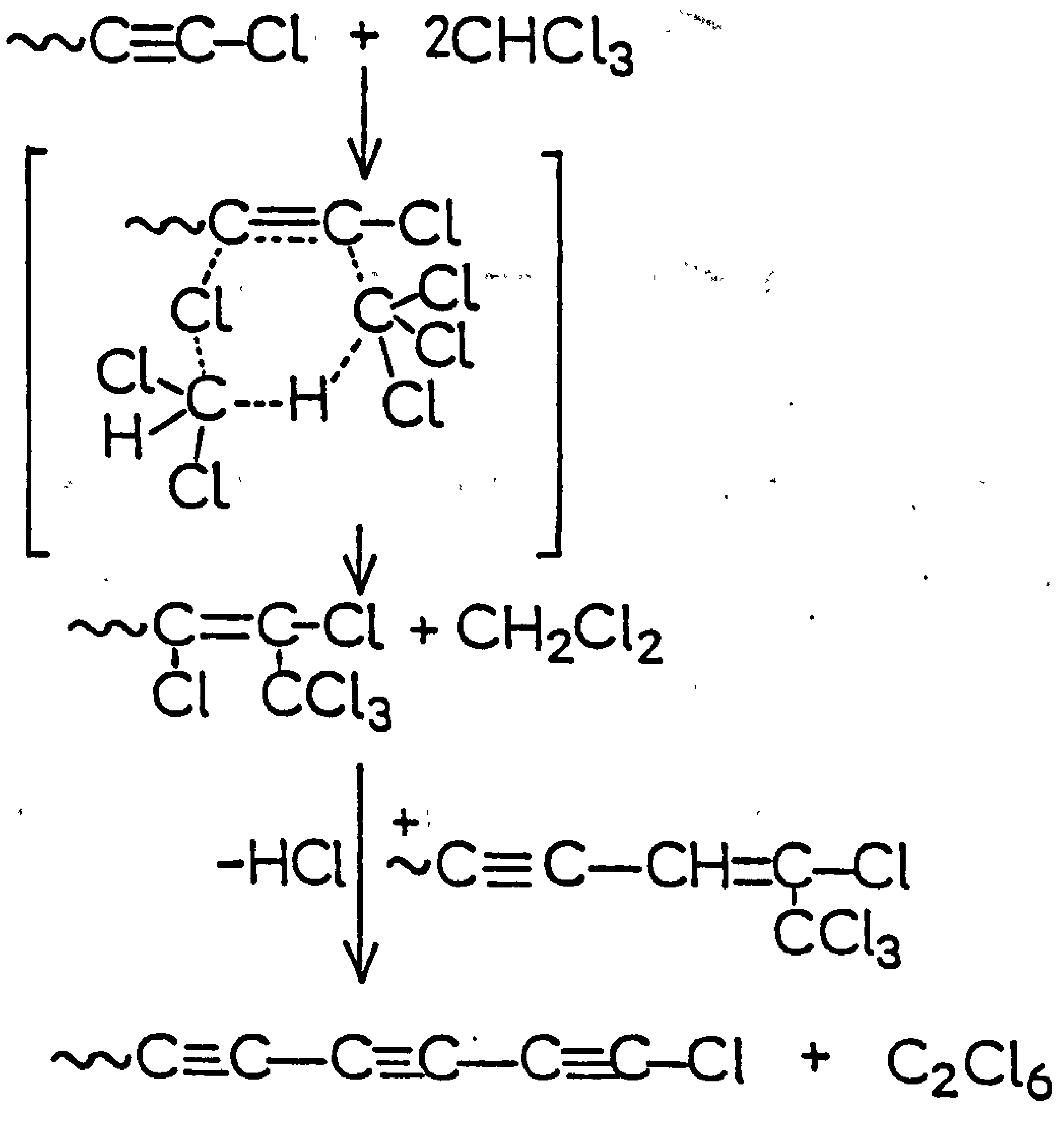
such a reaction could continue, eventually forming a polymeric carbon structure of the type $Cl{-}\left[C{\equiv}C\right]_n{-}Cl$, on the surface of the tube. Once formed the main reaction could then take place on the surface of this carbon polymer. This could explain why increasing the surface area resulted in an increase in reaction, since there was a larger area for the polymer to form on, thereby increasing the possible concentration of active sites. Pretreating the tube, or changing to a new tube had a negligible effect on the reaction, as would be expected, since it is the carbon rather than the silica itself which is acting as a catalyst. In other words, the reaction may be autocatalysed.

The following series of reactions could then occur.




~~C≡C–Cl + 2CHCl₃
~~C=C–Cl
H H
Cl Cl
Cl–C···C–Cl
Cl Cl
~~C=C–Cl + C₂Cl₆
H H
X8
–HCl
~~C≡C–H
+~~C≡C–Cl
-HCl
~~C≡C—C≡C~~
Cl Cl Cl Cl Cl Cl Cl Cl Cl Cl
H Cl Cl H H Cl Cl H H Cl
–5 HCl
GRAPHITE


~C≡C-Cl + 2CHCl3
~C=C-Cl + CCl4
Cl2HC H
X2
+Cl-C=CH-C≡C~
CCl3
-HCl
~C≡C-Cl + CH2Cl2
~C≡C-C≡C~ + CHCl2CHCl2
~C≡C-C≡C-C≡C-Cl + CHCl2CCl3

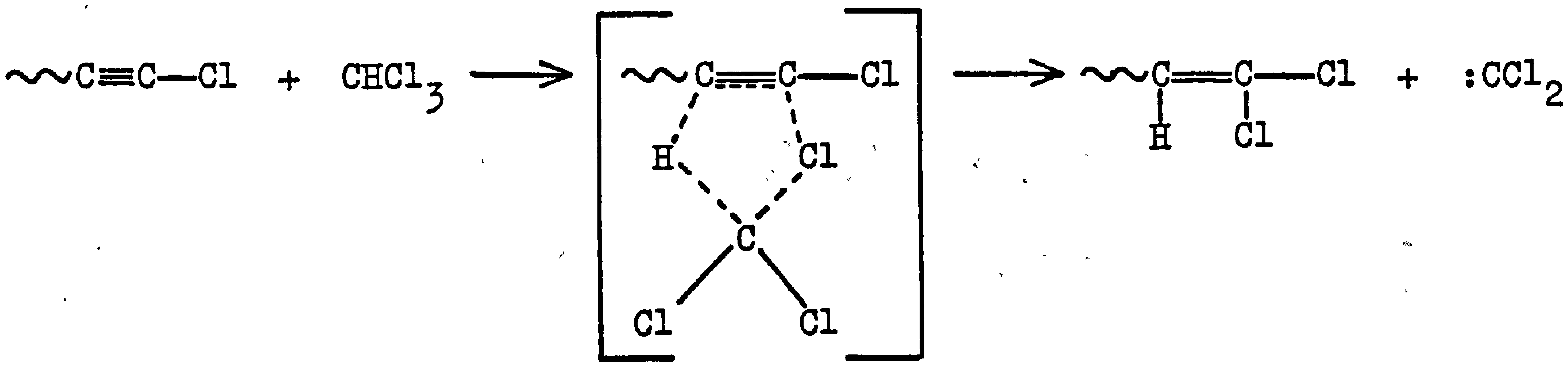

~C≡C-Cl + 2CHCl3
~C=C-Cl + CH2Cl2
Cl CCl3
-HCl
+ ~C≡C-CH=C-Cl
CCl3
~C≡C-C≡C-C≡C-Cl + C2Cl6

$$\mathrm{CHCl{=}CCl_2 + HCl \rightleftharpoons CHCl_2CHCl_2}$$

$$\mathrm{2CHCl{=}CCl_2 \longrightarrow C_4Cl_5}$$

$$\mathrm{Cl_2C{=}CHCl + Cl_2C{=}CCl_2 \longrightarrow C_4Cl_6 + HCl}$$

Alternatively, a single chloroform molecule may be adsorbed onto the surface and lose hydrogen chloride to give dichlorocarbene



Once formed, this may go on to react with other chloroform molecules, as has been suggested elsewhere[9,30,211].

The mechanism suggested by Dr. R.E. Busby may be summarised thus:

$$\mathrm{CHCl_3 + C_n \underset{k_{1r}}{\overset{k_1}{\rightleftharpoons}} CHCl_3{-}{-}{-}{-}C_n} \qquad (74)$$

$$\mathrm{CHCl_3{-}{-}{-}{-}C_n + CHCl_3 \xrightarrow{k_2} Products} \qquad (75)$$

where C_n is an active, possibly carbon polymer, site on the surface of the tube, since it is more likely that the two chloroform molecules are adsorbed consecutively, than that they are both adsorbed together.

The theoretical rate equation may therefore be derived,

$$\text{Rate} = \frac{-d[CHCl_3]}{dt} = k_1[CHCl_3][C_n] - k_{1r}[CHCl_3\text{----}C_n] + k_2[CHCl_3\text{----}C_n][CHCl_3] \quad (76)$$

Under steady state conditions,

$$\frac{d[CHCl_3\text{----}C_n]}{dt} = 0$$

$$\frac{d[CHCl_3\text{----}C_n]}{dt} = k_1[CHCl_3][C_n] - k_{1r}[CHCl_3\text{----}C_n] - k_2[CHCl_3\text{----}C_n][CHCl_3] \quad (77)$$

$$k_{1r}[CHCl_3\text{---}C_n] + k_2[CHCl_3\text{---}C_n][CHCl_3] = k_1[CHCl_3][C_n] \quad (78)$$

$$\therefore [CHCl_3\text{---}C_n] = \frac{k_1[CHCl_3][C_n]}{k_{1r} + k_2[CHCl_3]} \quad (79)$$

Substituting this expression into eq. (76)

$$\text{Rate} = \frac{-d[CHCl_3]}{dt} = k_1[CHCl_3][C_n] - \frac{k_{1r}k_1[CHCl_3][C_n]}{k_{1r} + k_2[CHCl_3]} + \frac{k_2k_1[CHCl_3]^2[C_n]}{k_{1r} + k_2[CHCl_3]} \quad (80)$$

Assuming that $k_2[CHCl_3] \gg k_{1r}$, eq.(80) becomes,

$$\text{Rate} = \frac{-d[CHCl_3]}{dt} = 2k_1[CHCl_3]\,C_n - \frac{k_{1r}k_1[C_n]}{k_2} \quad (81)$$

TEXT CUT OFF IN ORIGINAL

The theoretical rate equation based on the proposed mechanism therefore predicts a first order dependence on both the chloroform concentration and the concentration of reaction sites. It is likely, however, that the molecularity of the reaction is greater than one, and it is thought that two molecules are involved, as shown in the proposed mechanism.

Similarly, if the reaction were to involve the formation of dichlorocarbene on the surface of the vessel, which then reacted with a second molecule of chloroform, a similar theoretical rate equation could be derived.

$$CHCl_3 + C_n \underset{k_{1r}}{\overset{k_1}{\rightleftharpoons}} CHCl_3{-}{-}{-}{-}C_n$$

$$CHCl_3{-}{-}{-}{-}C_n \xrightarrow{k_2} C_n + HCl + :CCl_2$$

$$:CCl_2 + CHCl_3 \xrightarrow{k_3} \text{products}$$

$$\text{Rate} = \frac{-d[CHCl_3]}{dt} = k_1[CHCl_3][C_n] - k_{1r}[CHCl_3{-}{-}{-}{-}C_n] + k_3[:CCl_2][CHCl_3] \qquad (8$$

Applying steady state conditions,

$$\frac{d[CHCl_3{-}{-}{-}{-}C_n]}{dt} = \frac{d[:CCl_2]}{dt} = 0$$

$$\frac{d[CHCl_3{-}{-}{-}{-}C_n]}{dt} = k_1[CHCl_3][C_n] - k_{1r}[CHCl_3{-}{-}{-}{-}C_n] - k_2[CHCl_3{-}{-}{-}{-}C_n] \qquad (83)$$

$$\therefore [CHCl_3\text{-----}C_n] = \frac{k_1[CHCl_3][C_n]}{k_{1r} + k_2} \qquad (84)$$

$$\frac{d[:CCl_2]}{dt} = k_2[CHCl_3\text{-----}C_n] - k_3[:CCl_2][CHCl_3] \qquad (85)$$

$$\therefore [:CCl_2] = \frac{k_2[CHCl_3\text{-----}C_n]}{k_3[CHCl_3]} \qquad (86)$$

Substituting (84) into (86),

$$[:CCl_2] = \frac{k_2k_1[C_n]}{k_3(k_{1r} + k_2)} \qquad (87)$$

Substituting (84) and (87) into the rate expression (82) we obtain,

$$\text{Rate} = \frac{-d[CHCl_3]}{dt} = k_1[CHCl_3][C_n] - \frac{k_{1r}k_1[CHCl_3][C_n]}{k_{1r} + k_2} + \frac{k_3k_2k_1[CHCl_3][C_n]}{k_3(k_{1r} + k_2)} \qquad (88)$$

$$= \left(\frac{2k_2k_1}{k_{1r}+k_2}\right)[CHCl_3][C_n]$$

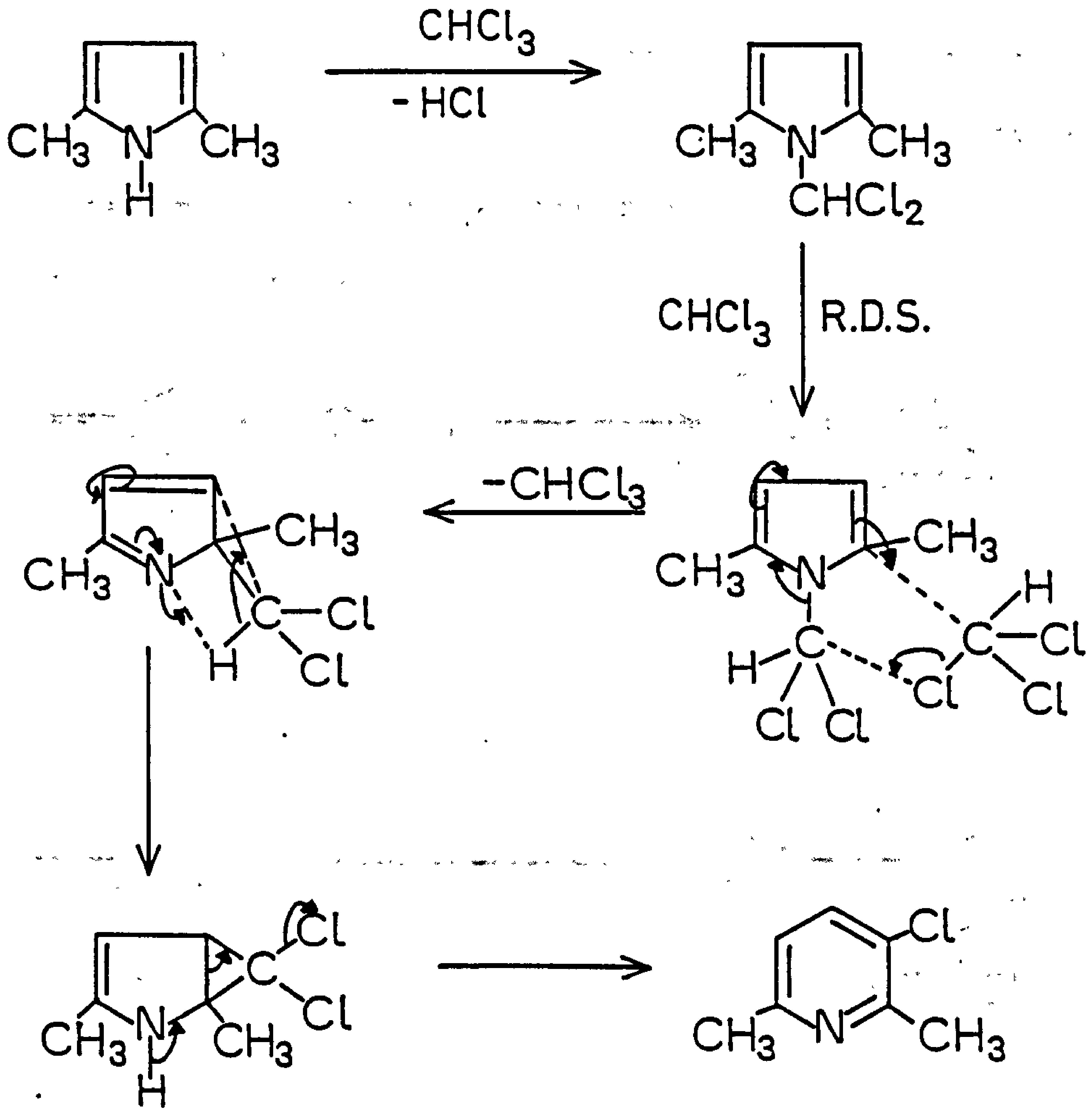
Again, the theoretical rate equation predicts a reaction which is first order with respect to both chloroform and the concentration of active sites. It is not possible therefore, to distinguish between the two mechanisms on this basis alone. In both cases the theoretical treatment predicts a first order reaction which is in agreement with the observed results, and also with what other authors have reported[5,9]. The fact that the rate is dependent on the concentration of reaction sites is also compatible with our findings, since we have shown that increasing the surface area of the reaction tube resulted in an increase in the rate of reaction. In order to explain the formation of two-carbon compounds in this reaction the molecularity of the reaction must be greater than one. Two molecules are more likely to be involved than three, since no three-carbon compounds are obtained from the reaction. In order for the reaction to occur two molecules must come together, and be held together long enough for reaction to take place. This is more likely to occur on a surface, which can hold the molecules together momentarily, than in the bulk of the gas, where they come together only by collision. For this reason, the mechanism suggested by Dr. R.E. Busby probably explains what is happening in the reaction, better than the formation of dichlorocarbene, unless the latter is also held on the surface long enough for the reaction to take place. However, dichlorocarbene would be expected to insert into pentachloroethane and hexachloroethane to give three-carbon species. Since no such compounds were found to be present, dichlorocarbene is probably not involved.

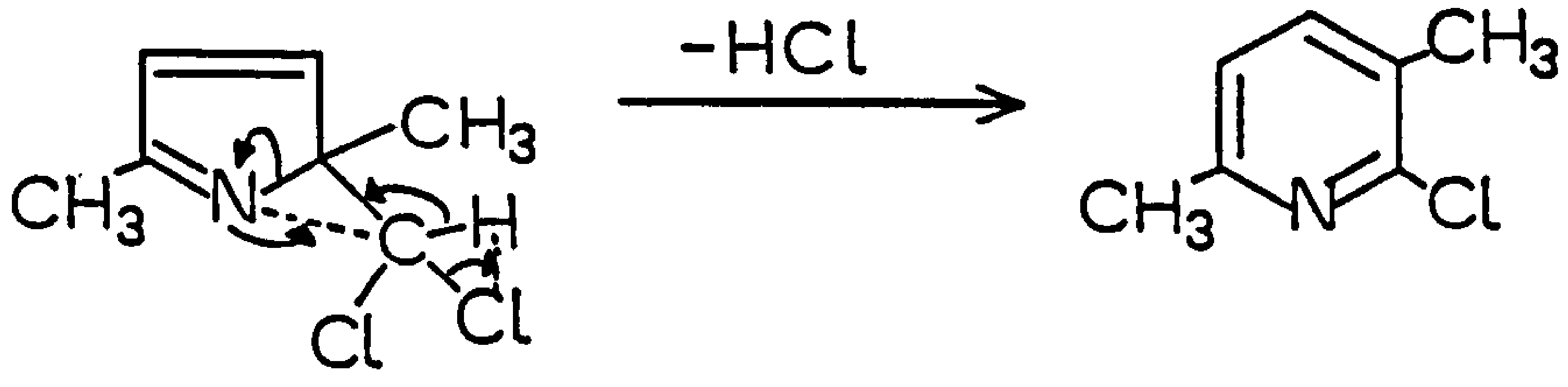
The rate of reaction was found to be faster when the tube was carbonised, than it was when the tube was cleaned between runs. The induction period was also higher in the carbonised tube, suggesting that the nature of the 'catalyst' may be changing. As the carbon is built up on the surface, the carbon polymer will begin to form a graphite-like structure. The region we are observing may be a region where this change-over is taking place, so that what we have is a mixture of carbon polymer and graphitic-type carbon which may be in equilibrium. Such a mixture may be a more active catalyst than either form alone. We have shown that when a carbonised surface becomes cracked and uneven, its catalytic activity increases considerably. This would account for the fact that we observe a higher rate of reaction. Once the surface has become completely graphitised the reaction may become slower, as has been reported elsewhere[5,9], since this may be a poorer catalyst.

The induction period observed in the reaction with a carbonised tube appeared to be longer than that in the clean silica tube, although it cannot be determined with the same degree of accuracy because of the greater amount of scatter. The species which is building up to steady state concentrations is no longer the carbon polymer, but possibly an equilibrium mixture of the carbon polymer with the graphitic-type carbon, and it may be that it takes longer for this to reach a steady-state, than the carbon polymer alone.

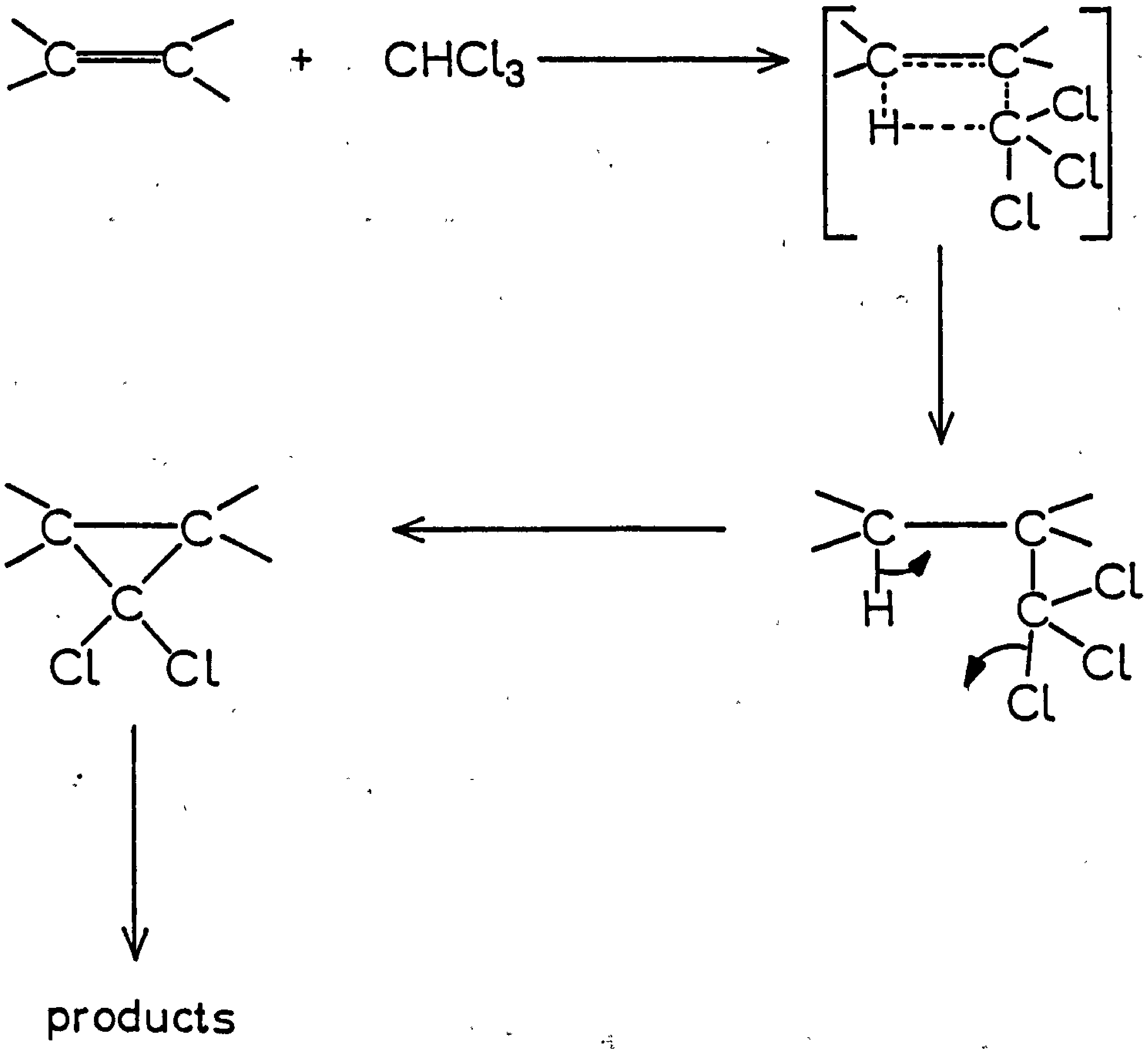
8.III.i. THE REACTION OF CHLOROFORM WITH A SUBSTRATE IN THE VAPOUR PHASE

A kinetic study has recently been carried out on the reaction between chloroform and 2,5-dimethylpyrrole in the vapour phase[31]. Earlier work had shown that the reaction is first order with respect to the pyrrole[30], and it is now known that the reaction is second order with respect to chloroform[31]. Existing mechanisms cannot account for this observation, so an alternative mechanism has been suggested[224].


CHCl3
-HCl
CH3
N
H
CH3
CHCl2
CHCl3
R.D.S.
-CHCl3
C
Cl
Cl


-HCl
CH3
N
C
H
Cl
Cl

The formation of cyclopropane adducts in the pyrolysis of chloroform with olefins can be explained by simple addition across the double bond, followed by dehydrohalogenation, without needing to invoke either free radicals or dichlorocarbene.



8.IV. CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

From the experimental results obtained during this investigation we have found that the decomposition of chloroform in the vapour phase is a first order reaction which is catalysed at the surface of the reaction tube. The main products of the reaction are hydrogen chloride, hexachloroethane, pentachloroethane and tetrachloroethylene. Hydrogen and chlorine were not detected amongst the reaction products, nor were any compounds containing three or five carbon atoms. This, together with the fact that the reaction is neither initiated nor inhibited by AIBN and phenol respectively has led us to reject the idea that the reaction proceeds entirely by a radical mechanism. The formation of dichlorocarbene cannot be entirely ruled out, although in this mechanism also, trichloromethyl radicals must be invoked to explain the formation of hexachloroethane, and this might be expected to give rise to three- and five-carbon species. Also, insertion of dichlorocarbene into pentachloroethane would be expected to give three-carbon species, which are not observed.

The reaction was preceded by an induction period, and both this and the rate of reaction increased when a carbonised tube was employed. Using a carbonised tube also gave rise to considerable scatter in the results since the amount of carbon deposited was not enough to form a reproducible surface, and the extent of carbonisation was no longer proportional to the space time, as in the clean silica tube. A mechanism involving the formation of a carbon polymer, which then enables chloroform to be adsorbed and react on the surface has been suggested.

Future work should be directed towards an increased understanding of the way in which the surface catalyses the reaction. It would be very difficult to study the reaction with a partly carbonised surface, since it would be difficult to ensure that the surface was reproducible. However, if this could be done accurately, it would be of great value to determine how the extent of carbonisation effected both the rate of the reaction and the induction period. If it were possible to treat the surface in some way, so that the adsorption of chloroform could be improved, this might result in an increased rate of reaction.

The reaction could also be studied in a reactor which had been sufficiently carbonised to produce a stable graphite type structure. These conditions would be similar to those used in other work, in which a slower reaction has been reported[5,9], compared to that observed under the conditions we have used. No induction periods have been reported under these conditions, and it would be interesting to see whether this is in fact the case. If under these conditions the reaction is catalysed solely by the graphite-type carbon, which would be present right from the beginning of the reaction, then no induction period would be expected. It would also be of interest to see whether this reaction would in fact be slower as we expect it to be.

By studying the effect of temperature on the induction period, an estimate of the activation energy associated with the processes involved in this part of the reaction could be made. This would give valuable information about the nature of these processes. It would also be of interest to determine the activation energy of the reaction proper in a clean silica tube, so that this could be compared with values obtained in the carbonised system.

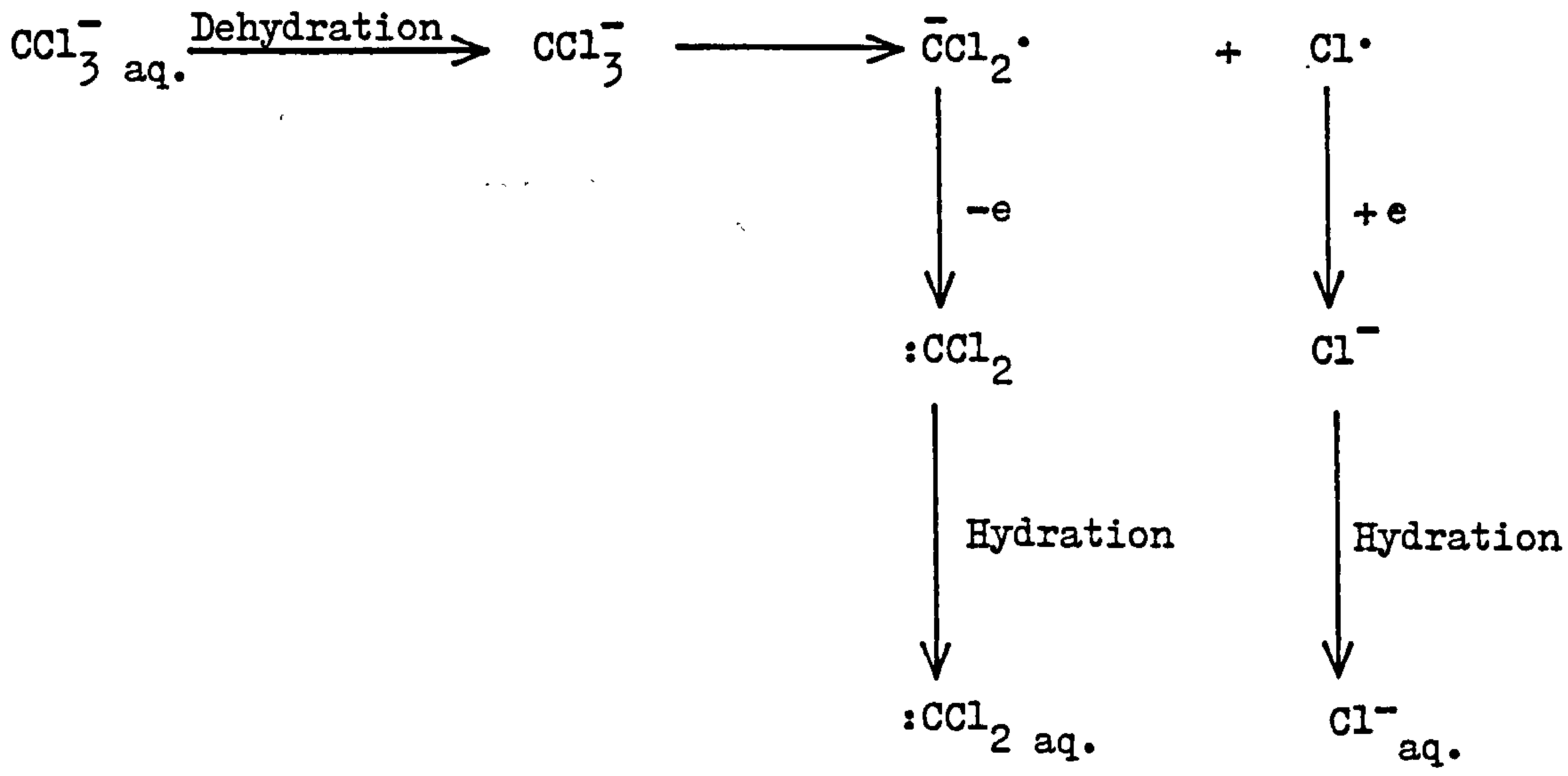
It is evident that the mechanism of the vapour phase decomposition of chloroform is more complex than had previously been imagined. Whilst it is not possible to state definitely that the mechanism we have proposed is the correct mechanism, we feel that it explains the observed results better than the existing mechanisms, and should therefore be considered as a possible alternative. It is felt that this reaction must be studied in still greater detail, before its mechanism can be fully understood.

CHAPTER 9

DISCUSSION OF THE HYDROLYSIS OF CHLOROFORM

The decision to investigate the kinetics of the basic hydrolysis of chloroform, was initiated by results obtained in a kinetic study of the breakdown of chloroform in the gas phase. Preliminary results suggested that this reaction, which had originally been believed to be first order, was in fact of a higher order with respect to chloroform. However, it has now been shown that this is not the case, and that the reaction is in fact first order in chloroform.

The most widely accepted mechanism for the alkaline hydrolysis of chloroform is that suggested by Hine and coworkers[92-99]. This involves the formation of a trichloromethyl anion, by rapid abstraction of a proton from chloroform, by a base, followed by the loss of a chloride ion, giving dichlorocarbene. However, no satisfactory explanation has been given to account for the energy required to break the carbon-chlorine bond, which would probably be similar in strength to the carbon-chlorine bond in chloroform (78 Kcal.mol.$^{-1}$). Loss of Cl^- from a trichloromethyl anion would involve the following processes.



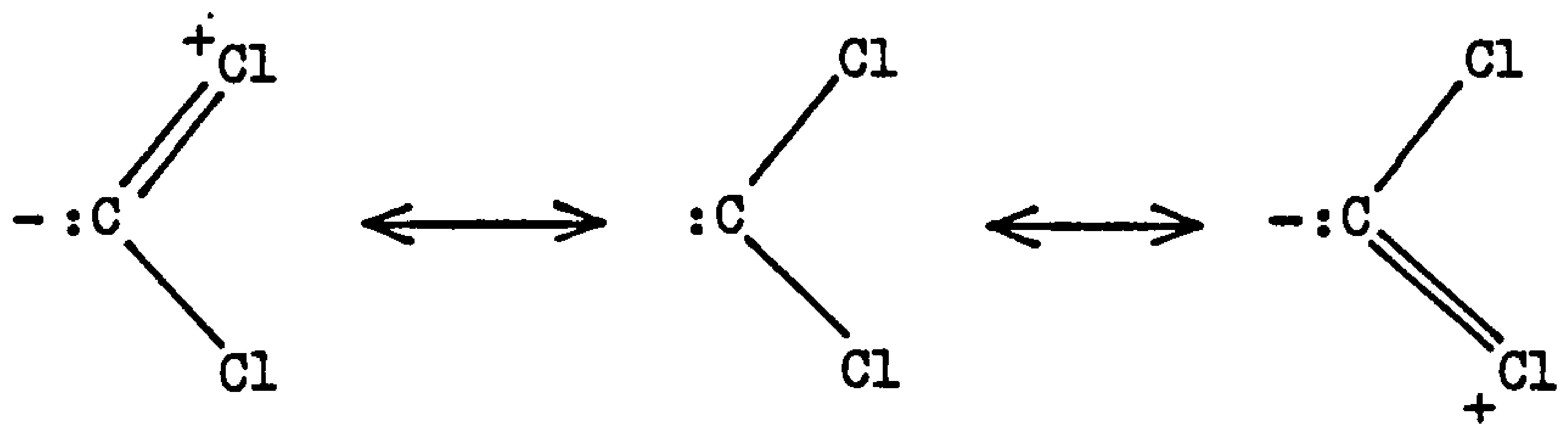
Therefore, the total energy involved would be,

$$H_{Total} = H_{Dehyd^{n}_{\cdot}CCl_3^-} + H_{C-Cl} + H_{-e} + H_{+e} + H_{Hyd^{n}_{\cdot}\,:CCl_2} + H_{Hyd^{n}_{\cdot}Cl^-}$$

where $Hyd^{n}_{\cdot}$ = hydration.

Such a process would, therefore, be endothermic to a degree which could not be accounted for by the activation energy observed (24.3-33.3 Kcal.mol.$^{-1}$)^{95,110,112}. The involvement of a second molecule of chloroform could help to make this process energetically more favourable.

Dichlorocarbene may be considered as a divalent, carbon intermediate, in which the carbon atom is covalently bonded to two chlorine atoms, leaving two non-bonding electrons which may have antiparallel spins (singlet state), or parallel spins (triplet state). Although dichlorocarbene is a very reactive intermediate, it is stabilised to some extent by the ability of the chlorine atoms to supply electrons to the electron-deficient carbon atom. Three possible resonance structures (42) increase the stability of the intermediate, thus decreasing the endothermicity of the rate controlling step.



(42)

However, this effect would be relatively small, and could not account for a significant proportion of the required energy.

The hydration energy of the chloride ion compared to the trichloromethyl ion could also help the reaction, if the former was significantly larger, but again this would not provide the necessary driving force.

The pyrolytic breakdown of chloroform had been found to be surface catalysed, and the possibility of the reaction in solution being similarly aided was considered. However, preliminary experiments to compare the rates of reaction in vessels made of glass (soda glass and pyrex), and polythene, showed that it was unaffected by the nature of the surface. The reaction was also independent of the surface area to volume ratio, since increasing the surface area by adding glass rings, had no effect on the reaction rate.

Lastly, other workers had followed the reaction by following the rate of disappearance of the sodium hydroxide, or the rate of formation of the products, whereas the method used in this work determines the rate of reaction of chloroform directly.

9.I. PROBLEMS ENCOUNTERED IN STUDYING THE REACTION

Certain difficulties had to be overcome in order to follow the reaction by g.l.c.. Although the dioxane used in this work was of analar grade, and repurified prior to use a very small amount of impurity remained which gave a peak on g.l.c. analysis, which interfered with the chloroform peak. A correction was made for this, by subtracting the area of the impurity peak from the chloroform peak, but this had to be done very accurately. If the size of the impurity peak was either overestimated or underestimated the resulting velocity constant was considerably changed, and the first order rate plot was non-linear. To overcome this the initial concentration of chloroform was kept high enough for the impurity peak to be less than 10 % of the initial chloroform peak, and by purifying the solvent so that the impurity concentration was as small as possible.

Similar problems were encountered as a result of the g.l.c. detector responding to water. Theoretically, flame ionisation detectors give no response to water, but in practice, a response is often observed, which is probably due to the stationary phase being washed off from the column. The magnitude of this response varies from one column to another, and becomes more severe as the column ages. It was important therefore, to find a column with which the detector did not respond to water, and to replace it as soon as it began to do so.

Another source of error was encountered when samples were incompletely neutralised before they were injected onto the column. This resulted in severe tailing of peaks, and a build up of alkali on the glass plug at the beginning of the column. In subsequent runs false values of chloroform concentration were obtained, because chloroform was reacting with alkali on the column, giving velocity constants which were falsely high, and non-linear rate plots. It was important therefore, to ensure that sufficient acid was used to neutralise the sample completely.

The reaction mixture was originally neutralised in small glass sample tubes with polythene stoppers, but it was found that the chloroform was rapidly absorbed by the polythene, thus reducing the chloroform concentration before it could be estimated. Alternative tubes with metal foil-lined tops were employed, but even when these were used, the solution was not allowed to come into contact with the top, before a sample was injected on to the chromatograph. The automatic pipette used to withdraw samples from the reaction mixture was fitted with polypropylene tips which did not absorb the chloroform.

In most of the runs carried out, an increase in chloroform concentration was observed between the first and the second injections. This was shown to be due to a small amount of chloroform being adsorbed on the syringe during the first injection. Once the barrel of the syringe had been saturated this was no longer a problem, unless the syringe was left for a long time between injections, allowing the chloroform to desorb from the surface. Since excellent straight line calibration curves were obtained this was thought to be unimportant.

9.II.i. DETERMINATION OF THE ORDER AND RATE OF REACTION

The results obtained from experiments to determine the order of the reaction, showed conclusively that the reaction was first order with respect to both chloroform and sodium hydroxide, and that three moles of sodium hydroxide reacted for every mole of chloroform. All runs gave straight line first order rate plots provided that the sodium hydroxide was present in large excess, whilst second order rate plots (with respect to chloroform) showed considerable curvature. A straight line was obtained for the overall second order rate plot, when comparable concentrations of the two reactants were used, and the change in the concentration of both the chloroform and the sodium hydroxide was taken into account.

Determination of the order by the method of fractional life also showed a first order dependence on chloroform, the time taken for the concentration of chloroform to be reduced by one-half, being independent of the initial concentration of chloroform. The first order velocity constant determined by this method was 1.52×10^{-4} sec.$^{-1}$, in good agreement with the value determined from the first order rate plot (1.59×10^{-4} sec.$^{-1}$).

It is difficult to compare the results obtained in this work with the values of velocity constants obtained by other workers, since their results were obtained under different experimental conditions. However, a summary of velocity constants obtained is given in Table 45.

TABLE 45

Comparison of second order velocity constants for the alkaline hydrolysis of chloroform

Temp.(°C)	Base	Solvent	$k_2 \times 10^4$ (mol.l.$^{-1}$sec.$^{-1}$)	Ref.
36.0	NaOH	32 % dioxane	6.50-2.55 *	This work
35.0	NaOH	67 % dioxane	3.19 ± 0.05	95
35.0	KOH	95 % ethanol	2.63	112
35.0	KOH	water	3.08 ± 0.09	110

* depending on the concentration of sodium hydroxide (0.05-1.50 M)

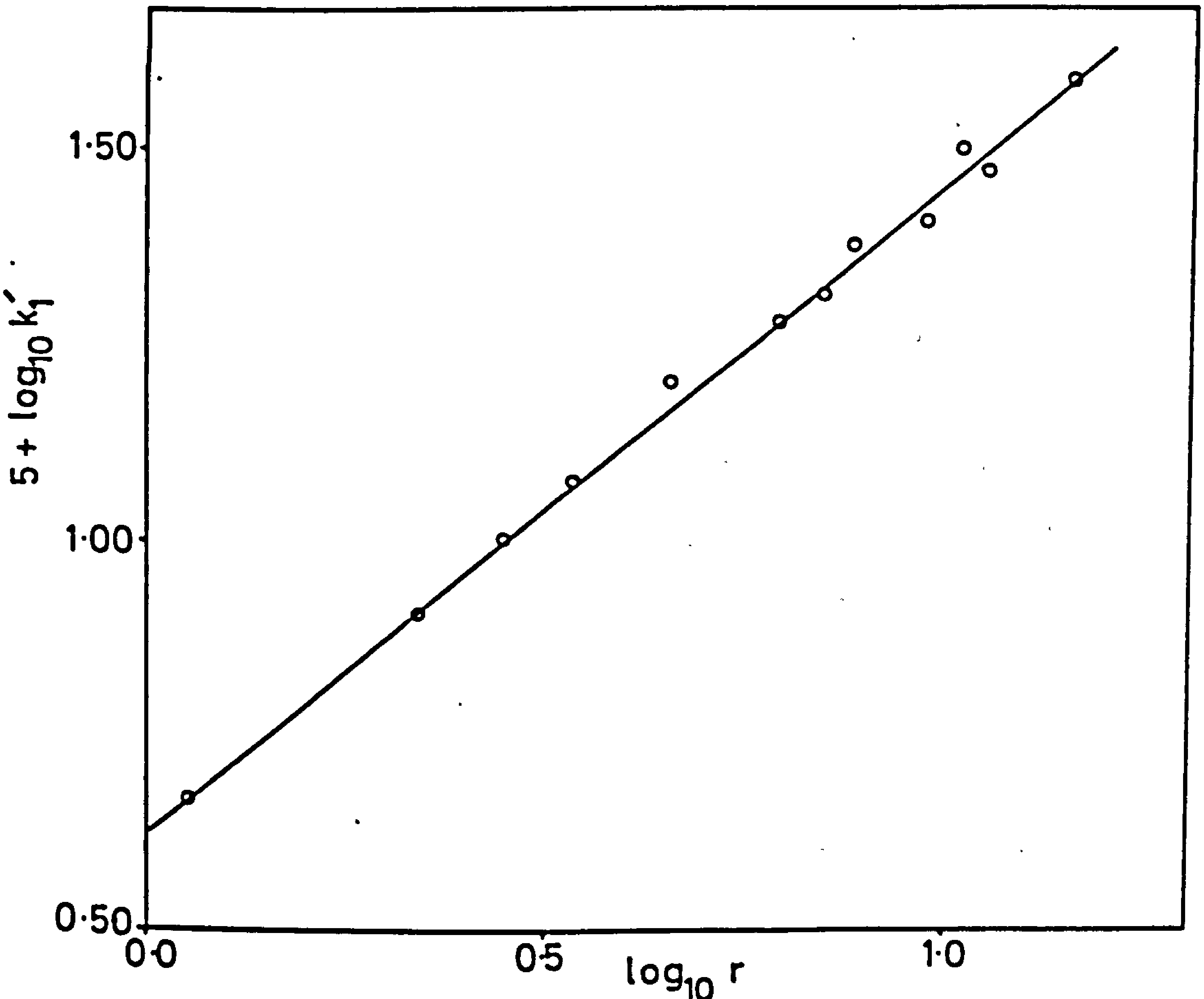
It can be seen from Table 45 that the second order velocity constants obtained in this work are of the same order of magnitude as those reported elsewhere. However, we have observed that k_2 varies from 6.50×10^{-4} mol.l.$^{-1}$sec.$^{-1}$ at 0.05 M sodium hydroxide, to 2.55×10^{-4}mol.l.$^{-1}$sec.$^{-1}$ at 1.50 M sodium hydroxide. Since others workers have not always quoted the concentration of base used to determine their values, it is difficult to make direct comparisons.

The possibility of the reaction being second order with respect to chloroform was considered, and the reaction mixtures were analysed for possible two carbon species such as pentachloroethane and tetrachloroethylene, but these were not found at any time.

Reactions such as the hydrolysis of chloroform, in which there is a fast pre-equilibrium involving proton transfer, followed by a slow, rate determining step may be classified as B-1 reactions. This is analogous to the A-1 reactions in acid solution[225], whose rate constants are known to be proportional to the acidity function of the medium. Since the basicities of the aqueous dioxane solutions used have been determined for a number of different hydroxide concentrations, it was possible to construct a plot of the log of the observed first order rate constants against basicity. Since pK_a is constant, any variation in the basicity function, H_-, will be due to the variation in $\log_{10}r$, therefore $\log_{10}r$ may be used instead of H_-, giving a plot of the same gradient.

FIGURE 42

Plot of $\log_{10}k_1'$ against basicity



The plot of $\log_{10}k_1'$ against basicity gave a straight line of gradient 0.81 (method of least squares). Similar plots have been constructed for the reactions of chloroform with alkoxides. More O'Ferall and Ridd[226] have studied the reaction in methanolic sodium methoxide. They found that a plot of $\log_{10}k_1$ against H_- was curved, with a mean slope of about 0.8 in the region $1\,M < C_{NaOMe} < 3\,M$. Barbaud[227] obtained a linear plot for the same reaction, with a similar slope (~0.7) to that obtained earlier. Again, linear correlation broke down at high concentrations of methoxide[228].

A study has recently been made of the reaction in strongly basic ethylene glycol-metal glycolate systems[229]. It was found that the plot of $\log_{10} k_1$ vs. H_- was linear with a slope of approximately 0.74, up to 2.0 M sodium glycolate. At concentrations above this it curved downwards. Points from the curves of three different metal glycolates (Na, Li or K), all lay on the same curve, providing extra evidence against the possibility of the proton abstracting step being rate determining[229].

The deviation of the gradients of the plots from unity, of all the reactions studied has been explained on the basis of the large difference in size and structure between chloroform and the indicators used to determine H_-. This could result in a large difference in the solvation requirements of CCl_3^- compared to the indicator anion. This would mean that the Zucker-Hammett hypothesis, $f_{SH}/F_{\ddagger} = f_{HA}/f_{A^-}$, where f values are the activity coefficients of the species concerned, was not completely valid.

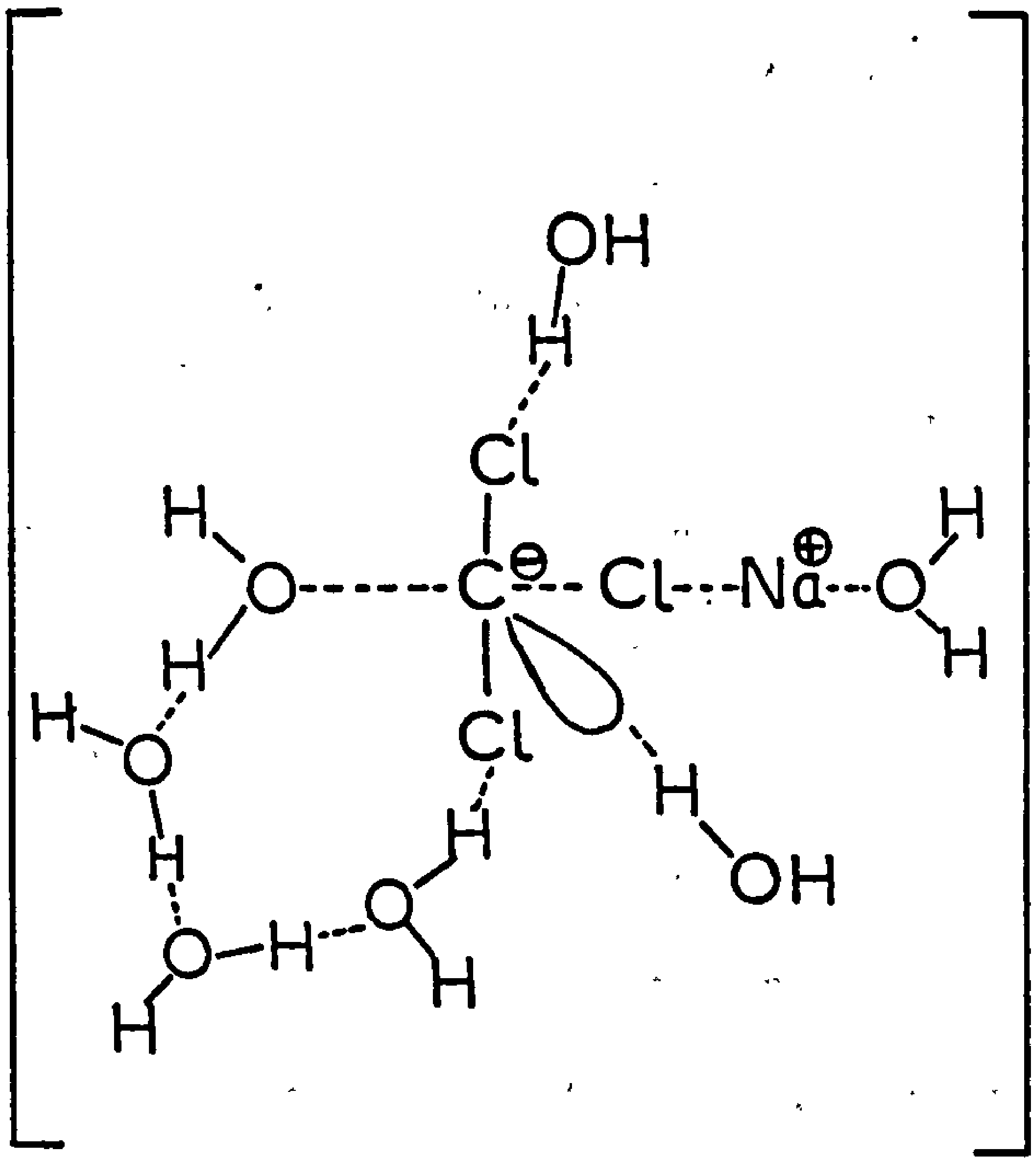
9.II.ii. APPLICATION OF THE YAGIL APPROACH

It is advantageous at this point to consider the results of the application of the Yagil approach to this reaction, since this gave information about the reaction mechanism which has helped to explain the effects observed. The method suggested by Yagil (see page 65) to determine the number of water molecules associated with the transition state of a reaction, is a relatively new idea, and as yet is probably not fully accepted, since it has only been applied to relatively few reactions. It was felt therefore, that by applying it to the hydrolysis of chloroform it would give more information about the usefulness of the method, as well as helping to gain further insight into the reaction mechanism.

A plot of k_1' against the initial concentration of sodium hydroxide was curved (see Fig.33), suggesting that another factor, other than the concentration of sodium hydroxide, was involved in determining the reaction rate.

The Yagil plot of $\log_{10} k_1'/C_{OH^-}$ against $\log_{10} C_w$ gave a straight line plot of slope + 3.14. Values of $\log_{10} k_1'/C_{OH^-}$ fell off rapidly at values of C_w greater than 0.974. This corresponds to sodium hydroxide concentrations of between 0 and 0.2 molar. It has been shown[103], that at values below 0.2 molar, the ionic strength has a severe effect on the rate of the reaction, and it is possible that such an effect is responsible for the observed deviation. At ionic strengths greater than 0.2 molar such effects are no longer important[103].

Positive values of slope are less common than negative values in the Yagil plot, but since relatively few reactions have been treated in this way it is not yet known whether the value we have obtained is particularly unusual. The highest positive value reported to date was +1, which was determined for the hydrolysis of aziridinium ions[166]. A slope of +3 means that an average of seven water molecules are associated with the transition state, (three molecules are given up by the hydroxide ion, and one is formed in the reaction). It is suggested therefore, that the reaction intermediate is a product formed by attack of water on the carbon atom of the trichloromethyl anion. This could be aided by the high degree of solvation of the transition state, and the fact that a sodium ion is helping to remove a chlorine atom. Several structures are possible for the transition state:-



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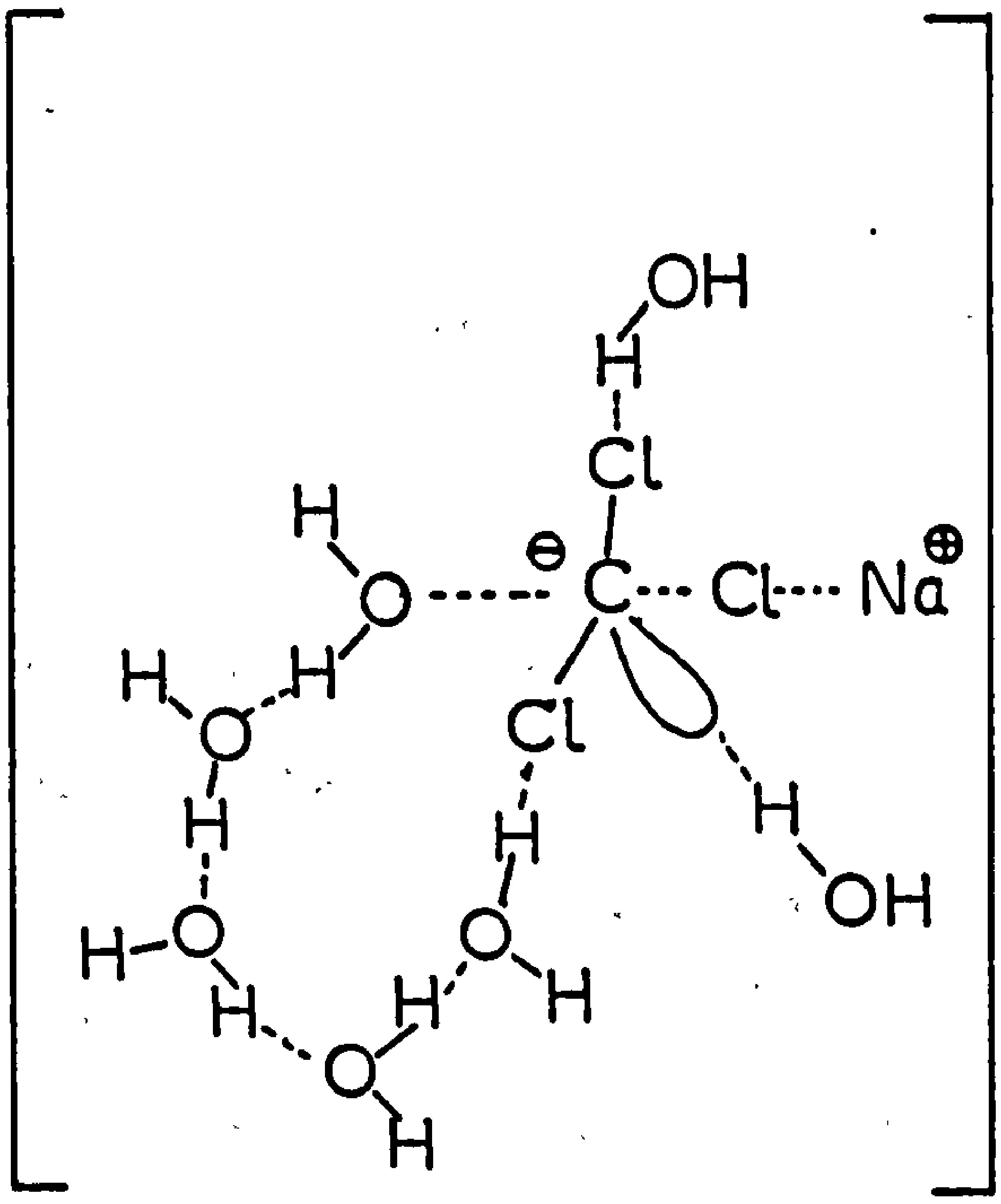

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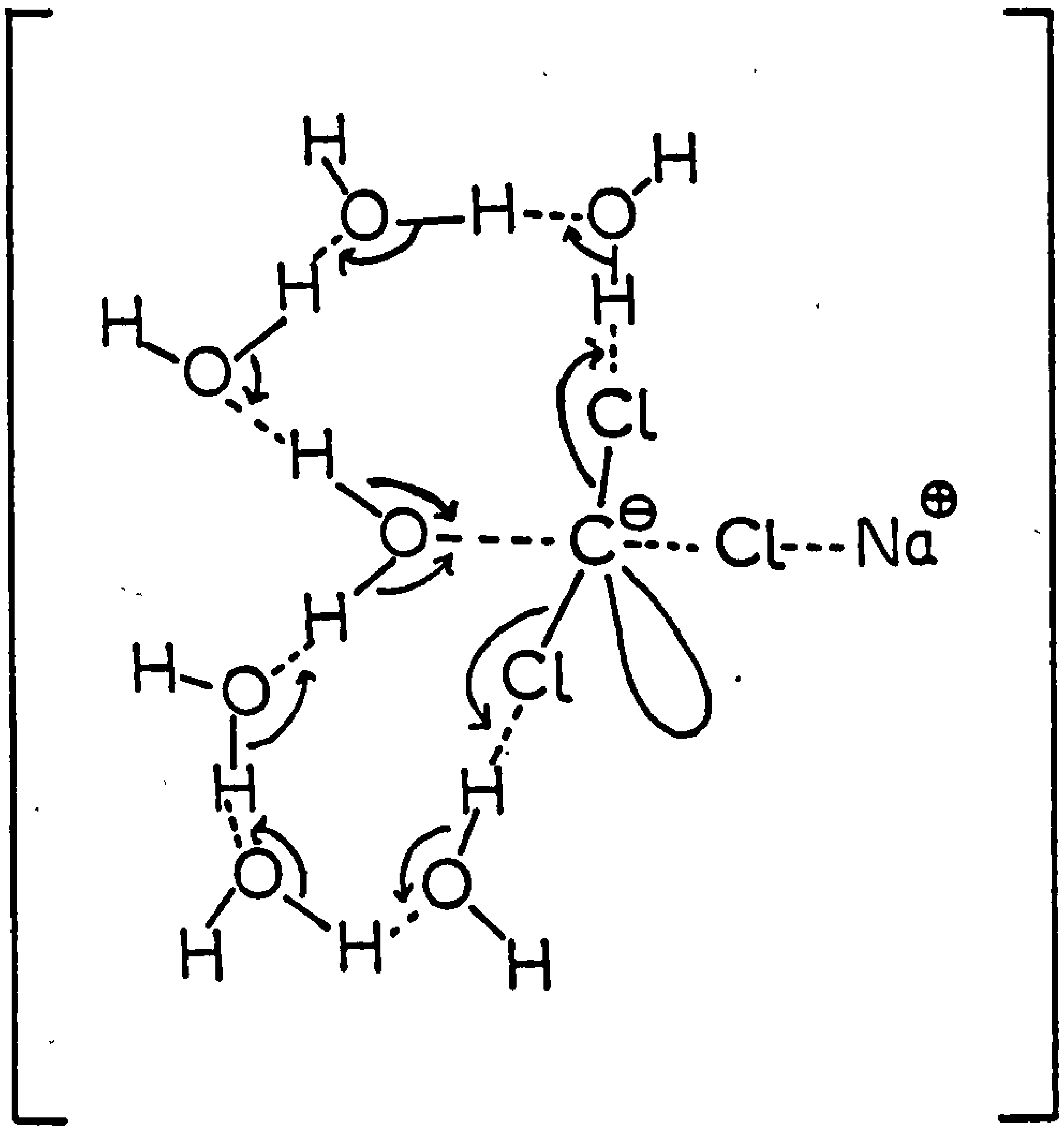
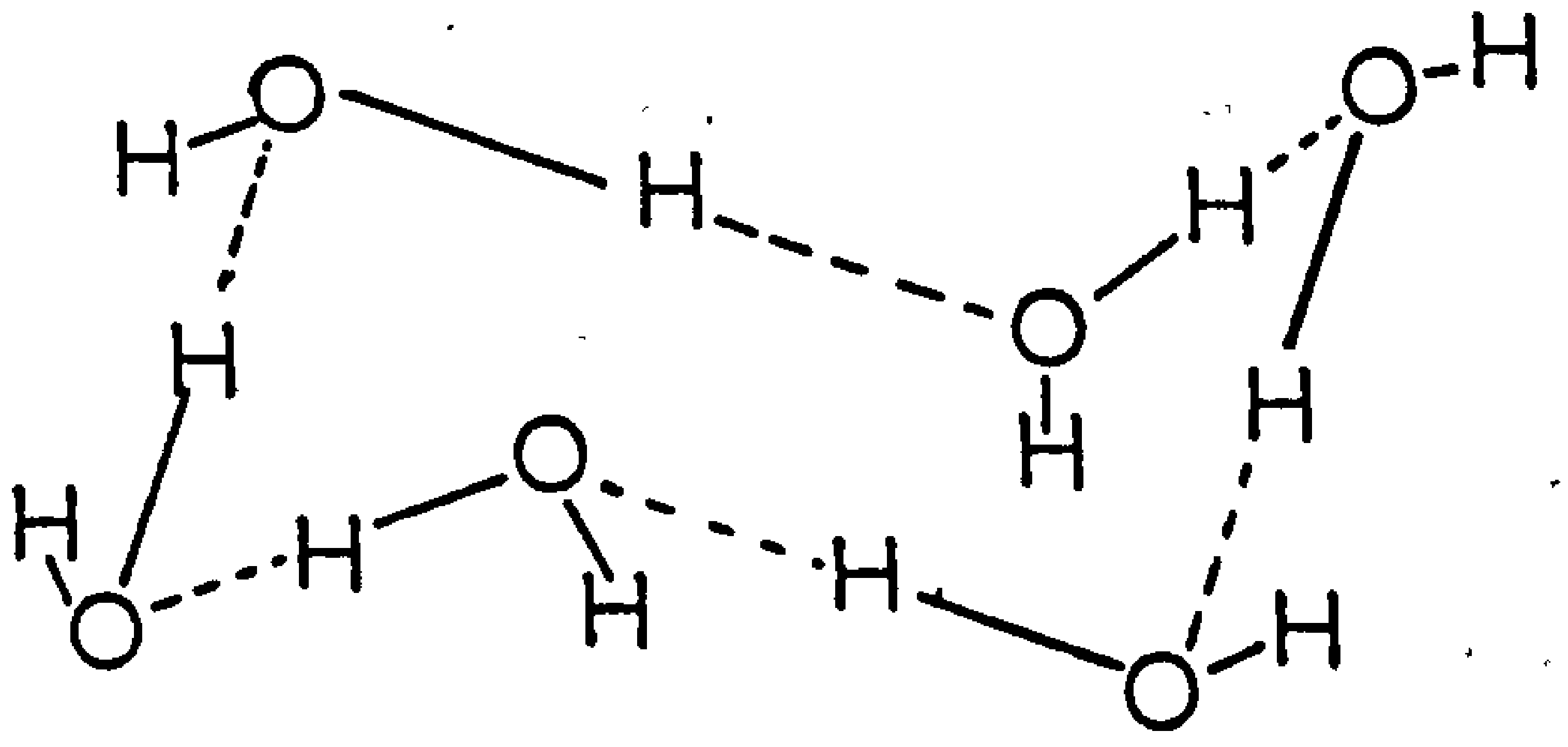


(45)

In all of the structures postulated the chlorine atoms are hydrogen bonded to water molecules, thus enhancing their tendency to pull electrons away from the carbon atom, making it more susceptible to nucleophilic attack. This pull of electronic charge can be transferred through the hydrogen bonded ring system, to the oxygen of the attacking water molecule as shown in (43-5), thereby increasing its nucleophilicity. In structure (45), which includes a bidentate hydrogen-bonded water molecule, this can occur through both rings, and it will therefore be a stronger effect than in either of the other two possible arrangements.

The hydrogen bonded ring structures proposed in (43) and (44) are both ten membered rings, whereas that proposed in (45) is a twelve membered ring. Similar ring systems (46) have been found in ice crystals, so that it does not seem unreasonable to suggest that a structure such as we have proposed (47) could occur in aqueous solutions.



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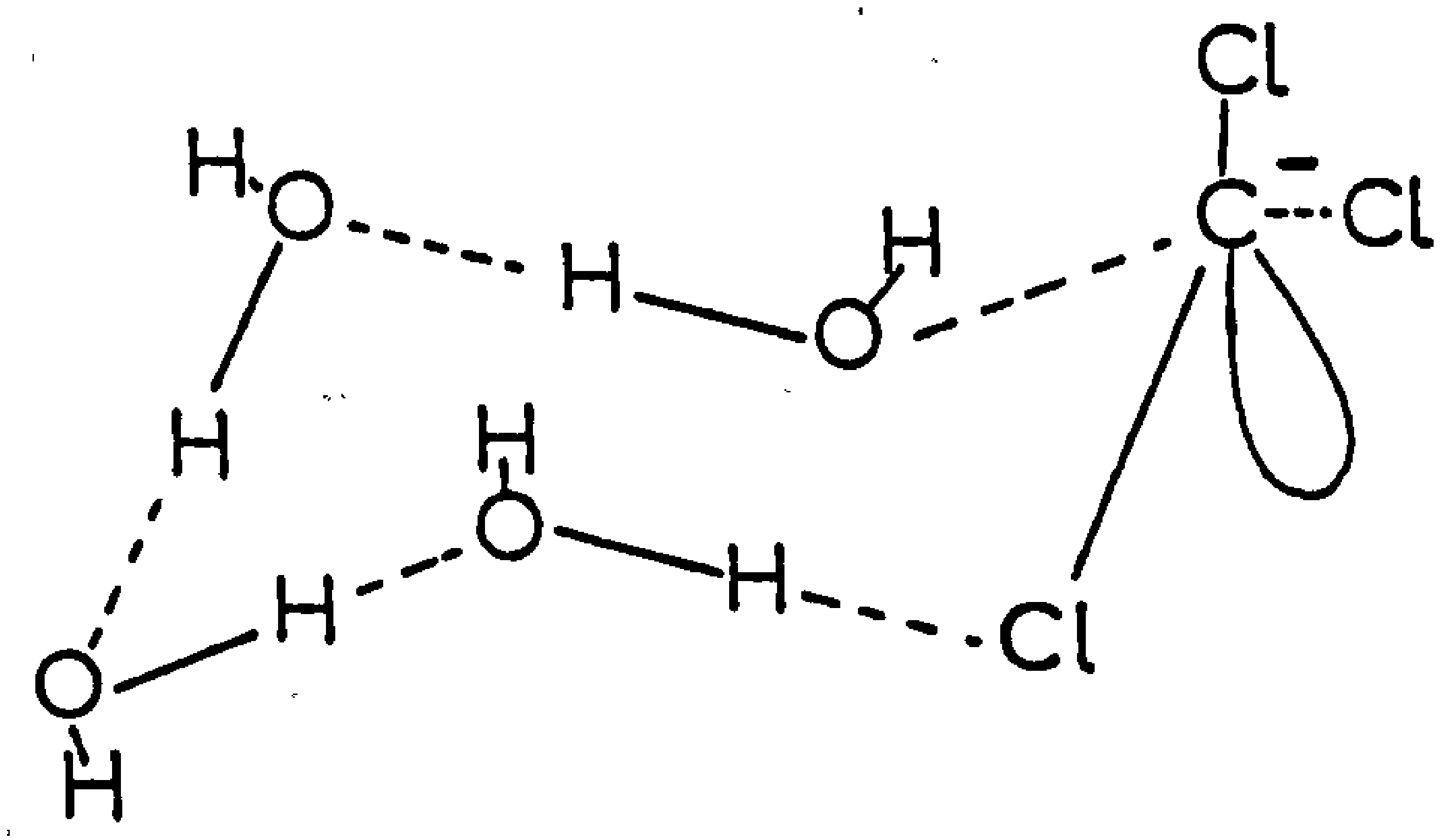
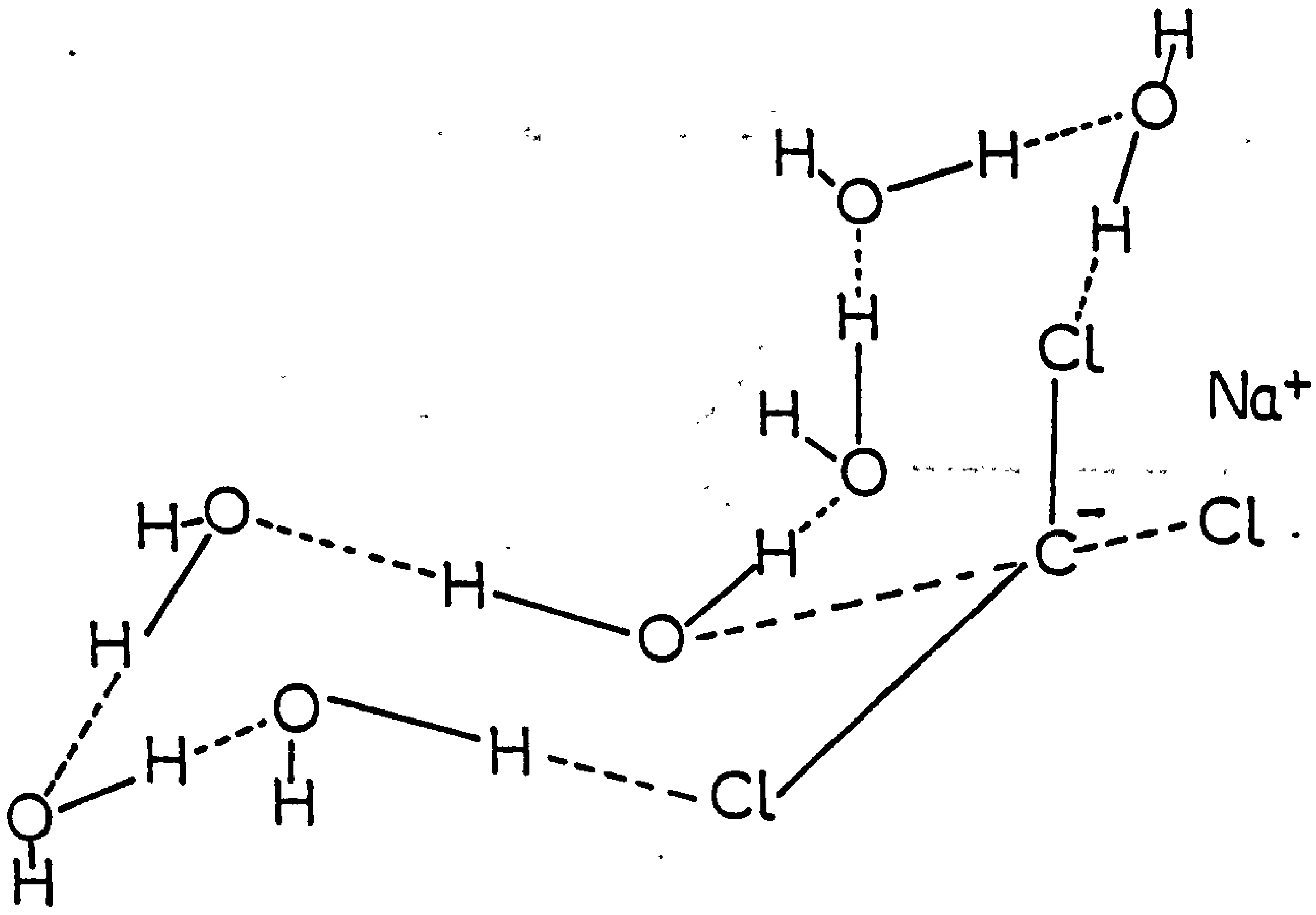


(47)

Structure (48) is analogous to that of *cis*-decalin.

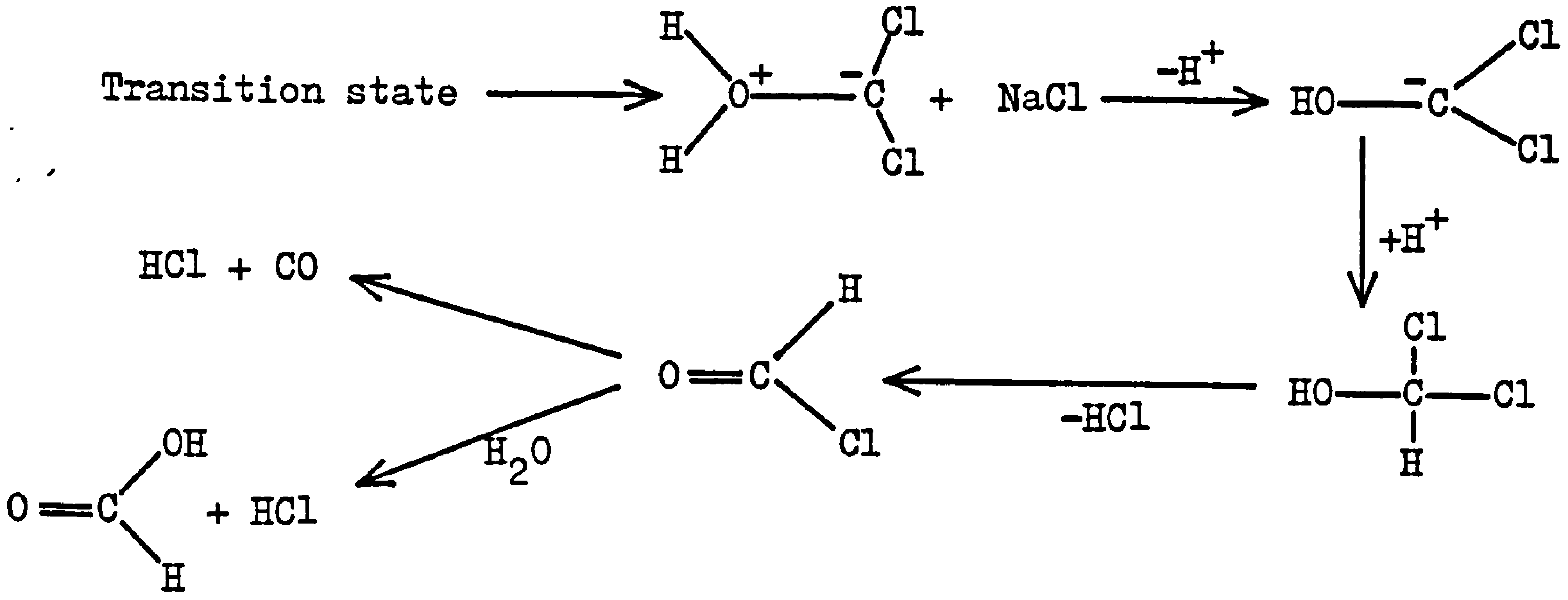


(48)

Attack by a water molecule appears to be more likely than attack by a hydroxide ion, despite the fact that the latter is a stronger nucleophile. Bringing a hydroxide ion close to a trichloromethyl anion would mean overcoming the electrostatic repulsion between the two negatively charged ions. However, halide ions have been shown[106] to react with trichloromethyl ions, so the reaction with hydroxide ions cannot be ruled out on these grounds.

Application of the transition state theory shows that only oppositely charged species can be involved in the transition state, since a negative salt effect is observed. The involvement of a second negatively charged species, that is a hydroxide ion, would predict a positive primary salt effect. This will be discussed in greater detail later on.

The intermediate formed from the postulated transition state, can then break down to give the reported products, according to the observed stoichiometry of the reaction.



Although the transition state involves an incipient dichlorocarbene, it is thought unlikely that free dichlorocarbene is formed. The formation of $H_2\overset{+}{O}—\overset{-}{C}Cl_2$ by a concerted mechanism such as that suggested would involve breaking a carbon-chlorine bond, together with the formation of a carbon-oxygen bond. There would also be favourable electrostatic interaction between the sodium and chloride ions, although this may not be as strong as the sodium chloride bond in the crystal lattice. This process would therefore appear to be energetically more favourable than formation of dichlorocarbene by loss of a chloride ion from a trichloromethyl anion.

9.II.iii. DETERMINATION OF THE ACTIVATION PARAMETERS

Activation parameters were determined for the hydrolysis of chloroform at two different sodium hydroxide concentrations, between 25°C and 41°C. The values obtained are compared with those reported elsewhere in Table 46.

TABLE 46

Comparison of activation parameters for
the hydrolysis of chloroform

Solvent/Base	E_{Act}.(Kcal.mol.$^{-1}$)	ΔH^{*}(Kcal.mol^{-1})	ΔS^{*}(e.u.)	Ref.
32 % dioxane/NaOH	25.0 ± 0.4 *	24.4 ± 0.4 *	+1.4 (0.4 M NaOH) +5.2 (0.8 M NaOH)	This work
67 % dioxane/NaOH	—	26.3 ± 0.8	+10.5 ± 3	95
95 % ethanol/KOH	33.3	32.7	+44	112
Water/KOH	24.3	—	—	110

* Average of two values.

The Arrhenius activation energy had an average value (2 determinations) of 25.0 Kcal.mol.$^{-1}$ in good agreement with the value of Fells and Moelwyn-Hughes[110]. A decrease in activation energy with increasing temperature has been reported[110], but we have not observed this effect. Since dE_{Act}/dT would be small (13.3 cal.deg.$^{-1}$)[110], the values of k_1 used to calculate the energies of activation would have to be determined very accurately, and over a wide range of temperatures.

The change in activation energy with temperature was explained on the basis of the rate determining step being a unimolecular reaction. It was suggested that the number of simple harmonic oscillators contributing to the decrease in activation energy with temperature, is greater for the breakdown of the solvated CCl_3^- ion than it is for chloroform, due to the effect of charge on solvation. However, a temperature effect on the equilibrium constant, may also have been involved[110].

The greatest variation in reported activation parameters, is in the values of entropy (+ 1.4 — + 44 e.u). This is not entirely unexpected since the different values were obtained under different experimental conditions. In the present work, an increase in entropy with increasing sodium hydroxide concentration was observed. It was originally thought that the formation of a highly hydrated transition state would result in a negative entropy of activation. However, since it is known that at low temperatures chloroform forms a hydrate with eighteen molecules of water[230], it is likely that the trichloromethyl anion will be associated with a large number of water molecules. Sodium ions will help to stabilise the anion, and they may also be hydrated, giving rise to a highly ordered system which fits in well with the structure of the medium. In going from the reactants to the transition state it is possible that a less ordered structure will result, and positive values of entropy will be obtained. This difference in entropy will become greater with increasing hydroxide concentration, because of the increase in the number of water molecules which are associated with hydroxide ions, resulting in a more ordered system initially.

9.II.iv. THE EFFECT OF ADDED SALTS

The addition of both potassium nitrate and sodium chloride to the reaction mixture resulted in a decrease in the reaction rate. Sodium chloride had a greater effect than potassium nitrate, as had been reported previously[92,93].

In the reaction mixture, negatively charged trichloromethyl ions will be stabilised by the presence of positively charged sodium ions, so that on increasing the concentration of these counter ions by adding salts to the mixture, the stability of the anion will be increased. The transition state, on the other hand, will not be affected to the same extent, since it more closely resembles a neutral species, as a result of the strong interaction between CCl_3^- and a sodium ion. Increasing the stability of the trichloromethyl anion will decrease the free energy of the system relative to the transition state. This will tend to increase the energy of activation, thereby decreasing the reaction rate. It can easily be shown that an increase of ~ 4 % in the Arrhenius activation energy will decrease the reaction rate by a factor of two. Stabilising CCl_3^- would also be expected to affect the initial equilibrium, but this effect would be very small compared to that on the activation energy.

The variation in rate observed when different salts are added, can be explained on the basis of competition between the trichloromethyl anion, and the anion of the added salt, for the oppositely charged cation. In the presence of sodium fluoride, the highly negatively charged fluoride ion is strongly bound to sodium ions, that is the free energy of the system can be lowered by the close approach of the small ions. Addition of sodium fluoride, therefore, will only increase the stability of the CCl_3^- ion by a small amount.

In the case of the iodide ion the free energy cannot be reduced so effectively, compared to smaller anions, since iodide anions cannot approach a sodium ion so closely. Furthermore, the interaction will be less stabilising, due to the greater spread of charge over the surface of a larger ion. This will result in an increase in the concentration of sodium ions available to stabilise CCl_3^-, giving a bigger increase in the activation energy, and a slower reaction, compared to the case where sodium fluoride is added. On this basis it must be assumed that nitrate and perchlorate ions act similarly to fluoride ions.

Results obtained by Hine and coworkers have shown that under similar experimental conditions, the addition of sodium salts consistently decreases the reaction rate more than potassium salts[92], which is compatible with the idea that counter ions are involved. Hine has in fact suggested that this difference may be due to the lessened tendency of the potassium ion to form ion-pairs with the trichloromethyl anion, thereby increasing the rate of chloride elimination from this anion[93].

Primary salt effects have been accurately predicted from transition state theory[231]. The rate of reaction is given by

$$\text{rate} = \nu[AB^{\ddagger}] \tag{89}$$

where $AB^{\ddagger}$ is the activated complex formed from the reaction between A and B.

$$K^{\ddagger} = \frac{\gamma_{AB^{\ddagger}}[AB^{\ddagger}]}{\gamma_A[A]\gamma_B[B]} \tag{90}$$

Solving eq.(90) for the concentration of $AB^{\ddagger}$, and substituting it into the rate equation, gives the Brønsted relationship;

$$\text{rate} = k[A][B] = \left(\frac{kT}{h}\right) K^{\ddagger} \frac{\gamma_A \gamma_B}{\gamma_{AB^{\ddagger}}} [A][B] \tag{91}$$

$$\therefore k = \left(\frac{kT}{h}\right) K^{\ddagger} \frac{\gamma_A \gamma_B}{\gamma_{AB^{\ddagger}}} \tag{92}$$

$$\therefore \log k = \log\left(\frac{kT}{h}\right) K^{\ddagger} + \log \gamma_A + \log \gamma_B - \log \gamma_{AB^{\ddagger}} \tag{93}$$

For reactions in dilute aqueous solutions, the activity coefficients of ions can be obtained from the Debye-Huckel limiting law,

$$\log \gamma_i = - A Z_i^2 \mu^{\frac{1}{2}} \tag{94}$$

where A is a term containing universal constants, the dielectric of the solvent, and the temperature, Z_i is the charge of the ion, and μ is the ionic strength. Eq.(94) can be introduced into eq.(93), and $Z_A + Z_B$ for $Z_{AB^{\ddagger}}$, since the charge of the transition state must equal the sum of the charges of the reactants.

$$\log k = \log\left(\frac{kT}{h}\right) K^{\ddagger} - A\mu^{\frac{1}{2}} [Z_A^2 + Z_B^2 - (Z_A + Z_B)^2] \tag{95}$$

which reduces to

$$\log k = \log\left(\frac{kT}{h}\right) K^{\ddagger} + 2AZ_A Z_B \mu^{\frac{1}{2}} \tag{96}$$

The first term on the right-hand side of this equation is the log of the rate constant k_o in the standard state, thus

$$\log \frac{k}{k_o} = 2AZ_AZ_B\mu^{\frac{1}{2}} \tag{97}$$

This is the Brønsted-Debye limiting rate equation which predicts that a plot of log k against the square root of the ionic strength, should be a straight line of slope $2AZ_AZ_B$. For water solutions at 25°C, $A = 0.509$, and the slope is Z_AZ_B. This equation has been shown to hold for many reactions[231]

This fits the Hughes-Ingold qualitative theory concerning medium polarity and reaction rates. Since the addition of an ionic substance increases the polarity of a reaction medium, a large positive salt effect would be predicted for a reaction between two similarly charged ions, and a large negative salt effect when the reacting ions are oppositely charged.

According to the mechanism proposed by Hine, the transition state is intermediate between a trichlorcmethyl anion and dichlorocarbene.

$$CCl_3^- \longrightarrow [CCl_3^{\ddagger}]^- \longrightarrow :CCl_2 + Cl^-$$

From eq.(91),

$$\text{Rate} = k[CCl_3^-] = \left(\frac{kT}{h}\right) K^{\ddagger} \frac{\gamma_{CCl_3^-}}{\gamma_{CCl_3^{-\ddagger}}} [CCl_3^-] \tag{98}$$

$$\therefore k = \left(\frac{kT}{h}\right) K^{\ddagger} \frac{\gamma_{CCl_3^-}}{\gamma_{CCl_3^{-\ddagger}}} \tag{99}$$

and, $$\log k = \log\left(\frac{kT}{h}\right) K^{\ddagger} + \log \gamma_{CCl_3^-} - \log \gamma_{CCl_3^{-\ddagger}} \qquad (100)$$

Substituting eq.(95)

$$\log k = \log\left(\frac{kT}{h}\right) K^{\ddagger} - A\mu^{\frac{1}{2}} [z_{CCl_3^-}^{2} - z_{CCl_3^-}^{2}] \qquad (101)$$

$$\log k = \log k_o - 0 \qquad (102)$$

Clearly, according to Hine's mechanism, no primary salt effect should be observed, although he has explained the retardation observed when fluoride, nitrate and perchlorate ions are added to the reaction, on the basis of a primary salt effect.

It may be argued, that a small negative salt effect could result from dispersion of the negative charge during the formation of the transition state. Since the negative charge will probably be delocalised over the CCl_3^- ion, by the electron withdrawing properties of the chlorine atoms, it is unlikely to be any more dispersed in the transition state. Thus even if this effect were apparent it would be small.

According to the mechanism we have postulated, a trichloromethyl anion and a sodium ion are involved in the formation of the transition state, predicting a definite negative salt effect. If hydroxide ions were attacking CCl_3^-, instead of water, the product of the ionic charges would be positive, predicting a positive salt effect.

A secondary salt effect is unlikely to be seen in the pre-equilibrium, since both sides of the equation involve a neutral molecule and a single negative charge.

$$CHCl_3 + OH^- \rightleftharpoons CCl_3^- + H_2O$$

Hine's evidence for the formation of dichlorocarbene, depends to a large extent on the effects of added salts[92,93]. He claimed the observed decrease in the reaction rate as being due to recombination of dichlorocarbene with halide ions, to reform trichloromethyl anions, and the increasing effect of different anions, $Cl^- < Br^- < I^-$, as being due to their increasing nucleophilicities. If this were the case, one would expect to see such a trend in reaction rate from the point of view of product formation or decrease in hydroxide concentration, but, if the reaction were studied by following the rate of loss of chloroform, this would not be the case. Recombination of bromide and iodide ions with $:CCl_2$ would not give trichloromethyl anions, so that the rate of formation of dichlorocarbene should not be affected, since Hine has reported that it is independent of the nature of ions present[92]. Accordingly, the rate of loss of chloroform should not be affected to any greater extent than it is by nitrate, perchlorate or fluoride ions.

$$OH^- + CHCl_3 \rightleftharpoons H_2O + CCl_3^- \rightleftharpoons :CCl_2 + Cl^-$$

$$OH^- + CHCl_3 \rightleftharpoons H_2O + CCl_3^- \rightleftharpoons :CCl_2 + Cl^- \xrightarrow{X^-} CXCl_2^-$$

Unfortunately, there was insufficient time to investigate the effects of bromide and iodide ions on the reaction, when the rate of chloroform loss is followed directly, but it is hoped that this will be carried out in the near future.

The isolation of mixed haloforms from the reaction of chloroform and alkali in the presence of other halide ions, has been quoted by several authors as evidence for the formation of dichlorocarbene[93,108,109]. However, Horiuti and coworkers have observed the chlorine exchange between chloroform and aqueous chloride solutions, and have deduced that the mechanism involves exchange of a chloride ion with a chlorine atom in the trichloromethyl anion[106].

$$Cl^{*-} + CCl_3^- \rightleftharpoons CCl^*Cl_2^- + Cl^- \quad (Cl^* \text{- chlorine from solution})$$

Bromide and iodide ions could similarly exchange, thus explaining the formation of mixed haloforms without the need to invoke dichlorocarbene. The exchange would obviously be base catalysed, since a base is required for the formation of the trichloromethyl anions.

The formation of mixed trihalomethyl anions when halide ions are added to the hydrolysis reaction will result in a gradual increase in the observed rate constant. Bromide and iodide ions are better leaving groups than chlorine, so that as the concentration of $CBrCl_2^-$ and $CICl_2^-$ builds up, its effect on the rate constant will gradually become apparent, as observed by Hine[93].

The effects of added thiophenolate ions have also been used by Hine to support his dichlorocarbene mechanism[92]. However, an alternative mechanism, based on the interaction of sodium thiophenolate as opposed to thiophenolate anions, with trichloromethyl anions, also explains the observed results.

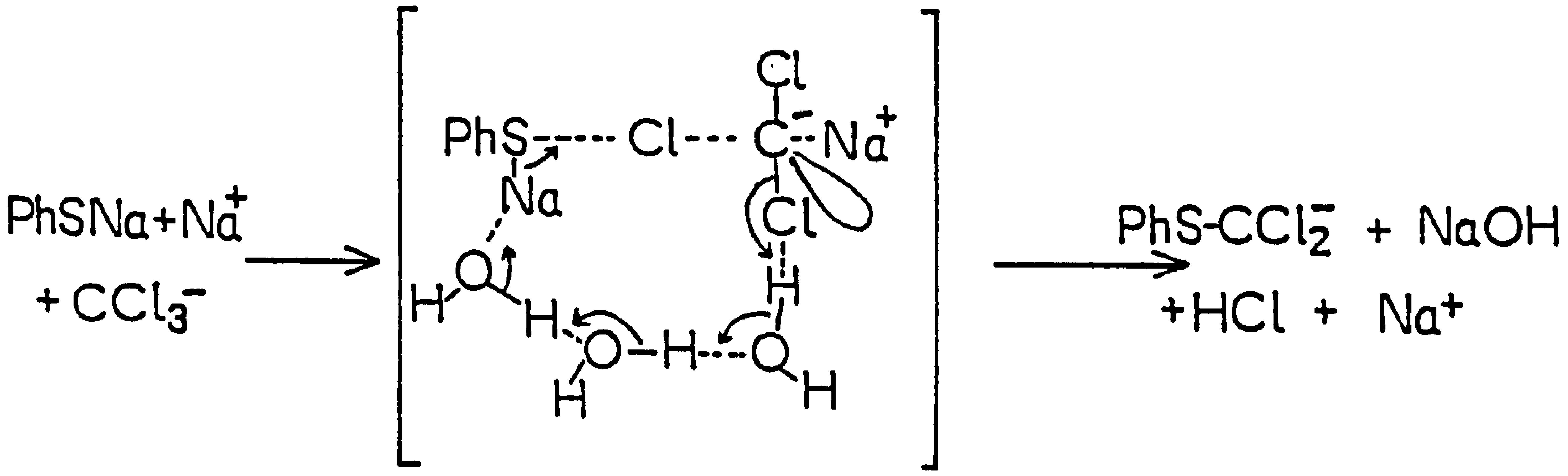
In an aqueous solution sodium thiophenolate will tend to dissociate into ions, eq.(103),

$$\mathrm{PhSNa} \rightleftharpoons \mathrm{PhS^-} + \mathrm{Na^+} \tag{103}$$

it will also be hydrolysed;

$$\mathrm{PhSNa} + \mathrm{H_2O} \rightleftharpoons \mathrm{PhSH} + \mathrm{NaOH} \tag{104}$$

The concentration of sodium thiophenolate in aqueous solution will therefore be low, and little reaction will occur. On addition of sodium hydroxide both equilibria (103) and (104) will be pushed over towards the left-hand side, which will tend to increase the concentration of sodium thiophenolate and the rate of reaction, thus explaining why the reaction is base catalysed. An analogous reaction to that observed with water can be postulated.



(49)

Since the reaction involves an undissociated ion pair, a negative trichloromethyl anion and a positive sodium ion it would be expected to show a negative salt effect. The reaction between CCl_3^-, water and a sodium ion would show a similar salt effect, explaining why the ratio of the rate of reaction with thiophenolate, to the rate of reaction with water (k_t/k_w), was found to be independent of ionic strength[92]. Hine's argument against a reaction between thiophenolate and trichloromethyl anions did not take into account any involvement of the sodium ions.

$$CCl_3^- + C_6H_5S^- \xrightarrow{k_t} C_6H_5SCCl_2^- + Cl^-$$

$$CCl_3^- + H_2O \xrightarrow{k_w} H_2\overset{+}{O}\text{—}\overset{-}{C}Cl_2 + Cl^-$$

Thus, he predicted that since the reaction between thiophenolate and trichloromethyl anions involves two negatively charged species it should show a larger positive salt effect than that between a trichloromethyl anion and a neutral water molecule. The ratio k_t/k_w would decrease with decreasing ionic strength[92]. However, this would not be the case if sodium ions were also involved.

LeNoble's determination of the volume of activation, showed that there was an increase in volume associated with the formation of the transition state[114,115]. This can be equally well explained by the formation of the transition state we have postulated, as by the formation of dichlorocarbene. The entropy of activation has shown that there is an increase in disorder during the formation of the transition state, suggesting that the trichloromethyl anion and sodium ion are part of a highly ordered system, which probably fits well into the structure of the medium. The formation of a bulky transition state with its hydrogen bonded rings such as has been suggested could therefore result in an increase in volume as well as an increase in entropy.

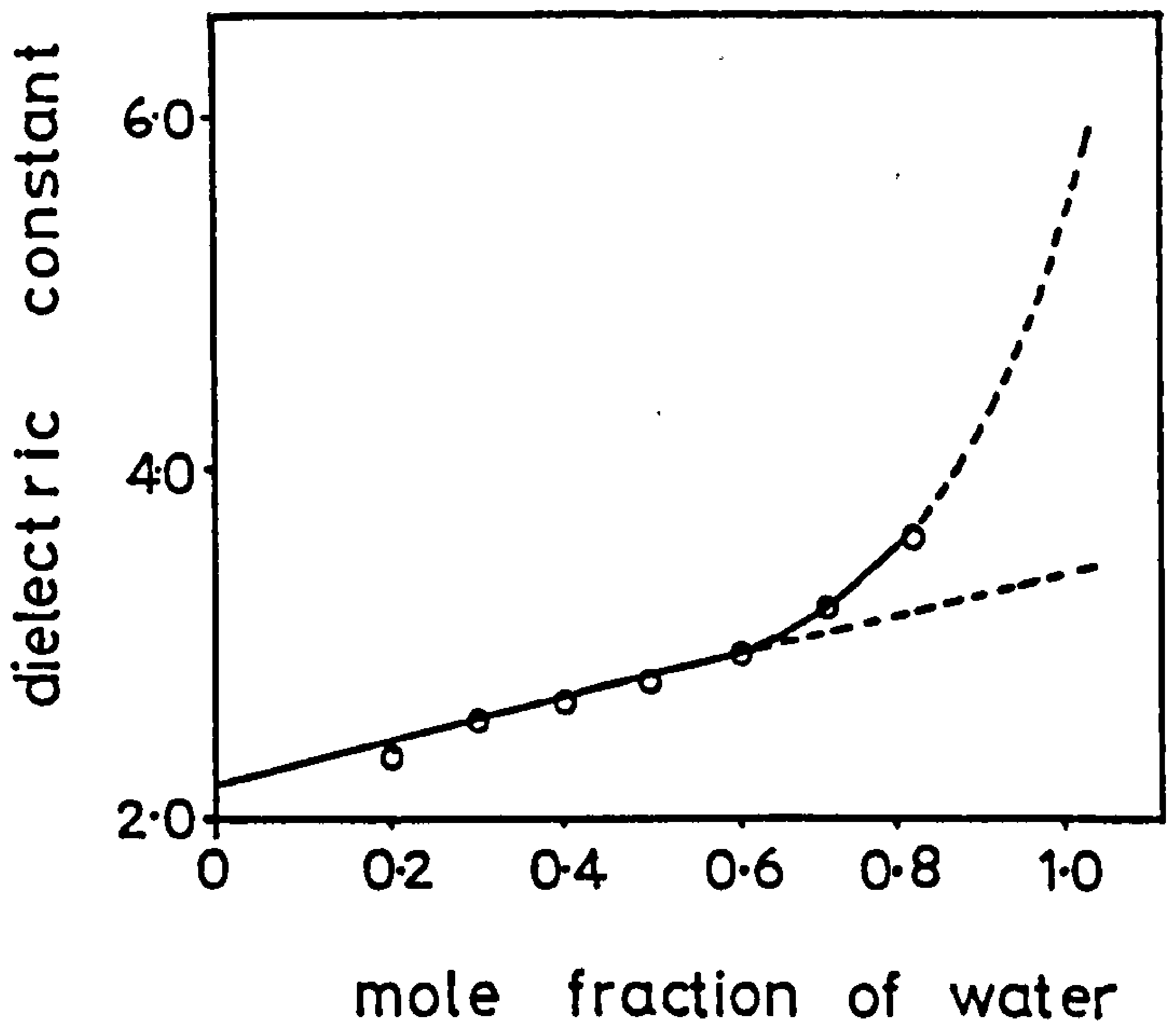
9.II.v. THE EFFECT OF CHANGING THE DIOXANE CONCENTRATION

The rate of reaction was decreased by increasing the concentration of dioxane in the reaction mixture from 32 % (3.79 M) to 35 % (4.12 M). This decrease varied from 9 % at 1.00 M sodium hydroxide to 14 % at 1.50 M sodium hydroxide. Increasing the concentration of dioxane in the solvent has two effects; it reduces the dielectric constant, and it reduces the concentration of unbound water, since each dioxane molecule associates with two water molecules. Both of these effects will tend to decrease the reaction rate, as was observed. This effect will be greater at higher concentrations of alkali, since hydroxide ions are hydrated by three water molecules, so that the concentration of free water will be lower to start with, and any further reduction will have a relatively greater effect.

Hine's results show that at 67 % dioxane, where the dielectric constant is considerably lower than at 32 % dioxane, the rate constant is reduced by approximately 51 %. Hine reported that under the experimental conditions he has used, the rate of the reaction was independent of solvent composition[95]. This may be explained by the change in dielectric with the change in mole fraction of water (Fig.43).

FIGURE 43

Plot of dielectric constant against mole fraction of water (10 - 55°C)[232]



Under the conditions Hine has used (67 % dioxane, ~ 0.7 mol. fraction of water), a small change in the dioxane concentration would have little effect on the dielectric of the solvent. At 32 % dioxane (~ 0.9 mol. fraction of water) any change in the solvent composition will result in a much bigger change in the dielectric which will be reflected in the reaction rate.

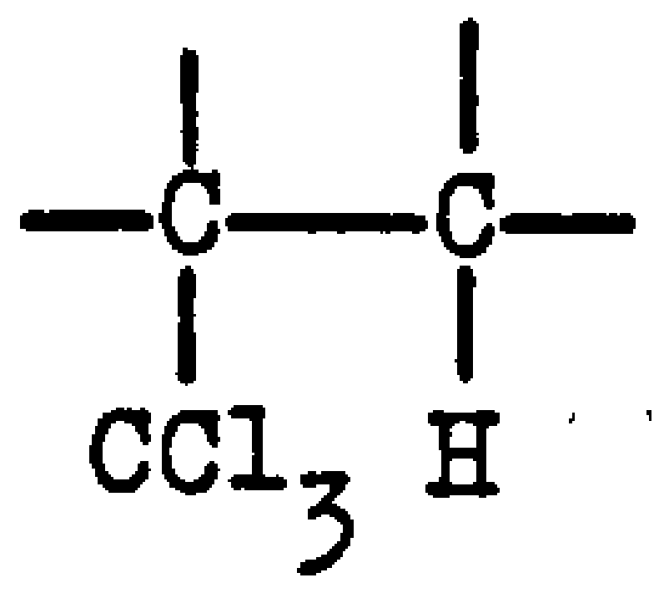
9.II.vi. THE REACTION OF DEUTEROCHLOROFORM WITH SODIUM DEUTEROXIDE

The reaction of deuterochloroform with sodium deuteroxide in deuterium oxide was 24 % faster than the equivalent reaction in the proton system. However, it is not possible to gain any definite information from this result. A possible explanation is that the pull of electrons away from the carbon atom of the trichloromethyl anion, is greater in the case of deuterium oxide, than it is with ordinary water. This might make the carbon atom more susceptible to nucleophilic attack in the deuterium system.

9.III. REACTIONS OF CHLOROFORM WITH A BASE IN THE PRESENCE OF SUBSTRATES

Any alternate mechanism proposed for the hydrolysis of chloroform, should also explain the reactions which occur in the presence of a substrate. The formation of dichlorocyclopropane derivatives has hitherto been explained by the addition of dichlorocarbene across a double bond, via a three-centre transition state, thus accounting for the stereospecificity of the reaction.

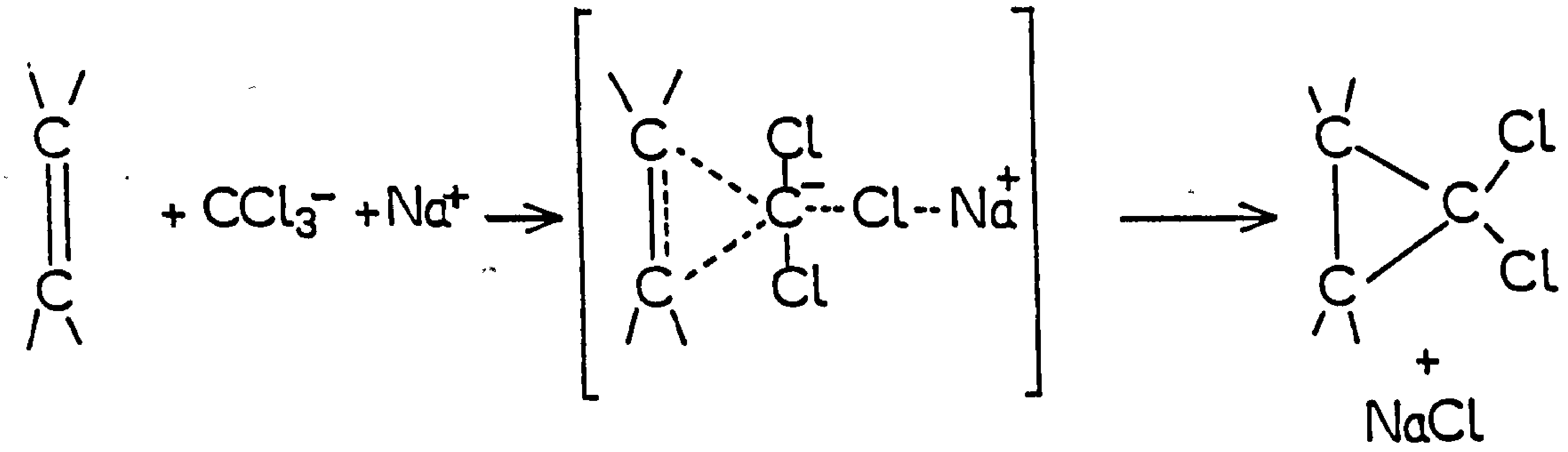
The formation of these compounds by addition of trichloromethyl anions was rejected, on the grounds that it had never been possible to isolate the saturated trichloromethyl derivative (25), formed by addition of CCl_3^- to one of the carbon atoms. However, this is possible in some reactions of carbonyl compounds with chloroform[119-121] and chloroform derivatives[122].



$$\begin{array}{cc} | & | \\ -C- & -C- \\ | & | \\ CCl_3 & H \end{array}$$

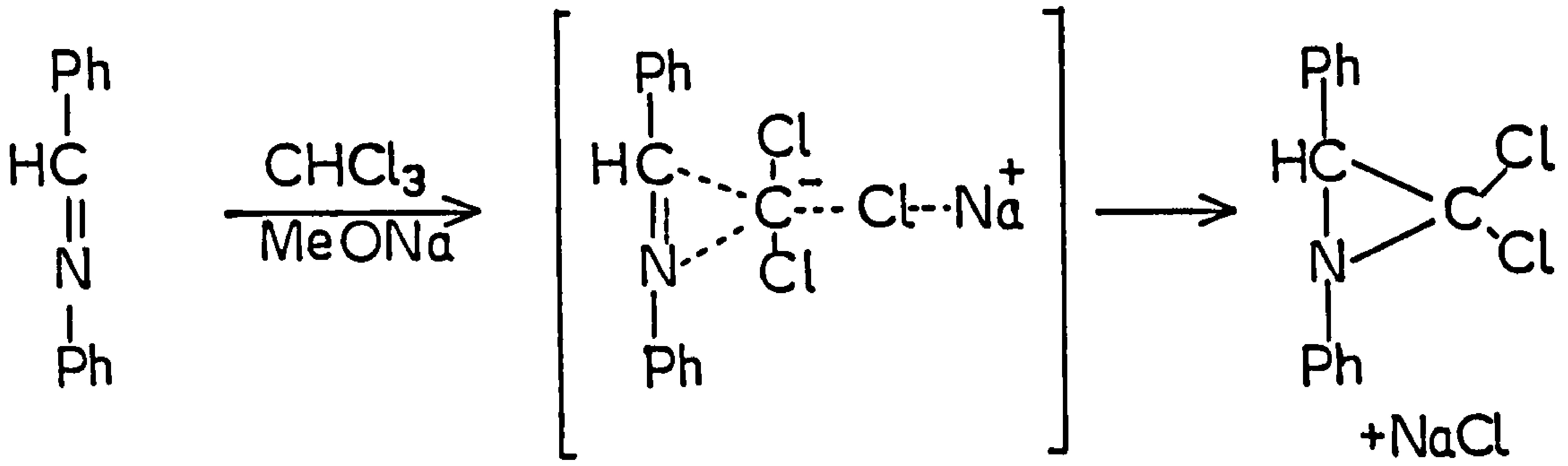
(25)

If, on the other hand, the anion added across the double bond to form a three centre transition state similar to that proposed in the addition of dichlorocarbene, this would account for the fact that (25) is not observed, and also explain the stereospecificity of the reaction.

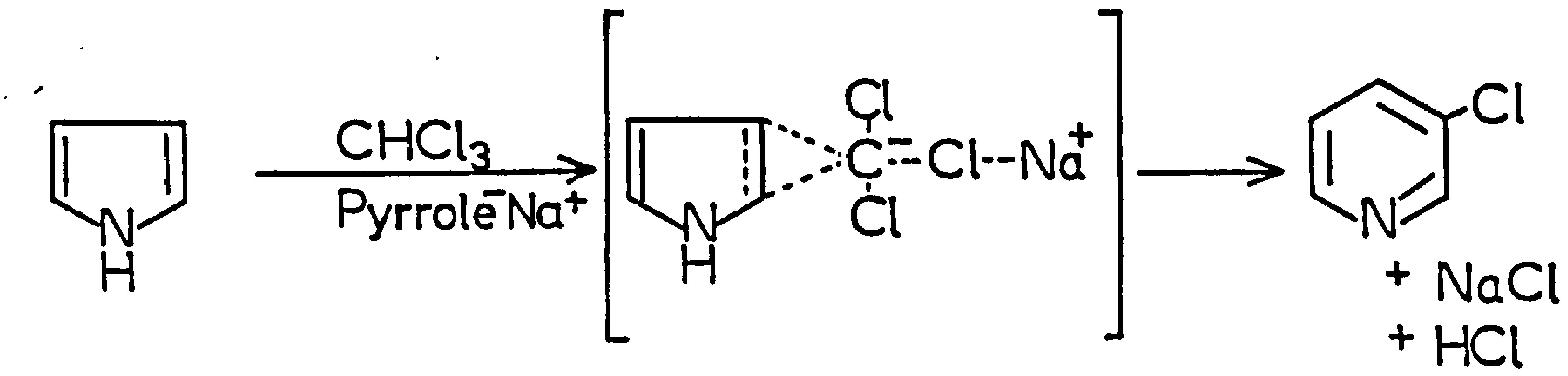


(50)

Similarly, in the addition to carbon-nitrogen double bonds,



and, in the ring expansion of heterocyclic compounds.

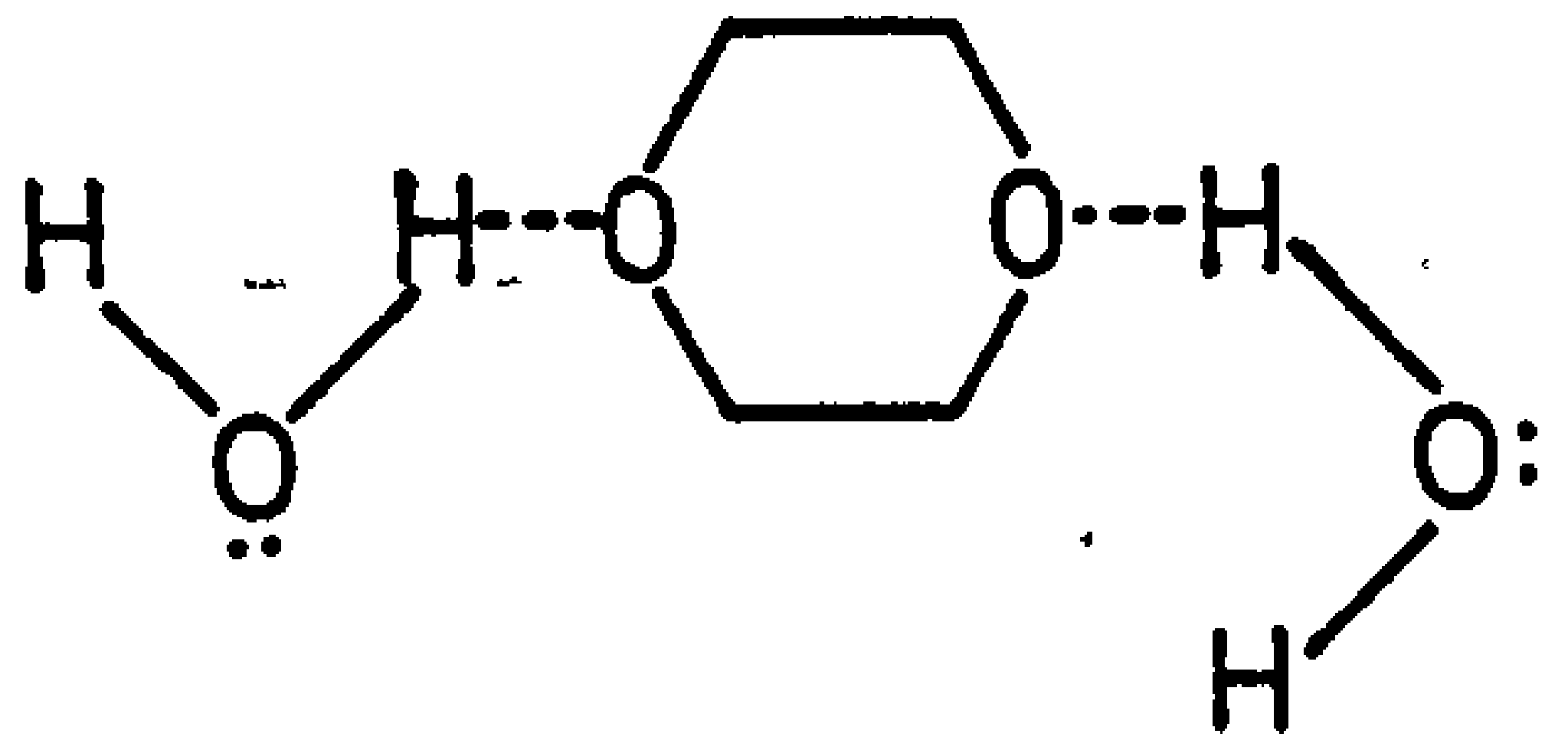


Many of these reactions have been carried out under anhydrous conditions. Since water plays an important role in the reaction in aqueous solution, it might be expected that other solvents employed, such as alcohols would act in a similar way in the absence of water. Alcohols may be able to form hydrogen bonds analogous to those formed between water molecules.

9.IV. DETERMINATION OF THE HYDRATION NUMBER OF DIOXANE

1,4-Dioxane was found to have an average hydration number of 2.25. This does not imply that each dioxane molecule is associated with a non-integral number of water molecules, simply that this is an average value for dioxane molecules in a 32 % aqueous solution. Results obtained in DMSO-water mixtures have also been shown to have non integral values, which gradually increased from 0.78 (81.4 % DMSO w/w), to 2.32 (38.3 % DMSO), remaining almost constant in more dilute solutions[188].

Other authors have also suggested that dioxane is associated with two water molecules[233,234] and they proposed the following type of interaction[233], (51).



(51)

The basicity of dilute sodium hydroxide solution was found to be considerably higher in an aqueous dioxane solution, compared to pure water. This is readily understood on the basis that dioxane molecules can compete with the hydroxide ions for free water, thereby decreasing the number of water molecules available for the hydroxide ions, and increasing their basicity.

Absolute values of H_- were not determined since this would have involved determining values of pK_a and H_- for a number of overlapping indicators, and there was not sufficient time available to do so. However, in anchoring H_- to the pH region, people have determined the pK_a of their most acid indicator in water, and then assumed that it is the same in their water-solvent mixture. We felt justified therefore, in making the same assumption for 6-bromo-2,4-dinitroaniline. Values of pK_a have been determined for this compound in a number of different solvents and these are in good agreement, as shown in Table 47.

TABLE 47

Comparison of pK_a's determined for
6-bromo-2,4-dinitroaniline in different solvents

Solvent	pK_a	Ref
Pyridine/water	13.66	180
Sulpholane/water	13.60	180
Sulpholane/water	13.71	182

Since the values above were determined at 25°C as opposed to 36°C, and pK_a is known to change with temperature, we have not used them. Instead, it was assumed that the value of pK_a was the same in 32 % dioxane as in pure water, and that any variation in basicity was due solely to a change in the ionisation ratio, r.

9.V. CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The hydrolysis of chloroform by a solution of sodium hydroxide in 32 % (w/v) dioxane has been studied and the reaction was found to be first order with respect to each of the two reactants. Activation parameters were determined in the temperature range 25-41°C, and these have been summarized in Table 35.

Application of the Yagil approach showed that the transition state was associated with seven water molecules, which is thought to make the formation of dichlorocarbene as a discrete entity unlikely. We have therefore suggested an alternative mechanism involving an intermediate formed by nucleophilic attack of water on a trichloromethyl anion which is closely associated with a cation (Na^+). This is also thought to be more likely from a thermodynamic point of view. The formation of dichlorocarbene from CCl_3^- by loss of a chloride ion would be expected to involve an activation energy considerably higher than that determined (25.0 Kcal.mol.$^{-1}$), and it is difficult to explain how this energy would be provided.

A definite negative salt effect was observed, which is compatible with a transition state formed from two oppositely charged species. This can only be explained on the basis of both a trichloromethyl ion and a sodium ion being involved.

The reaction between deuterochloroform and sodium deuteroxide in deuterium oxide and dioxane was found to be 24 % faster than the corresponding reaction in the proton system. This has been explained on the basis of stronger interaction between CCl_3^- ion and the water molecules in the transition state.

Further work must be done to investigate the salt effect in greater detail. By measuring the rate of the reaction at different concentrations of added salts, it would be possible to determine the number of charges involved in the formation of the transition state. Also, the relative effects of the different halide ions must be accurately determined since this would give strong evidence either for or against the formation of dichlorocarbene as suggested by Hine[92-99].

If, as we have suggested, the sodium ion is intimately involved in the formation of the transition state, changing this cation should also effect the rate of reaction, and this could easily be tested.

Although the dichlorocarbene mechanism suggested by Hine[92-99], has largely been accepted as correct, we do not feel that it is the only possible explanation for the observed reaction. Hine has considered the possibility of nucleophilic attack by water on a trichloromethyl anion, and although he favoured the formation of $:CCl_2$, he has been unable to rule the former out. We feel that this mechanism is a better explanation than the formation of dichlorocarbene.

PART FOUR

APPENDIX

APPENDIX ONE

NUMERICAL DETERMINATION OF THIRD ORDER RATE EQUATION FOR PLUG FLOW CONDITIONS.

For irreversible reactions of order n.

$$\tau = \frac{1}{kC_{A0}^{\,n-1}} \int_0^{X_A} \frac{(1-\varepsilon_A X_A)^n}{(1-X_A)^n}\, dX_A \qquad (50)$$

Hence, for an irreversible third order reaction,

$$\tau = \frac{1}{kC_{A0}^{\,2}} \int_0^{X_A} \frac{(1+\varepsilon_A X_A)^3}{(1-X_A)^3}\, dX_A \qquad (103)$$

Expanding $(1+\varepsilon_A X_A)^3$, this becomes

$$\tau = \frac{1}{kC_{A0}^{\,2}} \int_0^{X_A} \left\{ \frac{1}{(1-X_A)^3} + \frac{3\varepsilon_A X_A}{(1-X_A)^3} + \frac{3\varepsilon_A^{\,2} X_A^{\,2}}{(1-X_A)^3} + \frac{\varepsilon_A^{\,3} X_A^{\,3}}{(1-X_A)^3} \right\} dX_A \qquad (104)$$

Since terms in $\varepsilon_A^{\,3} X_A^{\,3}$ are very small these may be neglected.

$$\int_0^{X_A} \frac{dX_A}{(1-X_A)^3} = \left[\frac{1}{2(1-X_A)^2} \right]_0^{X_A} \qquad (105)$$

$$= \frac{1}{2(1-X_A)^2} - \frac{1}{2} \qquad (106)$$

$$\int_0^{X_A} \frac{3\varepsilon_A X_A}{(1-X_A)^3}\, dX_A = 3\varepsilon_A \left[-\frac{1}{(1-X_A)} + \frac{1}{2(1-X_A)^2} \right]_0^{X_A} \tag{107}$$

$$= 3\varepsilon_A \left\{ \frac{1}{2(1-X_A)^2} - \frac{1}{(1-X_A)} + \frac{1}{2} \right\} \tag{108}$$

$$\int_0^{X_A} \frac{3\varepsilon_A^{\,2} X_A^{\,2}}{(1-X_A)^3}\, dX_A = -3\varepsilon_A^{\,2} \left[\ln(1-X_A) + \frac{2}{(1-X_A)} - \frac{1}{2(1-X_A)^2} \right]_0^{X_A} \tag{109}$$

$$= -3\varepsilon_A^{\,2} \left\{ \ln(1-X_A) + \frac{2}{(1-X_A)} - \frac{1}{2(1-X_A)^2} - \ln 1 - \frac{3}{2} \right\} \tag{110}$$

Substituting eq.(106),(108) and (110) into (104),

$$\tau = \frac{1}{kC_{A0}^{\,2}} \left\{ \left(\frac{1}{2(1-X_A)^2} - \frac{1}{2} \right) + 3\varepsilon_A \left(\frac{1}{2(1-X_A)^2} - \frac{1}{(1-X_A)} + \frac{1}{2} \right) - 3\varepsilon_A^{\,2} \left(\ln(1-X_A) + \frac{2}{(1-X_A)} - \frac{1}{2(1-X_A)^2} - \frac{3}{2} \right) \right\} \tag{111}$$

which, on rearrangement gives,

$$\tau = \frac{1}{kC_{A0}^{\,2}} \left\{ \frac{(1+3\varepsilon_A + 3\varepsilon_A^{\,2})}{2(1-X_A)^2} - \frac{(3\varepsilon_A + 6\varepsilon_A^{\,2})}{(1-X_A)} - 3\varepsilon_A^{\,2} \ln(1-X_A) - \frac{1}{2}(1 - 3\varepsilon_A - 9\varepsilon_A^{\,2}) \right\} \tag{112}$$

TABLE 48

Numerical determination of third order rate plot for non-carbonised tube

Run No.	τ (sec.)	$\left[\frac{1}{C_{A0}^{2}}\left\{\frac{(1+3\varepsilon_A+3\varepsilon_A^{2})}{2(1-X_A)^{2}} - \frac{(3\varepsilon_A+6\varepsilon_A^{2})}{(1-X_A)} - 3\varepsilon_A^{2}\ln(1-X_A) - \frac{1}{2}(1-3\varepsilon_A-9\varepsilon_A^{2})\right\}\right] \times 10^{-3}$
1	3.01	0.17
2	3.19	0.20
3	5.49	2.77
4	4.52	0.72
5	4.86	1.25
6	4.06	0.70
7	4.29	0.78
8	3.82	0.57
9	4.60	1.13
10	5.58	1.74
11	7.17	17.32
12	3.57	0.39
13	7.21	8.61

(Cont'd.....)

TABLE 48 (Cont'd)

Run No.	τ (sec.)	$\left[\frac{1}{C_{A0}^2}\left\{\frac{(1+3\varepsilon_A+3\varepsilon_A^2)}{2(1-X_A)^2} - \frac{(3\varepsilon_A+6\varepsilon_A^2)}{(1-X_A)} - 3\varepsilon_A^2 \ln(1-X_A) - \frac{1}{2}(1-3\varepsilon_A-9\varepsilon_A^2)\right\}\right] \times 10^{-3}$
14	7.67	6.47
15	8.05	89.90
16	6.69	7.40
17	6.18	3.73
18	6.35	2.31
19	6.70	6.82
20	7.33	16.80
21	7.66	29.32
22	7.93	45.51
C.T.8	3.96	0.50
C.T.12	4.92	1.59
C.T.16	4.77	1.33
C.T.23	4.97	1.29

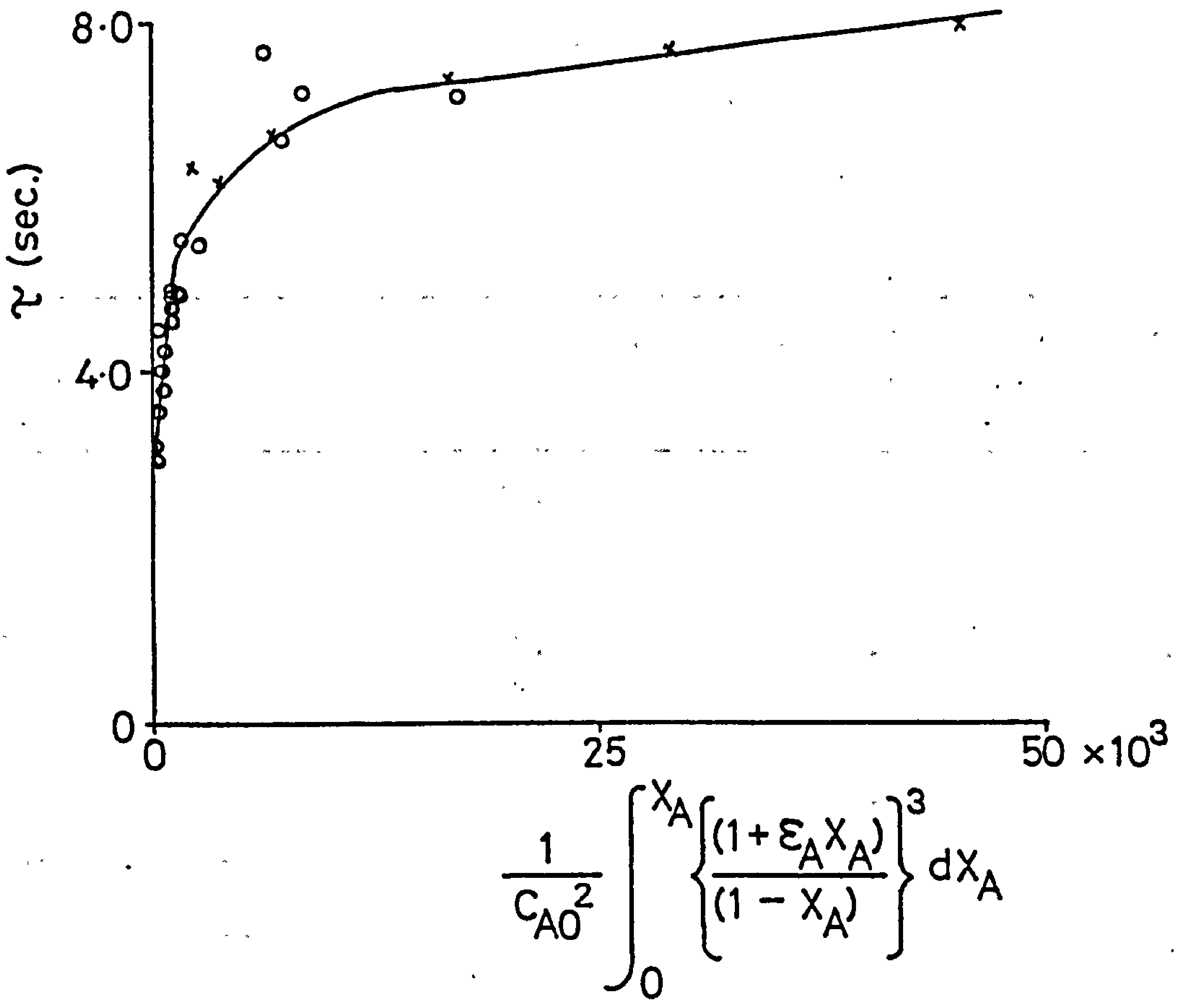


Fig. 44 Third order rate plot — integral determined numerically

APPENDIX TWO

RESULTS FROM THE HYDROLYSIS OF CHLOROFORM

RUN 67

Initial concentration $CHCl_3$: 0.0115 mol. $l.^{-1}$

Initial concentration NaOH : 0.5057 mol. $l.^{-1}$

Temperature : 36 ± 0.1°C

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
90	425198	11.26	11.26	1.9485
960	354485	9.38	9.38	2.0278
1950	293528	7.76	7.76	2.1101
2880	241762	6.39	6.39	2.1945
3810	207772	5.50	5.50	2.2596
4950	159379	4.21	4.21	2.3757
5940	137366	3.60	3.60	2.4437
7170	110718	2.92	2.92	2.5346
8160	93584	2.48	2.48	2.6055
9450	68687	1.81	1.81	2.7423
11760	46470	1.22	1.22	2.9136
13290	35934	0.94	0.94	3.0269
14520	23865	0.62	0.62	3.2076
15840	22460	0.58	0.58	3.2366
16740	17286	0.46	0.46	3.3372

RUN 68

Initial concentration $CHCl_3$: 0.0109 mol.l.$^{-1}$

Initial concentration NaOH : 1.4950 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
90	398871	10.57	10.57	1.9759
270	379329	10.03	10.03	1.9988
1020	293800	7.76	7.76	2.1101
1590	229872	6.09	6.09	2.2154
2160	195122	5.16	5.16	2.2874
2640	178847	4.71	4.71	2.3270
3120	130962	3.47	3.47	2.4597
3600	113065	2.96	2.96	2.5287
4290	88084	2.31	2.31	2.6364
5310	52499	1.38	1.38	2.8601
6330	35754	0.95	0.95	3.0223
6540	39033	1.01	1.01	2.9957

RUN 69

Initial concentration $CHCl_3$: 0.0107 mol.l.$^{-1}$

Initial concentration NaOH : 1.2956 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
90	384369	10.17	10.17	1.9928
1230	273106	7.19	7.19	2.1433
2430	178691	4.72	4.72	2.3261
3870	106104	2.80	2.80	2.5528
4980	71017	1.87	1.87	2.7281
6000	48474	1.27	1.27	2.8962
7050	32209	0.85	0.85	3.0706
7950	22933	0.60	0.60	3.2218
9240	12840	0.33	0.33	3.4815

RUN 70

Initial concentration $CHCl_3$: 0.0085 mol.l.$^{-1}$

Initial concentration NaOH : 0.7942 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.23 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
60	260049	6.87	8.45	2.0731
900	201770	5.34	6.57	2.1824
2760	139181	3.67	4.51	2.3458
3540	115136	3.03	3.73	2.4283
4380	90944	2.40	2.95	2.5302
5160	71589	1.88	2.31	2.6364
5940	57960	1.49	1.83	2.7375
6780	49047	1.29	1.59	2.7986
7620	40354	1.05	1.29	2.8894
8520	30023	0.78	0.96	3.0177
9300	25262	0.66	0.81	3.0915
10110	14722	0.39	0.48	3.3188
11130	15946	0.41	0.50	3.3010
12060	12527	0.32	0.39	3.4089
12930	9204	0.25	0.31	3.5086

RUN 72

Initial concentration $CHCl_3$: 0.0097 mol.l.$^{-1}$

Initial concentration NaOH : 0.9998 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Volume after netralisation : 1.30 ml.

Time (sec.)	Peak Area	Conc^n $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd to 1 ml. (M x 10^3)	$\log_{10}$ (a-x)
90	274895	7.25	9.43	2.0255
870	230401	6.10	7.93	2.1007
1860	166656	4.31	5.60	2.2518
2670	129260	3.42	4.45	2.3516
3450	99527	2.63	3.42	2.4660
4260	82025	2.16	2.81	2.5513
5130	61400	1.62	2.11	2.6757
5940	48568	1.28	1.66	2.7799
6750	36533	0.98	1.27	2.8962
7500	29747	0.79	1.03	2.9872
8310	23566	0.61	0.79	3.1024

RUN 73

Initial concentration $CHCl_3$: 0.0101 mol.l^{-1}

Initial concentration NaOH : 0.6952 mol.l^{-1}

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.20 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
60	318099	8.39	10.07	1.9971
750	270101	7.11	8.53	2.0691
1500	214925	5.68	6.82	2.1662
2160	183897	4.87	5.84	2.2336
2940	145668	3.85	4.62	2.3354
3690	113676	3.00	3.60	2.4437
4650	86961	2.28	2.74	2.5622
5340	78150	2.05	2.46	2.6091
6390	62102	1.63	1.96	2.7077
7110	58912	1.55	1.86	2.7304
8040	39671	1.03	1.24	2.9066
8700	37509	0.98	1.18	2.9281

RUN 74

Initial concentration $CHCl_3$: 0.0103 mol.l.$^{-1}$

Initial concentration NaOH : 0.2017 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.065 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
60	371719	9.83	10.47	1.9801
900	331819	8.76	9.33	2.0301
1680	312730	8.25	8.79	2.0560
2520	292447	7.71	8.21	2.0857
3420	275481	7.26	7.73	2.1118
4260	260359	6.88	7.33	2.1349
5070	232405	6.15	6.55	2.1838
5940	219314	5.81	6.19	2.2083
6750	205490	5.45	5.80	2.2366
7560	184055	4.88	5.20	2.2840
8610	178111	4.70	5.01	2.3002
9450	158209	4.18	4.45	2.3516
10380	155246	4.10	4.37	2.3595
11910	137623	3.62	3.86	2.4134
12870	126970	3.36	3.58	2.4461
13650	118137	3.11	3.31	2.4802
14820	109086	2.86	3.05	2.5157
15570	101543	2.71	2.89	2.5391
16320	95383	2.51	2.67	2.5735
17160	89423	2.37	2.52	2.5986
17910	83839	2.20	2.34	2.6308
18820	77252	2.03	2.16	2.6655
19740	73112	1.83	1.95	2.7100

RUN 75

Initial concentration $CHCl_3$: 0.0103 mol.l.$^{-1}$

Initial concentration NaOH : 0.3047 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.09 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	-$\log_{10}$ (a-x)
90	351511	9.28	10.12	1.9949
930	303488	8.00	8.72	2.0595
1710	278496	7.34	8.00	2.0969
2580	248707	6.56	7.15	2.1457
3480	223191	5.91	6.44	2.1911
4740	204712	5.42	5.91	2.2284
5670	172719	4.56	4.97	2.3036
6510	156027	4.12	4.49	2.3478
7560	142288	3.77	4.11	2.3862
8910	121785	3.21	3.50	2.4559
9660	112018	2.96	3.23	2.4908
11160	93753	2.47	2.69	2.5702
12090	85657	2.25	2.45	2.6108
12870	78601	2.06	2.25	2.6478
13740	69832	1.83	1.99	2.7011
14580	63836	1.69	1.84	2.7352
16020	55439	1.47	1.60	2.7959
17010	49868	1.30	1.42	2.8477
17910	44933	1.17	1.28	2.8928
18690	40335	1.05	1.14	2.9431

RUN 76

Initial concentration $CHCl_3$: 0.0102 mol.l.$^{-1}$

Initial concentration NaOH : 0.4026 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.12 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
60	341680	9.00	10.08	1.9967
810	298773	7.88	8.83	2.0540
1620	270763	7.13	7.99	2.0975
2370	241746	6.40	7.17	2.1445
3150	200580	5.31	5.95	2.2255
3840	181740	4.80	5.38	2.2692
4710	155321	4.10	4.59	2.3382
5430	148695	3.93	4.40	2.3565
6150	115180	3.05	3.42	2.4660
7590	97927	2.59	2.90	2.5376
8370	85510	2.26	2.53	2.5969
9120	75295	1.99	2.23	2.6517
9900	69962	1.83	2.05	2.6882
10650	61323	1.61	1.80	2.7447
11400	52382	1.37	1.53	2.8153
12150	48497	1.26	1.41	2.8508
13230	45599	1.20	1.34	2.8729
14250	34883	0.91	1.02	2.9914

RUN 77

Initial concentration $CHCl_3$: 0.0100 mol.l.$^{-1}$

Initial concentration NaOH : 0.1527 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.065 ml.

Time (Sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	-$\log_{10}$ (a-x)
90	322117	8.50	9.05	2.0434
870	332295	8.78	9.35	2.0292
1560	319540	8.43	8.98	2.0467
2280	299740	7.90	8.41	2.0752
3090	285842	7.53	8.02	2.0958
3810	274521	7.23	7.70	2.1135
4530	249631	6.59	7.02	2.1537
5220	236241	6.25	6.66	2.1765
5940	226369	5.99	6.38	2.1952
6720	211993	5.61	5.97	2.2240
7440	206012	5.47	5.83	2.2343
17610	127860	3.38	3.60	2.4437
18570	121780	3.21	3.42	2.4660
19380	115632	3.04	3.24	2.4895
20160	111260	2.95	3.14	2.5031
20880	101847	2.69	2.86	2.5436
21570	94782	2.50	2.66	2.5751
22350	92420	2.43	2.59	2.5867
23250	87898	2.31	2.46	2.6091
24000	80953	2.13	2.27	2.6440

RUN 78

Initial concentration $CHCl_3$: 0.0091 mol.l.$^{-1}$

Initial concentration NaOH : 0.1020 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.065 ml.

Time (sec.)	Peak Area	conc^{n}. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
4440	304271	8.01	8.53	2.0691
5250	289885	7.65	8.15	2.0888
6150	278982	7.35	7.83	2.1062
7050	265763	7.00	7.46	2.1273
7830	254792	6.73	7.17	2.1445
8670	241932	6.40	6.82	2.1662
9810	239510	6.35	6.76	2.1701
10620	221303	5.86	6.24	2.2048
11490	218262	5.78	6.16	2.2104
12450	200668	5.33	5.68	2.2457
13410	198058	5.24	5.58	2.2534
14430	186365	4.94	5.26	2.2790
15300	178800	4.73	5.04	2.2976
16170	173876	4.69	4.99	2.3019
17160	166964	4.42	4.71	2.3270
18030	154772	4.08	4.35	2.3615
18840	150267	3.98	4.24	2.3726
19590	148717	3.93	4.19	2.3778

RUN 79

Initial concentration $CHCl_3$: 0.0110 mol.l.$^{-1}$

Initial concentration NaOH : 0.0511 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.065 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
60	383728	10.16	10.82	1.9658
870	376245	9.97	10.62	1.9739
1710	368597	9.75	10.38	1.9839
2460	346654	9.16	9.76	2.0106
3270	352270	9.31	9.92	2.0035
4020	338778	8.95	9.53	2.0209
4740	332352	8.78	9.35	2.0292
5550	313268	8.27	8.81	2.0550
6300	309327	8.16	8.69	2.0610
7080	283683	7.49	7.98	2.0980
7770	302510	7.99	8.51	2.0701
8880	287786	7.59	8.08	2.0926
10710	284339	7.50	7.99	2.0975
11400	270502	7.11	7.57	2.1209
12210	256531	6.77	7.21	2.1421
12960	247478	6.53	6.95	2.1580
13740	242183	6.41	6.83	2.1656
14460	226923	6.00	6.39	2.1945
15270	225575	5.98	6.37	2.1959

RUN 80

Initial concentration $CHCl_3$: 0.0097 mol.l.$^{-1}$

Initial concentration NaOH : 1.3025 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.28 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
120	278244	7.33	9.38	2.0278
930	216849	5.74	7.35	2.1337
1740	179180	4.75	6.08	2.2161
2580	149015	3.94	5.04	2.2976
3660	110532	2.94	3.76	2.4248
4410	89047	2.36	3.02	2.5200
5220	72494	1.91	2.44	2.6126
5970	60945	1.60	2.05	2.6882
6720	49400	1.30	1.66	2.7799
7500	37856	1.00	1.28	2.8928
8250	30723	0.80	1.02	2.9914
9210	24765	0.65	0.83	3.0799

RUN 81

Initial concentration $CHCl_3$: 0.0100 mol.l.$^{-1}$

Initial concentration NaOH : 1.2733 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.35 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	-$\log_{10}$ (a-x)
90	272688	7.19	9.71	2.0128
810	210807	5.57	7.52	2.1238
1620	169202	4.47	6.03	2.2197
2370	133743	3.52	4.75	2.3233
3420	100770	2.65	3.58	2.4461
4170	78084	2.04	2.75	2.5607
4890	63537	1.68	2.27	2.6440
5670	47382	1.24	1.67	2.7773
6390	41828	1.10	1.49	2.8268
7230	33135	0.87	1.17	2.9318
7980	23341	0.60	0.81	3.0915
8760	16219	0.42	0.57	3.2464
9600	12440	0.32	0.43	3.3665

RUN 82

Initial concentration $CHCl_3$: 0.0104 mol.l.$^{-1}$

Initial concentration NaOH : 0.9687 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.28 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
60	326512	8.68	11.11	1.9543
930	231427	6.12	7.83	2.1062
1740	188608	4.99	6.39	2.1945
2580	139627	3.69	4.72	2.3261
3360	117650	3.10	3.97	2.4012
4290	93627	2.47	3.16	2.5003
5070	74798	1.97	2.52	2.5986
6210	55987	1.49	1.91	2.7190
7020	45403	1.19	1.52	2.8182
7830	33732	0.89	1.14	2.9431
9180	23650	0.70	0.90	3.0458
9960	21330	0.55	0.70	3.1549

RUN 83

Initial concentration $CHCl_3$: 0.0103 mol.l.$^{-1}$

Initial concentration NaOH : 1.4332 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.41 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
90	263594	6.96	9.81	2.0083
780	213433	5.65	7.97	2.0985
1500	161919	4.28	6.03	2.2197
2370	126108	3.32	4.68	2.3298
3210	99012	2.60	3.67	2.4353
3990	71636	1.88	2.65	2.5768
4740	60637	1.60	2.26	2.6459
5520	46452	1.22	1.72	2.7645
6540	32751	0.86	1.21	2.9172
7320	25419	0.66	0.93	3.0311

RUN 84

Initial concentration $CHCl_3$: 0.0110 mol.l.$^{-1}$

Initial concentration NaOH : 1.3540 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.40 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
60	292234	7.71	10.79	1.9669
750	229018	6.05	8.47	2.0721
1500	177760	4.70	6.58	2.1818
2340	139057	3.66	5.12	2.2907
3180	105723	2.78	3.89	2.4101
3990	76632	2.00	2.80	2.5528
4890	57663	1.51	2.11	2.6757
5790	44783	1.17	1.64	2.7852
7380	28374	0.74	1.04	2.9830

RUN 85

Initial concentration $CHCl_3$: 0.0106 mol.l.$^{-1}$

Initial concentration NaOH : 1.1555 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.83 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
60	303375	8.00	10.64	1.9730
840	239255	6.33	8.42	2.0747
1830	174355	4.60	6.12	2.2132
2640	139084	3.66	4.87	2.3125
3360	115298	3.03	4.03	2.3947
4170	92472	2.45	3.26	2.4868
4890	74925	1.97	2.62	2.5817
5640	59088	1.55	2.06	2.6861
6390	48084	1.25	1.66	2.7799
7140	37138	0.97	1.29	2.8894
8010	31037	0.80	1.06	2.9747
8820	23371	0.60	0.80	3.0969

RUN 86

Initial concentration $CHCl_3$	:	0.0099 mol.l.$^{-1}$
Initial concentration NaOH	:	0.8949 mol.l.$^{-1}$
Temperature	:	36 ± 0.1°C
Volume after neutralisation	:	1.26 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
60	290881	7.67	9.66	2.0150
870	227432	6.01	7.57	2.1209
1740	170880	4.52	5.70	2.2441
2550	139217	3.67	4.62	2.3354
3300	113396	3.00	3.78	2.4225
4020	92524	2.43	3.06	2.5143
4770	75267	1.98	2.49	2.6038
5460	59236	1.56	1.97	2.7055
6360	45738	1.20	1.51	2.8210
7500	35674	0.94	1.18	2.9281
8580	26158	0.69	0.87	3.0605

RUN 87

Initial concentration $CHCl_3$	:	0.0097 mol.l.$^{-1}$
Initial concentration NaOH	:	1.1996 mol.l.$^{-1}$
Temperature	:	36 ± 0.1°C
Volume after neutralisation	:	1.33 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
60	279704	7.38	9.82	2.0079
810	189370	5.00	6.65	2.1772
1650	152579	4.02	5.35	2.2716
2610	115434	3.03	4.03	2.3947
3540	83241	2.19	2.96	2.5287
4320	66333	1.74	2.35	2.6289
5010	49956	1.31	1.77	2.7520
5730	40937	1.07	1.44	2.8416

RUN 88

Initial concentration $CHCl_3$: 0.0096 $mol.l.^{-1}$

Initial concentration NaOH : 0.5975 $mol.l.^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.18 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) ($M \times 10^3$)	(a-x) corr'd. to 1 ml. ($M \times 10^3$)	$-\log_{10}$ (a-x)
90	276360	7.29	8.60	2.0655
810	258801	6.83	8.06	2.0937
1710	211799	5.60	6.61	2.1798
2460	184128	4.88	5.76	2.2396
3240	162682	4.30	5.07	2.2950
3990	138638	3.66	4.32	2.3645
4800	111862	3.06	3.61	2.4425
5550	99679	2.52	2.97	2.5272
6270	81608	2.14	2.53	2.5969
6960	76040	2.00	2.36	2.6271
7710	63747	1.68	1.98	2.7033
8730	53150	1.39	1.64	2.7852
9240	46781	1.23	1.45	2.8386

RUN 89

Initial concentration $CHCl_3$: 0.0098 $mol.l.^{-1}$

Initial concentration NaOH : 1.0894 $mol.l.^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.32 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) ($M \times 10^3$)	(a-x) corr'd. to 1 ml. ($M \times 10^3$)	$-\log_{10}$ (a-x)
90	289106	7.79	10.28	1.9881
840	217528	5.76	7.60	2.1192
1530	181564	4.80	6.34	2.1979
2280	137761	3.62	4.78	2.3206
3000	108066	2.84	3.75	2.4260
3720	90800	2.40	3.17	2.4989
4470	70759	1.87	2.47	2.6073
5190	53336	1.40	1.85	2.7328
5910	45741	1.20	1.58	2.8013
6660	36295	0.96	1.27	2.8962

RUN 90

Initial concentration $CHCl_3$: 0.0091 mol.l.$^{-1}$

Initial concentration NaOH : 0.40 mol.l.$^{-1}$

Temperature : 41 ± 0.1°C

Volume after neutralisation : 1.15 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
60	309325	8.16	9.38	2.0278
840	245027	6.48	7.45	2.1278
1620	188968	5.00	5.75	2.2403
2370	163602	4.28	4.92	2.3080
3090	131451	3.48	4.00	2.3979
3840	104750	2.77	3.19	2.4962
4560	87910	2.31	2.66	2.5751
5910	63035	1.66	1.91	2.7190
6690	47431	1.25	1.44	2.8416
7920	36338	0.95	1.09	2.9626
8880	28012	0.72	0.83	3.0809
9840	22005	0.57	0.66	3.1805

RUN 91

Initial concentration $CHCl_3$: 0.0094 mol.l.$^{-1}$

Initial concentration NaOH : 0.80 mol.l.$^{-1}$

Temperature : 41 ± 0.1°C

Volume after neutralisation : 1.24 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
60	277126	7.30	9.05	2.0434
390	236484	6.26	7.76	2.1101
960	175146	4.63	5.74	2.2411
1170	136275	3.60	4.46	2.3507
1680	119585	3.15	3.91	2.4078
2400	83193	2.19	2.72	2.5654
3240	53204	1.39	1.72	2.7645
4200	33675	0.88	1.09	2.9626
4950	23033	0.60	0.74	3.1308
5730	14807	0.39	0.48	3.3188

RUN 92

Initial concentration $CHCl_3$	:	0.0093 mol.l.$^{-1}$
Initial concentration NaOH	:	0.40 mol.l.$^{-1}$
Temperature	:	30 ± 0.1°C
Volume after neutralisation	:	1.15 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) ($M \times 10^3$)	(a-x) corr'd. to 1 ml. ($M \times 10^3$)	$-\log_{10}$ (a-x)
90	275745	7.28	8.37	2.0773
1320	290669	7.67	8.82	2.0545
2460	255395	6.75	7.76	2.1101
3480	220249	5.84	6.72	2.1726
4800	228049	6.02	6.92	2.1599
5850	199745	5.28	6.07	2.2168
6900	193783	5.12	5.89	2.2299
8070	184652	4.90	5.64	2.2487
9060	176623	4.77	5.49	2.2604
10080	162884	4.30	4.95	2.3054
12000	143778	3.80	4.37	2.3595
12990	134074	3.53	4.06	2.3914
14010	123150	3.25	3.74	2.4271
15120	119064	3.13	3.60	2.4437
16050	107334	2.83	3.25	2.4881
17490	96523	2.54	2.92	2.5346
18690	95356	2.51	2.89	2.5391
19590	88947	2.34	2.69	2.5702
20580	82309	2.17	2.50	2.6021

RUN 93

Initial concentration $CHCl_3$: 0.0098 mol.l.$^{-1}$

Initial concentration NaOH : 0.80 mol.l.$^{-1}$

Temperature : 30 ± 0.1°C

Volume after neutralisation : 1.24 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
90	299394	7.90	9.80	2.0088
1110	272941	7.20	8.93	2.0491
2100	236005	6.24	7.74	2.1113
3210	201910	5.34	6.62	2.1791
4170	183104	4.84	6.00	2.2218
5220	155930	4.11	5.10	2.2924
6300	147039	3.88	4.81	2.3179
7320	126340	3.33	4.13	2.3840
9000	108525	2.86	3.55	2.4498
10290	81486	2.13	2.64	2.5784
11310	79881	2.10	2.60	2.5850
12240	72013	1.90	2.36	2.6271
13140	65740	1.72	2.13	2.6716
14880	54702	1.44	1.79	2.7471
15870	46184	1.21	1.50	2.8239
16830	44014	1.15	1.43	2.8447
17790	38768	1.00	1.24	2.9066
19650	33168	0.87	1.08	2.9666

RUN 94

Initial concentration $CHCl_3$: 0.0099 mol.l.$^{-1}$

Initial concentration NaOH : 0.80 mol.l.$^{-1}$

Temperature : 25 ± 0.1°C

Volume after neutralisation : 1.24 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
90	288951	7.53	9.34	2.0297
990	281212	7.43	9.21	2.0357
1980	260301	6.88	8.53	2.0691
2940	258037	6.80	8.43	2.0742
3870	240059	6.35	7.87	2.1040
4890	227012	6.00	7.44	2.1284
5940	211225	5.59	6.93	2.1593
6960	199147	5.27	6.53	2.1851
7860	187438	4.97	6.16	2.2104
9720	176919	4.67	5.79	2.2373
10590	158721	4.20	5.21	2.2832
11490	154465	4.08	5.06	2.2958
12390	144450	3.81	4.72	2.3261
13260	136904	3.61	4.48	2.3487
14280	125988	3.32	4.12	2.3851
15240	119881	3.16	3.92	2.4067
16170	116487	3.00	3.72	2.4295
17250	111014	2.93	3.63	2.4401

RUN 95

Initial concentration $CHCl_3$: 0.0100 mol.l.$^{-1}$

Initial concentration NaOH : 0.40 mol.l.$^{-1}$

Temperature : 25 ± 0.1°C

Volume after neutralisation : 1.15 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
90	315727	8.32	9.57	2.0191
690	319037	8.42	9.68	2.0141
1950	305097	8.10	9.32	2.0306
2820	294320	7.77	8.94	2.0487
3690	286432	7.55	8.68	2.0615
4680	281357	7.44	8.56	2.0675
5640	272597	7.19	8.27	2.0825
6510	259479	6.85	7.88	2.1035
7320	248500	6.57	7.56	2.1215
8160	247849	6.55	7.53	2.1232
8970	240216	6.36	7.31	2.1361
10140	230539	6.10	7.02	2.1537
11010	221899	5.88	6.76	2.1701
11820	212462	5.62	6.46	2.1898
12660	198138	5.24	6.03	2.2197
13620	189661	5.01	5.76	2.2396
14790	197099	5.22	6.00	2.2218
15720	184569	4.90	5.64	2.2487
16620	177266	4.66	5.36	2.2708
17640	177137	4.65	5.35	2.2716
18480	165311	4.37	5.03	2.2984

RUN 95 (cont)

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
19620	162244	4.29	4.93	2.3072
20910	156747	4.13	4.75	2.3233
21780	147878	3.90	4.49	2.3478
22920	147191	3.88	4.46	2.3507
23700	140881	3.72	4.28	2.3686
24480	136669	3.61	4.15	2.3820
25560	131778	3.49	4.01	2.3969
26520	126319	3.33	3.83	2.4168
27360	124400	3.29	3.78	2.4225
28200	115341	3.03	3.48	2.4584
28980	115092	3.02	3.47	2.4597

RUN 96

Initial concentration $CDCl_3$: 0.0083 $mol.l.^{-1}$

Initial concentration NaOD : 0.80 $mol.l.^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.24 ml.

Time (sec.)	Peak Area	Concn. $CHCl_3$ (a-x) ($M \times 10^3$)	(a-x) corr'd. to 1 ml. ($M \times 10^3$)	$-\log_{10}$ (a-x)
60	248374	6.56	8.13	2.0899
1080	181514	4.80	5.95	2.2255
2130	126527	3.34	4.14	2.3830
3360	80347	2.12	2.63	2.5800
4440	60564	1.60	1.98	2.7033
5460	44192	1.16	1.44	2.8416
6780	27831	0.71	0.88	3.0555
7860	20672	0.54	0.67	3.1739
8880	15417	0.39	0.48	3.3188
10290	10251	0.27	0.33	3.4815

RUN 97

Initial concentration $CHCl_3$	:	0.0133 mol.l.$^{-1}$
Initial concentration NaOH	:	0.40 mol.l.$^{-1}$
Temperature	:	36 ± 0.1°C
Volume after neutralisation	:	1.15 ml.

Time (sec.)	Peak Area	Conc^{n}. $CHCl_3$ (a-x) ($M \times 10^3$)	(a-x) corr'd. to 1 ml. ($M \times 10^3$)	$-\log_{10}$ (a-x)
60	4262	11.36	13.06	1.8841
540	4130	11.02	12.67	1.8972
1020	3750	10.03	11.53	1.9382
1410	3557	9.52	10.95	1.9606
1800	3301	8.84	10.17	1.9927
2160	3198	8.55	9.83	2.0075
2550	2921	7.80	8.97	2.0472
2940	2841	7.60	8.74	2.0585
3360	2723	7.29	8.38	2.0768
3720	2436	6.52	7.50	2.1249
4170	2401	6.42	7.38	2.1319
4530	2136	5.75	6.61	2.1798
4920	1891	5.10	5.87	2.2314
5280	1865	5.00	5.75	2.2403
5640	1684	4.50	5.18	2.2857

RUN 98

Initial concentration $CHCl_3$: 0.0182 mol.l.$^{-1}$

Initial concentration NaOH : 0.40 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.15 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
60	5861	15.65	18.00	1.7447
750	5371	14.33	16.48	1.7830
1200	4978	13.30	15.30	1.8153
1560	4659	12.45	14.32	1.8441
2010	4438	11.86	13.64	1.8652
2610	3917	10.38	11.94	1.9230
3030	3472	9.28	10.67	1.9718
3690	3436	9.20	10.58	1.9755
4080	3133	8.35	9.60	2.0177
4530	2987	8.00	9.20	2.0362
5010	2801	7.50	8.63	2.0640
5430	2614	7.00	8.05	2.0942
5880	2481	6.63	7.62	2.1180
6360	2250	6.02	6.92	2.1599
6780	2165	5.80	6.67	2.1759
7140	2135	5.75	6.61	2.1798
7860	1779	4.77	5.49	2.2604

RUN 99

Initial concentration $CHCl_3$: $0.0056\ mol.l.^{-1}$

Initial concentration NaOH : $0.40\ mol.l.^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.15 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) ($M \times 10^3$)	(a-x) corr'd. to 1 ml. ($M \times 10^3$)	$-\log_{10}$ (a-x)
90	1637	4.40	5.06	2.2959
450	1701	4.55	5.23	2.2815
810	1667	4.47	5.14	2.2890
1140	1471	3.97	4.57	2.3401
1530	1448	3.88	4.46	2.3507
2160	1286	3.45	3.97	2.4012
2610	1252	3.35	3.85	2.4145
3180	1204	3.22	3.70	2.4318
3570	1026	2.77	3.19	2.4962
3960	891	2.42	2.78	2.5560
4350	904	2.45	2.82	2.5498
4800	858	2.33	2.68	2.5719
5400	773	2.08	2.39	2.6216
5820	728	1.99	2.29	2.6402
6330	693	1.88	2.16	2.6655

RUN 100

Initial concentration $CHCl_3$: 0.0092 mol.l.$^{-1}$

Initial concentration NaOH : 0.40 mol.l.$^{-1}$

Temperature : 36 ± 0.1°C

Volume after neutralisation : 1.15 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
60	2792	7.48	8.60	2.0655
450	2778	7.45	8.57	2.0670
840	2633	7.06	8.12	2.0904
1260	2404	6.41	7.37	2.1325
1860	2154	5.77	6.64	2.1778
2280	1991	5.32	6.12	2.2132
2760	1856	5.00	5.75	2.2403
3150	1714	4.59	5.28	2.2774
3540	1624	4.35	5.00	2.3010
3960	1510	4.06	4.67	2.3307
4380	1478	3.99	4.59	2.3382
4860	1381	3.70	4.26	2.3706
5280	1296	3.50	4.03	2.3947

RUN 101

Initial concentration CHCl$_3$: 0.0115 mol.l.$^{-1}$

Initial concentration NaOH : 0.0375 mol.l.$^{-1}$

Temperature : 41 ± 0.1°C

Volume after neutralisation : 1.06 ml.

Time (sec.)	Peak Area	Conc^n. CHCl$_3$ (a-x) (M x 10^3)	(a-x) corr'd to 1 ml. (M x 10^3)	-log$_{10}$ (a-x)
90	4918	13.12	13.91	1.8567
480	4412	11.79	12.50	1.9031
960	4154	11.18	11.85	1.9262
1350	3421	9.15	9.70	2.0132
1770	3587	9.60	10.18	1.9923
2190	3478	9.30	9.86	2.0061
2640	3310	8.85	9.38	2.0278
3420	3092	8.25	8.75	2.0580
3870	2884	7.70	8.16	2.0883
4470	2787	7.49	7.94	2.1002
5940	2555	6.84	7.25	2.1397
6840	2463	6.57	6.96	2.1574
7350	2338	6.26	6.64	2.1778
7830	2300	6.15	6.52	2.1858
8310	2184	5.85	6.20	2.2076
8850	2190	5.88	6.23	2.2055
9330	2137	5.75	6.10	2.2147
9810	1852	4.98	5.28	2.2774
10290	1960	5.24	5.55	2.2557
10890	1950	5.23	5.54	2.2565
11310	1874	5.02	5.32	2.2741

RUN 102

Initial concentration $CHCl_3$: 0.0100 mol.l.$^{-1}$

Initial concentration NaOH : 0.0375 mol.l.$^{-1}$

Concentration KNO_3 : 0.01 mol.l.$^{-1}$

Temperature : 41 ± 0.1°C

Volume after neutralisation : 1.06 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
120	3374	9.00	9.54	2.0205
570	3384	9.04	9.58	2.0186
1020	3265	8.78	9.31	2.0311
1500	3190	8.53	9.04	2.0438
1980	3051	8.14	8.63	2.0640
2490	3041	8.13	8.62	2.0645
2970	2903	7.75	8.22	2.0851
3450	2859	7.65	8.11	2.0910
4020	2800	7.50	7.95	2.0996
4620	2730	7.30	7.74	2.1113
5280	2582	6.90	7.31	2.1361
5880	2446	6.54	6.93	2.1593
6360	2510	6.71	7.11	2.1481
6870	2370	6.33	6.71	2.1733
7530	2359	6.31	6.69	2.1746
8010	2234	5.99	6.35	2.1972
8490	2129	5.70	6.04	2.2190
8970	2081	5.48	5.81	2.2358
9480	2158	5.80	6.15	2.2111
9990	2009	5.40	5.72	2.2426
10440	2008	5.40	5.72	2.2426
10950	1823	4.89	5.18	2.2857
11580	1820	4.88	5.17	2.2865

RUN 103

Initial concentration $CHCl_3$: 0.0076 mol.l.$^{-1}$

Initial concentration NaOH : 0.0375 mol.l.$^{-1}$

Temperature : 41 ± 0.1°C

Volume after neutralisation : 1.06 ml.

Time (sec.)	Peak Area	Conc^n. $CHCl_3$ (a-x) (M x 10^3)	(a-x) corr'd. to 1 ml. (M x 10^3)	$-\log_{10}$ (a-x)
120	2542	6.80	7.21	2.1421
1050	2220	5.95	6. 31	2.2000
1380	2194	5.89	6.24	2.2048
1800	2106	5.65	5.99	2.2226
2160	2057	5.43	5.76	2.2396
2580	1748	4.69	4.97	2.3036
3240	1669	4.48	4.75	2.3233
3750	1619	4.35	4.61	2.3363
4200	1538	4.13	4.38	2.3585
4680	1507	4.03	4.27	2.3696
5100	1241	3.32	3.52	2.4535
5760	1238	3.32	3.52	2.4535
6360	1063	2.85	3.02	2.5200
6750	950	2.57	2.72	2.5654
7170	892	2.40	2.54	2.5952
7560	859	2.34	2.48	2.6055
7950	798	2.16	2.29	2.6402

RUN 104

Initial concentration $CHCl_3$: 0.0076 $mol.l.^{-1}$

Initial concentration NaOH : 0.0375 $mol.l.^{-1}$

Concentration NaCl : 0.01 $mol.l.^{-1}$

Temperature : 41 ± 0.1°C

Volume after neutralisation : 1.06 ml.

Time (sec.)	Peak Area	$Conc^n$. $CHCl_3$ (a-x) ($M \times 10^3$)	(a-x) corr'd. to 1 ml. ($M \times 10^3$)	$-\log_{10}$ (a-x)
90	2624	7.02	7.44	2.1284
960	2561	6.85	7.26	2.1391
2100	2338	6.26	6.64	2.1778
2550	2084	5.57	5.90	2.2291
3540	2061	5.53	5.86	2.2321
3960	2054	5.50	5.83	2.2343
4470	1979	5.30	5.62	2.2503
4890	1965	5.26	5.58	2.2534
5490	1660	4.56	4.83	2.3161
6210	1483	4.00	4.24	2.3726
6870	1449	3.90	4.13	2.3840
7530	1458	3.91	4.14	2.3830
8610	1455	3.90	4.13	2.3840
9390	1260	3.40	3.60	2.4437
9960	1368	3.66	3.88	2.4112
10560	1166	3.00	3.18	2.4976
11040	1231	3.31	3.51	2.4547
11580	1289	3.47	3.68	2.4343

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