KINETICS AND THERMODYNAMIC STUDIES
ON
CHLOROFORMATES

A thesis submitted by
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To my Parents and my Family
for their support and encouragement.

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ABSTRACT

The purpose of this study is to explore the nature of the reactions of n-propyl and benzyl chloroformates with tetra-n-butylammonium nitrate in actonitrile as a reaction medium. A thermodynamic investigation associated with the enthalpy of formation and vaporization of these chloroformates has also been undertaken.

The reaction kinetics were determined at various concentrations of chloroformates and tetra-n-butylammonium nitrate at different temperatures. The reactions have been found to be second-order and to follow pseudo-first-order rate coefficients proportional to the nitrate ion concentration. The changes in entropies, $\Delta S^{\ddagger}$, ranged from -59.5 for n-C_3H_7OCOCl to -14.5 J mol^{-1} deg^{-1} for $C_6H_5CH_2OCOCl$, which indicates that the reaction proceeded by a bimolecular S_N2 mechanism. The studies give evidence that the rate-determining step is the initial reaction between the chloroformates and NO_3^- to give nitratocarbonate via a tetrahedral intermediate.

The expected products, nitrate ester and carbon dioxide, are obtained in maximum yields of 18-20% and 61% respectively. Addition of pyridine or tetra-n-butylammonium perchlorate, has little effect on the yield of nitrate ester product.

The tetra-n-butylammonium chloride product is more reactive towards both n-propyl and benzyl chloroformates than the corresponding nitrate.

The enthalpies of solution of n-propyl and benzyl chloroformates in sodium hydroxide (1 mol dm^{-3})

have been measured over a range of concentrations at 298.15 K, using a solution reaction calorimeter.

The variation with the concentration of the enthalpy of hydrolysis was not significant over the concentration ranges studied $\Delta H_f^\ominus$ (C_3H_7OCOCl, l) = -524.396 ± 0.767 kJ mol^{-1} for $5791 < n < 19593$ and $\Delta H^\ominus$ ($C_6H_5CH_2OCOCl, l$) = -375.244 ± 1.088 kJ mol^{-1} for $36804 < n < 52495$

Enthalpies of vaporization have been obtained from measurements of vapour pressure over the temperature range 293.13 to 306.30 K, $\Delta H_v^\ominus$ (n-C_3H_7OCOCl, 298.15 K) = 40.676 ± 0.450, and 293.770 to 302.34 K, $\Delta H_v^\ominus$ ($C_6H_5CH_2OCOCl$, 298.15K) = 38.527 ± 0.110 kJ mol^{-1}.

Enthalpies of vaporization were also obtained using a vaporization calorimeter, giving $\Delta H_v^\ominus$ (n-C_3H_7OCOCl, 298.15 K) = 40.742 ± 0.403 kJ mol^{-1}.

These values of $\Delta H_v^\ominus$, obtained from the vapour pressure measurements, are combined with the enthalpies of formation of $\Delta H_f^\ominus$ (l) values to give enthalpies of formation in the gaseous state at 298.15 K viz.,

$\Delta H_f^\ominus$ (n-C_3H_7OCOCl, g) = -483.720 ± 0.864 kJ mol^{-1}

$\Delta H_f^\ominus$ ($C_6H_5CH_2OCOCl$, g) = -336.717 ± 1.094 kJ mol^{-1}

CONTENTS

Kinetics work — Page No.

CHAPTER I

I. INTRODUCTION

CHAPTER II.

CHAPTER III

III. EXPERIMENTAL TECHNIQUES

Thermodynamic work

CHAPTER IV

IV. INTRODUCTION

Page No.

CHAPTER V

V. THERMODYNAMICS RESULTS AND DISCUSSION

CHAPTER VI

VI. EXPERIMENTAL TECHNIQUES

KINETICS WORK

CHAPTER I

INTRODUCTION

CHAPTER I

I. INTRODUCTION

I.1 . Synthesis of Chloroformates.

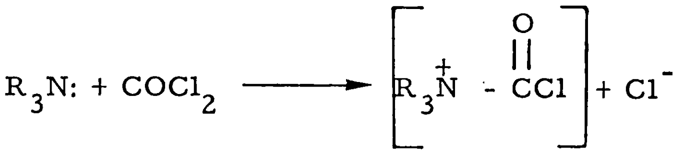
I.1.1 Alkyl Chloroformates.

Alkyl and cycloalkyl chloroformates (i.e. esters of carbonochloridic acid) have been conveniently prepared (1), (2) by the reaction of phosgene with the corresponding alcohols. This reaction can be simply represented as follows:

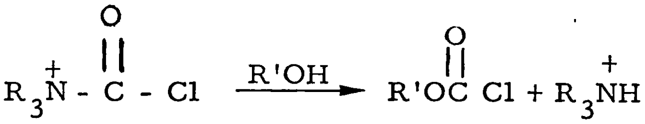
$$ROH + COCl_2 \longrightarrow ROCOCl + HCl\uparrow \qquad (1)$$

The reaction has been investigated and reported (3) to give good yields subject to careful control of the reaction temperature. Typically, phosgene is passed into the alcohols with cooling to room temperature or below, to minimise the formation of the corresponding dialkyl carbonates; the hydrogen chloride produced is removed under reduced pressure to yield the chloroformates.

A variation of this reaction has been to carry out the process in the presence of a tertiary amine. Here the chloroformates are formed when a tertiary amine is slowly added to a non-aqueous solution containing equivalent quantities of phosgene and the alcohol. This procedure has been patented (4), and tested for a wide variety of bases and alcohols. The yields are invariably as high as 75%. The use of tertiary amines (preferable when acid-sensitive groups are present), has been found in many cases to be essential for the reaction to occur at reasonable rates and it has been postulated (5) that the function of the amine initially is to form a complex with phosgene. This intermediate subsequently acts as a very effective acylating agent:



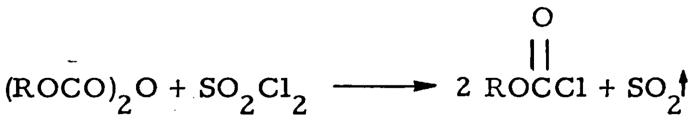
$$R_3N: + COCl_2 \longrightarrow \left[R_3\overset{+}{N} - \overset{O}{\overset{\|}{C}}Cl\right] + Cl^- \qquad (2)$$



$$R_3\overset{+}{N} - \overset{O}{\overset{\|}{C}} - Cl \xrightarrow{R'OH} R'O\overset{O}{\overset{\|}{C}}\,Cl + R_3\overset{+}{N}H \qquad (3)$$

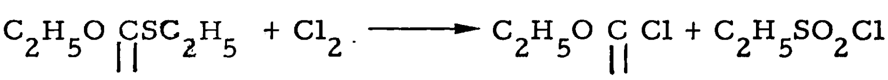
Jain (6) in his preparation of iso-propyl chloroformate has observed an alternative catalysis by Lewis acids: e. g. aluminium trichloride, liquified phosgene added to iso-propyl alcohols containing certain amounts of $AlCl_3$ at 10-20°C. to give iso-propyl chloroformate in 80-85% yield, compared with 60% yield without the $AlCl_3$ catalyst.

Alkyl chloroformates have also been prepared (7) by the reaction between dialkyl pyro-carbamates and thionyl chloride. After all the sulphur dioxide was evolved, the residue was distilled, the main fraction being identified as the alkyl chloroformates.



$$(ROCO)_2O + SO_2Cl_2 \longrightarrow 2\,RO\overset{O}{\overset{\|}{C}}Cl + SO_2\uparrow \qquad (4)$$

In addition, Douglas (8) has indicated that the direct chlorination of either ethyl or potassium ethylxanthate can give ethyl chloroformate, but in low yields.



$$C_2H_5O\underset{O}{\underset{\|}{C}}SC_2H_5 + Cl_2 \longrightarrow C_2H_5O\underset{O}{\underset{\|}{C}}\,Cl + C_2H_5SO_2Cl^{*} \qquad (5)$$

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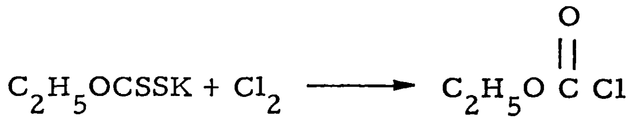
[*] The overall reaction is not understood.



$$C_2H_5OCSSK + Cl_2 \longrightarrow C_2H_5O\overset{O}{\overset{\|}{C}}\,Cl \qquad (6)$$

33%

It should be recognised, however, that most of the aforementioned methods have resulted in low yields of chloroformates. On the other hand, Strain (3) has pointed out that, when an alcohol is reacted with phosgene, a very considerable quantity of heat is evolved, and if this heat is not efficiently removed from the reaction mixture, over-heating of the reaction mixture easily occurs with consequential undesirably low yields. Following this observation, it is interesting to note that a new process has been devised by Strain in which the chloroformates may be prepared in improved yields and purities. According to this process, the chloroformates are prepared by establishing a liquid chloroformate solution of phosgene and adding both alcohol to be chloroformylated and phosgene to the solution. Phosgene is allowed to be vaporised from the solution thereby absorping at least a major proportion of the heat evolved. Further, this allows controlling of the concentration of phosgene so that the temperature of the solution remains above that at which phosgene normally is liquid (10°C.) but below that at which excessive by-product formation occurs.

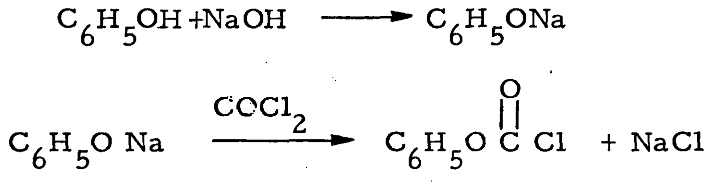
It might be useful to recognise that Strain's article includes many examples to clarify the above mentioned process. It has been applied to many alkyl chloroformates (methyl, ethyl, propyl, butyl), but not to benzyl chloroformate (9) which has been prepared by using a toluene solution of phosgene. Phosgene was passed into benzyl alcohol with cooling, at such a rate that the internal temperature remained between -20 and -30°C. This gave benzyl chloroformate in 91-94% yield.

Recently (10) (1976) however, chloroformates have been shown to be produced commercially by treating alcohols with less than one proportion of phosgene in the gas phase. The products have been shown not to be contaminated by carbonate esters. Propyl alcohol when reacted with phosgene at 120°C in a spherical reactor yields propyl chloroformate in 95% yield. Alternatively, alkyl, hexyl, cyclohexyl and benzyl chloroformates can be produced commercially in tube type reactors (11) at 20 to 60°C. / 20 to 150 atms. to give the chloroformates in 94.5% yields.

I.1.2 Aryl chloroformates.

Aryl chloroformates may be synthesized (12) by the addition of dimethylaniline to solutions of phenols and liquid phosgene in either benzene or toluene solution at temperatures greater than 75°C; phenols are inert towards phosgene at temperatures below 75°C. This method has also been used in the presence of a variety of bases, the yields of aryl chloroformates ranging from 40 to 60%. It was shown that the formation of considerable quantities of the normal carbonate were responsible for the low yields.

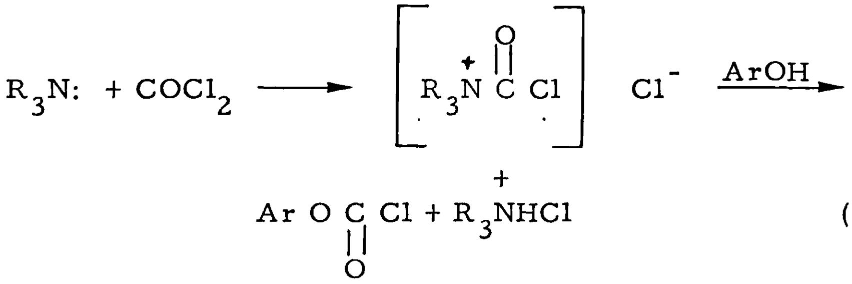
Furthermore, aryl chloroformates (13, 14) have also been prepared by shaking a solution of phosgene in toluene with a solution of phenols in aqueous sodium hydroxide (i. e. sodium phenate). The aryl chloroformates were purified by distillation under reduced pressure.



$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa$$

$$C_6H_5O\,Na \xrightarrow{COCl_2} C_6H_5O\overset{O}{\overset{\|}{C}}\,Cl + NaCl \qquad (7)$$

Amines of the N, N-dimethylaniline and pyridine type have been usefully used as acid acceptors in the preparation of aryl chloroformates in a wide range of organic solvents (15, 16). The effectiveness of tertiary amines in the preparation of aryl chloroformates is again enhanced further by the formation of an intermediate complex salt which behaves as a very reactive acylating agent for the phenol.



$$R_3N: + COCl_2 \longrightarrow \left[R_3\overset{+}{N}\overset{\overset{\displaystyle O}{\|}}{C}Cl \right] Cl^- \xrightarrow{ArOH} ArO\underset{\underset{\displaystyle O}{\|}}{C}Cl + R_3\overset{+}{N}HCl \qquad (8)$$

I. 2. Infrared spectra and structure of chloroformates.

I. 2. 1 Infrared spectra of chloroformates, carbonates and related compounds.

Several researchers have examined the frequencies of carbonyl absorption of the above compounds. They anticipated the influence of the two alkoxy oxygen atoms in carbonates (17) would be to raise the frequency of the carbonyl absorptions above that of the corresponding esters (18, 19). A similar effect due to the chlorine atom would be expected for chloroformates. It was found that for most alkyl and aryl carbonates the carbonyl absorption appears between 1787 and 1757 cm^{-1} (20).

As part of a study of carbonyl group vibration frequencies and intensities in various compounds, the infrared absorption spectra of some chloroformates have been determined with reference to the C=O and C-O vibrations. The absorption spectra of a series of chloroformates (21, 22, 23) have been studied in detail in the range 4000-400 cm^{-1}, both in the vapour state and in solution. Carbon tetrachloride was used as the solvent for the range 4000-1400 cm^{-1} and carbon disulphide for the range 1400 - 400 cm^{-1}. The main bands in the ranges 1850 - 1700 cm^{-1} and 1300 - 950 cm^{-1} of the spectra of these series of chloroformates have been reported and compared with their corresponding carbonates. The results confirm that:

i) $\nu_{c=o}$ for alkyl chloroformates is observed in the relatively narrow range between 1780 and 1775 cm^{-1}, while for dialkyl carbonates it occurred between 1740 and 1755 cm^{-1};

ii) the examination of the spectral bands in the region between 1250 and 1050 cm^{-1} showed that methyl chloroformate has its strongest ν_{c-o} band at 1215 cm^{-1}, the corresponding band occurring at 1195 cm^{-1} in ethyl chloroformate. Further, methyl chloroformate gives rise to two bands, at 1200 and 1147 cm^{-1}, the latter being more intense, whereas ethyl chloroformate has two bands of comparable intensity, 1160 and 1140 cm^{-1}. In other alkyl chloroformates the main ν_{c-o} band is observable , ca. 1160 cm^{-1}.

Moreover, Ory (24) and Potts (25) in their studies of a series of chloroformates, thiol chloroformates, carbamyl chlorides and their derivatives reported that the presence of a carbon-carbon double band, e. g. in phenyl and allyl chloroformates, raises the value of $\nu_{c=o}$ similar to that observed in alkenyl carbonates and vinyl esters (2). Thus, allyl chloroformates absorb at 1799 cm^{-1} and phenyl chloroformates at 1784 cm^{-1} (22).

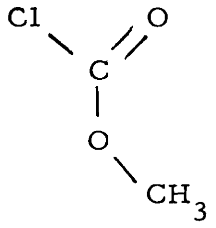
Potts (25), Katritzky (26) and Baker (27) in their investigation of alkyl and aryl thiol chloroformates found that alkyl derivatives absorb between 1772 and 1766 cm^{-1} and the aryl compounds absorb between 1775 and 1769 cm^{-1}. These values for $\nu_{C=O}$ were found to be reasonable in relation to the chloroformates. Morevoer, they quote that carbonyl frequencies of alkyl and aryl derivative in carbamyl chlorides ($R_2N\ CO\ Cl$) occur in the region 1745 - 1739 cm^{-1}. Halogen substitution on the alkyl substituents raises the carbonyl frequencies in carbonates to 1832 cm^{-1}, and for chloroformates α-halogen substitution raised the carbonyl absorption to 1973-1806 cm^{-1}, whilst a similar β substitution has no effect (23).

The carbonyl vibration absorption bands of methyl, (28), ethyl, n-butyl and sec-butyl chloroformates were investigated (19), in carbon tetrachloride solution and compared to a series of analogous carbonates, ring-substituted N-methyl benzamides and N-methyl acetanilides. These investigations suggested that the inductive effect is responsible more for the variation in vibration frequencies whilst the mesomeric effect affects more the intensities of the absorption bands. The use of band intensities accordingly can sometimes solve problems in structural determination where different groups share the same vibration frequency.

I. 2.2 Structure of chloroformates

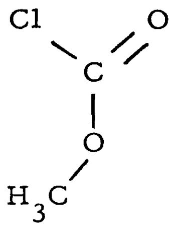
The Raman and infrared spectra of methyl chloroformate in carbon tetrachloride (3600 - 1400 cm^{-1}) and in carbon disulphide (1400 - 400 cm^{-1}) have been studied by Collingwood, Lee and Wilmshurst (29). They showed that there was a barrier to rotation around the carbonyl carbon-ether oxygen bond. Accordingly, they pointed out that there are two possible conformations for the methyl chloroformate molecule, viz. cisoid and transoid, illustrated as follows:

cisoid conformation



I. 2.1

transoid conformation



I. 2.2

Their study sought to determine whether the molecule normally existed in the cisoid or the transoid conformation and they concluded that methyl chloroformate exists normally in the cisoid conformation. This observation was based on the analysis of the fundamental vibrational frequencies of methyl chloroformate, methyl formate and methyl acetate.

Further, the vapour state spectrum showed the three types of bands expected for molecules having the cisoid conformation and none of those expected for the transoid conformation.

Electron diffraction (30, 31) has also been used to confirm the cisoid conformation of the methyl chloroformate molecule. By such means also the bond distances and bond angles were ascertained (32) for methyl together with those for ethyl and iso-propyl chloroformates.

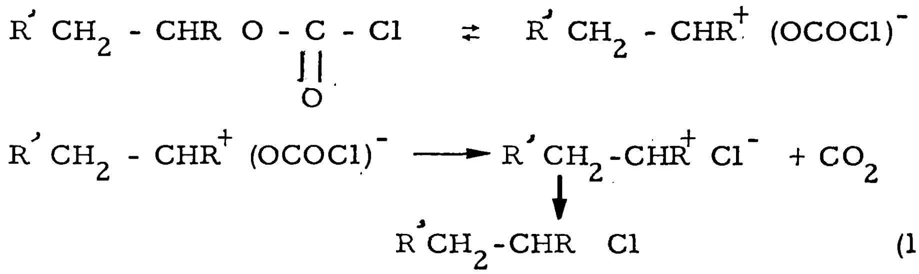
I. 3 Decomposition of chloroformates.

Generally, alkyl and arylalkyl chloroformates evolve carbon dioxide on strong heating and furnish the corresponding alkyl chloride (5, 33). This reaction may be catalysed by tertiary bases, aluminium chloride, and boron trifluoride. An alternative to the chloride formation, i. e. by a substitution reaction, elimination products may be obtained. These two overall processes are illustrated as follows:-

$$R'CH_2\text{-}CHR\ OCOCl \xrightarrow{\Delta} \begin{cases} R'CH_2\text{-}CHR\ Cl + CO_2 & (9) \\ R'CH=CHR + CO_2 + HCl & (10) \end{cases}$$

The decomposition of alkyl chloroformates (34) to yield the corresponding chloride and carbon dioxide, has been expressed in terms of two alternative mechanisms:

a) Tight ion-pair process:

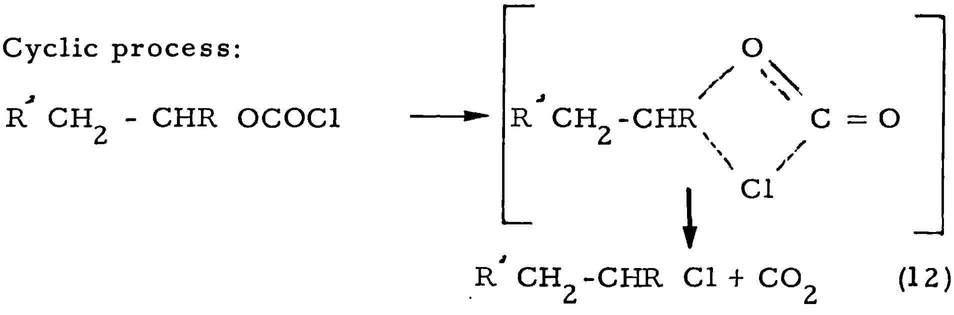


$$R'CH_2 - CHR\ O - \underset{\underset{O}{\|}}{C} - Cl \rightleftharpoons R'CH_2 - CHR^+\ (OCOCl)^-$$

$$R'CH_2 - CHR^+\ (OCOCl)^- \longrightarrow R'CH_2\text{-}CHR^+\ Cl^- + CO_2 \longrightarrow R'CH_2\text{-}CHR\ Cl \qquad (11)$$

This ionic process will indicate a large increase in rate as the solvent ionizing power is increased (35).

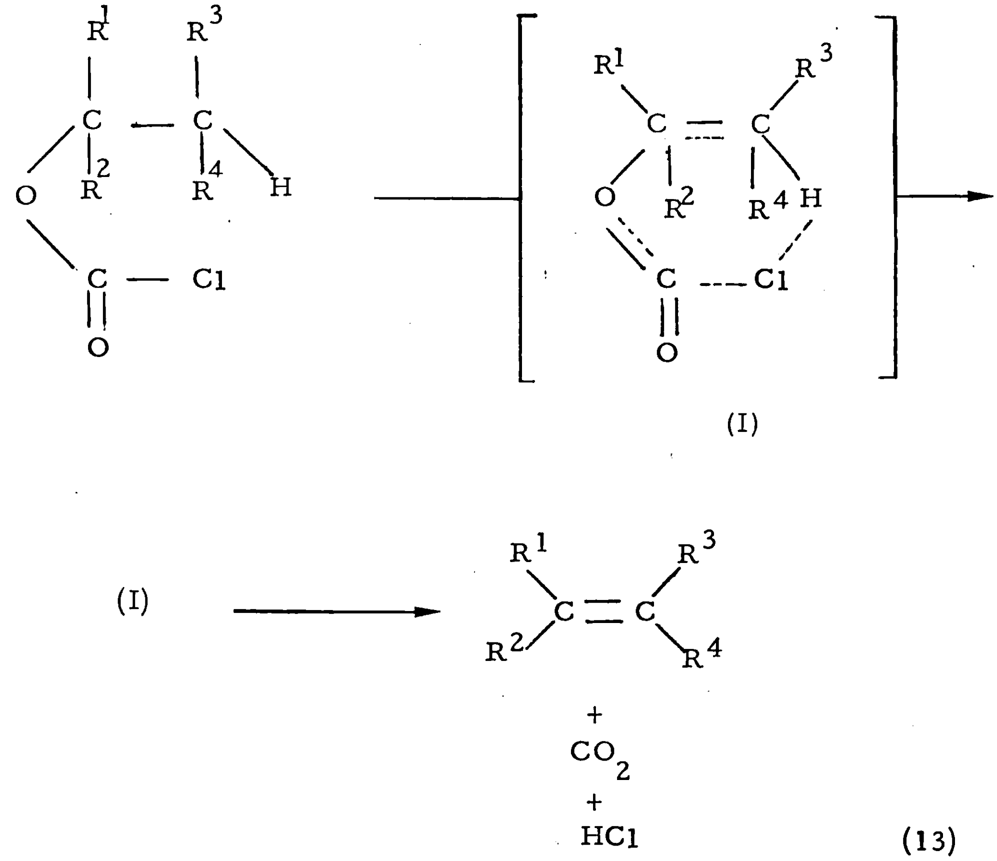
b) Cyclic process:



(12)

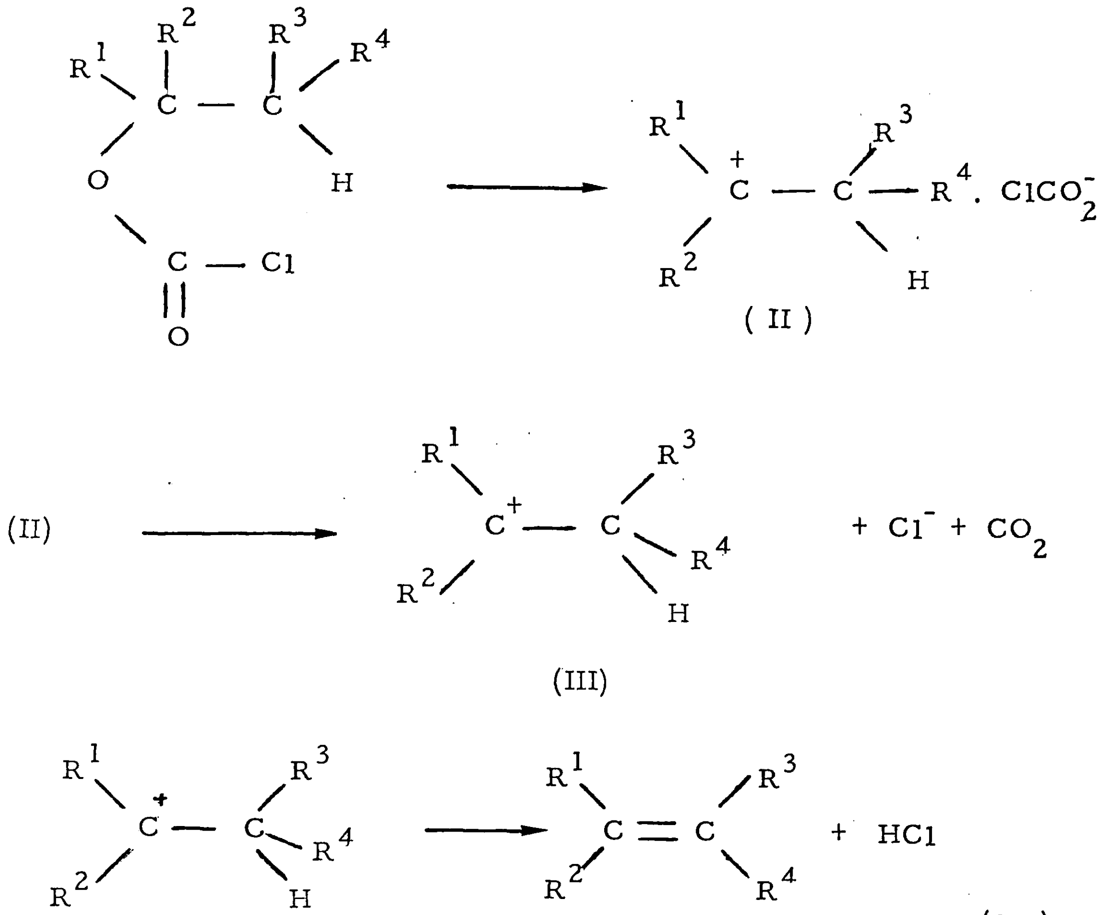
This covalent process will show only a moderate response to variation in solvent-ionizing power (35).

If β-hydrogens are present then there can be competition between the four-centred transition state (36) leading to substitution (equation 12) and a six-centred transition state leading to elimination (equation 13). This elimination reaction has been shown to be completely stereospecific giving syn-elimination. The transition states have been described as possessing substantial charge separation leading to the formation of different alkenes by loss of different β-hydrogens



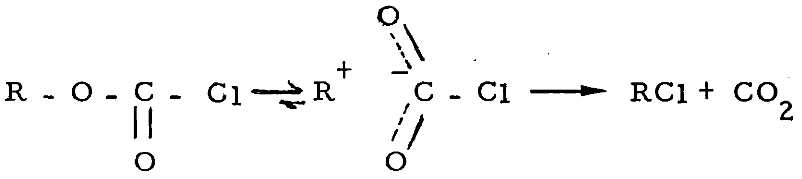
(13)

Alternatively, if an ionic process operates, there will be a common step involving formation of the ion-pair. This ion-pair (37, 38) may either collapse to a substitution product or else the counter ion abstracts a proton from the carbonium ion (39). While an ionic process does not demand a syn-elimination, it is possible to visualise if a very rapid proton extraction occurs, it could find the chloride ion ideally situated for this type of process:



(14)

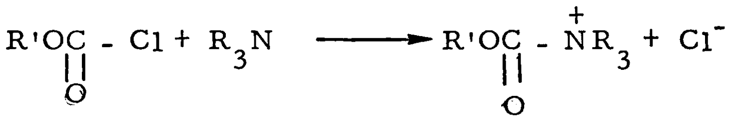
Some of the important results of mechanistic studies are now reported. The rates of decomposition of a number of substituted α-phenylethyl chloroformates (33) were determined in both toluene and dioxan solution by the rate of the formation of carbon dioxide. First-order rate plots were obtained. Good Hammett plots (40, 41) gave ρ values of -3.86 in dioxan and -3.56 in toluene. The values of the enthalpies and entropies of activation were found to be lower in toluene than in dioxan (42, 43). Benzyl chloroformate was found to decompose in dioxan, slower than the α-phenylethyl chloroformate (44) whereas neopentyl chloroformate was found to be unreactive. These data presented evidence of a carbonium ion process:



$$R-O-\underset{\underset{O}{\|}}{C}-Cl \rightleftharpoons R^{+}\ {}^{-}\overset{O}{\underset{O}{C}}-Cl \longrightarrow RCl + CO_2$$

(15)

The presence of tertiary amines (45, 46, 47) was found to assist the decomposition of chloroformates. A nucleophilic substitution at the acyl carbon, is followed by nucleophilic substitution by the displaced chloride ion at the α-carbon.



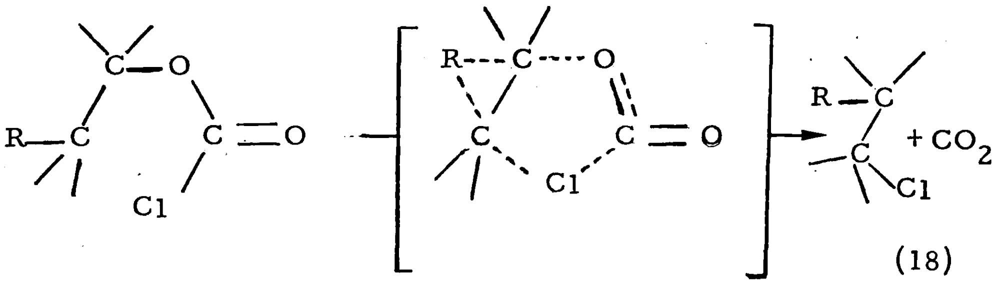
$$R'O\underset{\underset{O}{\|}}{C}-Cl + R_3N \longrightarrow R'O\underset{\underset{O}{\|}}{C}-\overset{+}{N}R_3 + Cl^-$$

(16)

$$\overset{-}{Cl} + R'O\underset{\underset{O}{\|}}{C}-\overset{+}{N}R_3 \longrightarrow ClR + CO_2 + R_3N$$

(17)

This mechanism is proposed from observations of the effect of the presence of chloride ion or addition of pyridine hydrochloride to the decomposing of n-butyl, iso-butyl, n-pentyl and iso-pentyl chloroformates. An alternative process involving a concerted displacement rearrangement was also mentioned (56) as a possibility. Such a process could proceed by way of a five-centred transition state:



(18)

Olefin by-products may arise by elimination from a carbonium ion, possibly after the rearrangement particularly in secondary chloroformates which give alkenes as the main by-products.

The decomposition of neopentyl chloroformate (33) was found to be very slow and the products were completely rearranged with 20 parts of t-pentyl chloride for each part of alkene (19% 2-methyl-1-buene; 81% 2-methyl-2-butene).

Olivier and Young (48) noted the similarity between the relative rates of liquid-phase decomposition of chloroformates and the stability of carbonium ions (as indicated by the behaviour of alkyl chloride in hydrolysis (49)). They found them to be in the sequence: triphenylmethyl (50) > benzhydryl (50) > t. alkyl (51, 52, 53) α-phenylethyl (33) > 1-adamantyl > 1-methylallyl > 3-methyl allyl (48) > benzyl(33), secondary alkyl(54) > primary alkyl(54) ≫ phenyl (5).

t-Alkyl chloroformates have been studied by Choppin and Frediani (55) who reported that s-butyl chloroformate decomposes rapidly above 10°C to yield carbon dioxide, isobutylene and hydrogen chloride rather than t-butyl chloride; t-pentyl chloroformate also has been reported, by Sakakibara (53), to be slightly more stable.

Kevill (106) has reported that iso-propyl chloroformate decomposes in acetonitrile at 25°C, slowly producing chloride ion. He observed a first-order rate coefficient of 2.0×10^{-7} sec.$^{-1}$ Later, (34) he reported that 1-adamantyl chloroformate decomposes in n-decane giving only 1-adamantyl chloride but in benzene solution it gives a very small amount of hydrochloric acid (0.5% at 25.2°) with a 94% yield of 1-adamantyl chloride. Although still generally small, increased amounts of acid production accompany the decomposition in nitrobenzene and in mixtures of nitrobenzene with benzene. At 54.2°C.,it has been found that the relative rates of decomposition of 0.06M solution in decane, benzene, and nitrobenzene are 1:1260:205,000. Further, the addition of tetra n-butylammonium chloride modestly accelerated the decomposition of 1-adamantyl chloroformate in nitrobenzene.

Gas-phase reactions of chloroformate esters have been studied in detail (55) and led to a general pattern of molecular elimination reactions (57). These can proceed, as in the liquid phase, to both substitution and elimination products.

$$\mathrm{R\,CH_2 - CHR'\,OCOCl} \xrightarrow{\Delta} \begin{cases} \mathrm{R\,CH_2CHR'\,Cl + CO_2} & (19) \\ \mathrm{R\,CH{=}CHR' + HCl + CO_2} & (20) \end{cases}$$

Since gas phase decompositions of chloroformates have been carried out at higher temperatures than in the liquid phase, and the elimination reactions usually have higher activation energies than the corresponding substitutions (58), elimination in the gas phase accounts for a greater proportion of the overall decomposition products.

Lewis and Witte (59) studied benzyl and allylic chloroformates and they found that only allyl chloroformate decomposed with exhibition of a linear Arrhenius plot, even at lower temperatures whereas benzyl,1-methylallyl and 3-methylallyl all gave curved Arrhenius plots. The curvature indicated the reactions proceeded by both low activation energy heterogenity, and a high activation energy homogeneity.

Alkyl chloroformates have been studied in a wide range from (1940-1969) Ref. (60-65, 67 and 68) by Choppin, Lewis and Matzner (5). For ethyl chloroformate, Choppin et al.(55, 62) found decomposition to take place at $150-195^{\circ}$ in an all glass system, with ethyl chloride and carbon dioxide the only products and having $10^4 k_1 = 1.3$ and 30 s^{-1} at 150° and 195° respectively. Roberts et al. (63) found it somewhat unreliable but slower decompositions at 280 - 330°C gave ethylene as well as ethyl chloride.

Later Johnson (69), Johnson and Stimson (70) in their investigation of the decomposition of ethyl chloroformates, (followed by means of pressure change measurements (± 0.2 mm Hg). They reported that ethyl chloroformate decomposes at measurable rates between 286 and 535°C, in agreement with the results of Roberts et al. (63). The products were, ethylene, ethyl chloride, hydrogen chloride and carbon dioxide. The elimination of ethylene, always the main reaction (2), equation (20) obeyed first-order kinetics over the extent of the reaction and independent of initial pressure. Moreover, they reported (71) that the only product of decomposition of methyl chloroformates was methyl chloride and carbon dioxide as this compound cannot undergo elimination. The rate constants at 240°C were found to be 1.170 and 0.533 10^{-5} sec^{-1} for ethyl and methyl chloroformates respectively. The lower rate for methyl chloroformate may be in part due to the lower electron release (Me $<$ Et).

Isopropyl chloroformate was similarly investigated (72) and was found to decompose in clean glass vessels, at least in part, by a heterogeneous reaction. Both substitution and elimination products were observed in the temperature range of 220 - 232°C., with 45 - 52% of overall reaction being elimination.

The relative rates observed (73) for decomposition of ROCOCl at 240°, as R is varied, were Me. 1, Et. 2.2 (74), iso-pr. 220, sec. but. 640 s^{-1} (1). The acceleration by α-substitutions was considered to indicate a rather polar transition state with positive charge development on the α-carbon. Maccoll (75) in his studies of ethyl, iso-propyl and sec-butyl chloroformates found the rates of decompositions parallelled very closely those of the corresponding chlorides and suggested an ion-pair transition state of the type $R^{+}\ CO_2Cl^{-}$ in the case of chloroformates analogous to $R^{+}\ X^{-}$ in the case of halides.

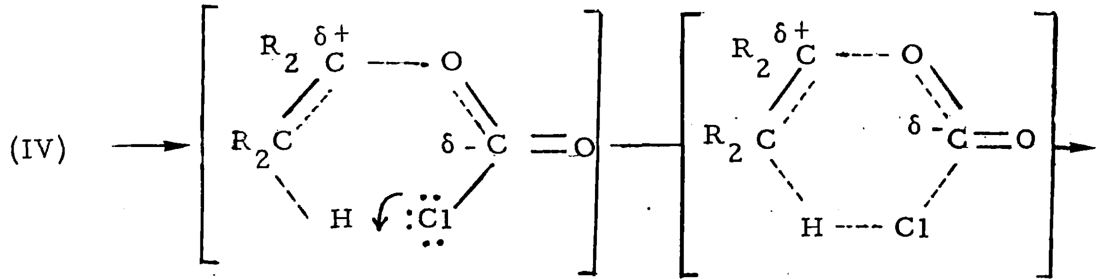
Stereochemical studies (76, 77 and 64) of the decomposition of chloroformate esters, showed that optically active sec.butyl chloroformates gave sec.butyl chloride with complete retention of configuration. Erytho- and threo- sec. butyl-3-d, chloroformates had deuterium contents (78) requiring a completely stereospecific syn-elimination. The observation of a small kinetic isotope effect suggests the formation of intermediate having the some charge separation.

The stereochemistry was consistent with four- and six-membered cyclic transition states for substitution and elimination following a reversible charge separation (See IV).

$$R_2CH\text{-}R_2COCOCl \underset{fast}{\overset{slow}{\rightleftharpoons}} R_2CH\text{-}R_2\overset{\delta+}{C}\text{----}\overset{\delta-}{O}COCl \qquad (21)$$

(IV)

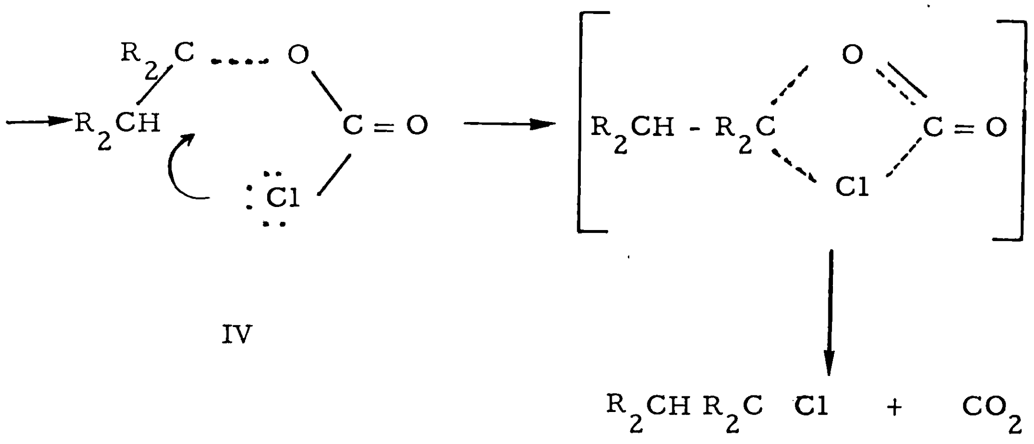
The elimination scheme (competitive with the substitution process) can be visualized as follows:



(22)

$$(V) \longrightarrow R_2C = CR_2 + CO_2 + HCl$$

The mechanisms to give the substitution product with retention of configuration and without rearrangement, and which also incorporate the observed facilitation by alkyl group substituents, could be illustrated as follows:



(23)

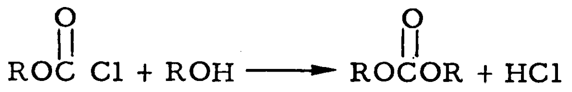
I. 4 Hydrolysis of alkyl chloroformates

I. 4. 1. In the aqueous medium

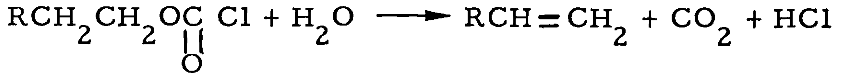
Roese (79) and Nekrassow et al. (80) stated early in the nineteenth century that chloroformate esters react with water to give the corresponding alcohol or phenol and hydrogen chloride, with evolution of carbon dioxide:

$$ROCOCl + H_2O \longrightarrow ROH + HCl + CO_2 \qquad (24)$$

The reaction of water with alkyl chloroformates was found to be complicated by the presence of a side reaction. This may be explained as resulting from the reaction between the alcohol, first formed in the hydrolysis, with further chloroformate, giving a disubstituted carbonate (eqn. 25). In addition, the probability exists for the formation of alkenes during the hydrolysis, (eqn. 26).

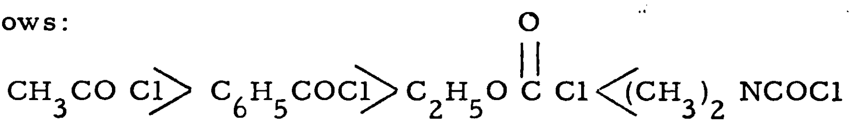


$$\mathrm{ROC(=O)Cl + ROH \longrightarrow ROC(=O)OR + HCl} \qquad (25)$$



$$\mathrm{RCH_2CH_2OC(=O)Cl + H_2O \longrightarrow RCH{=}CH_2 + CO_2 + HCl} \qquad (26)$$

Hall (81), in his investigations of the kinetics and mechanisms of the hydrolysis of ethyl chloroformate,undertook parallel investigations with acetyl-,benzoyl-, dimethylcarbamyl- chlorides. The rate sequence for the above series was found to be as follows:



$$\mathrm{CH_3CO\,Cl > C_6H_5COCl > C_2H_5OC(=O)Cl < (CH_3)_2NCOCl}$$

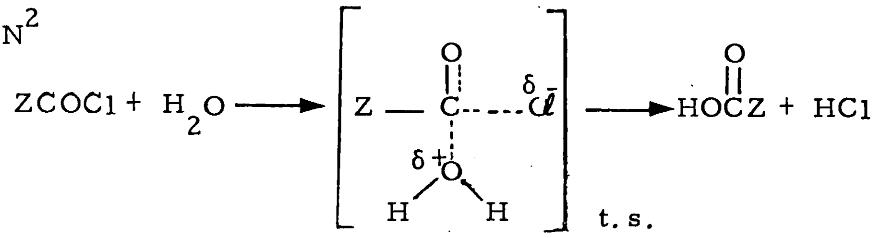
Ethyl chloroformate has a first-order hydrolysis rate constant of 3.5×10^{-4} $\mathrm{sec^{-1}}$ in water at 25°C., which can be increased by the addition of alkali, sodium chloride or sodium perchlorate. The hydrolysis of ethyl chloroformate in pure water has an activation energy of 79.49 k Joule $\mathrm{mole^{-1}}$ and an entropy of activation of -51.9 J $\mathrm{mol^{-1}K^{-1}}$. The entropy of activation for dimethyl carbamyl chloride was +23.4 J $\mathrm{mol^{-1}K^{-1}}$. Both the sequence in reaction rates and the differences in the entropies suggest a change in the mechanism of hydrolysis from acetyl chloride and ethyl chloroformate to dimethylcarbamyl chloride. It is suggested that carbamyl chloride hydrolyses by an S_N1 mechanism, whereas ethyl chloroformate and carboxylic acid chlorides hydrolyse by an S_N2 mechanism as follows:

S_N1

$$\mathrm{(CH_3)_2NCO\,Cl \rightleftarrows (CH_3)_2\overset{+}{\overset{\frown}{NCO}} + Cl^-}$$

$$\xrightarrow{H_2O} \mathrm{(CH_3)_2NCOOH + H^+} \qquad (27)$$

S_N2



(28)

$Z = CH_3, C_6H_5$ and C_2H_5O

Fourholt (82) in his study of the bimolecular hydrolysis of ethyl chloroformate pointed out that the ethyl hydrogen carbonate (HOCOZ with $Z = OC_2H_5$) formed in the first step, decomposes rapidly to yield ethanol and carbon dioxide. This can be represented by equation 29 .

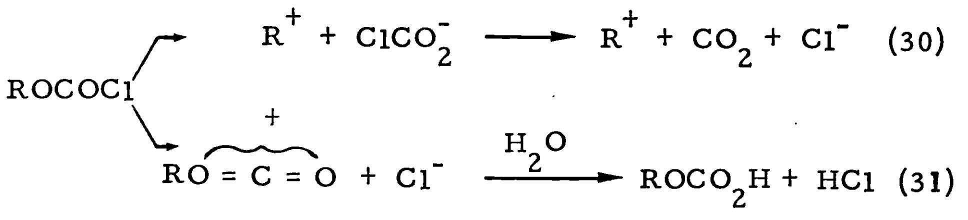
$$C_2H_5OCOOH \longrightarrow C_2H_5OH + CO_2 \qquad (29)$$

The hydrolysis of several alkyl chloroformates (e.g. methyl, ethyl and iso-propyl) have been studied by Crundon and Hudson (83). In 65% aqueous acetone they obtained the rate sequence for the hydrolysis $CH_3 > C_2H_5 < iso\text{-}C_3H_7$ but in formic acid containing 1% water they observed the rates $CH_3 < C_2H_5 \ll iso\text{-}C_3H_7$. This reaction when carried out in the presence of sodium formate shows only small increases in their respective rates, viz. 7% (iso-Pr) and 27% (Et).

Crunden and Hudson concluded from their investigations that increasing the electron donation to the carbonyl group, changes the mechanism of the hydrolysis from a bimolecular displacement at the carbonyl group, i.e. as observed with methyl and ethyl chloroformates in aqueous acetone, to a unimolecular process, i.e. with iso-propyl chloroformate.

Two postulated mechanisms have been reported for the S_N1 hydrolysis as follows:

(R = iso-Pr)

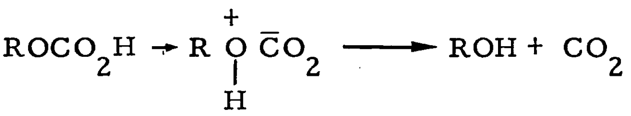


$$ROCOCl \rightarrow R^{+} + ClCO_2^{-} \longrightarrow R^{+} + CO_2 + Cl^{-} \qquad (30)$$

$$ROCOCl \rightarrow \overset{+}{RO}=C=O + Cl^{-} \xrightarrow{H_2O} ROCO_2H + HCl \qquad (31)$$

Two steps have been reported for the bimolecular process. The first step of the reaction gives the monoalkyl carbonate and the second step decomposition of that intermediate.

$$ROCOCl + H_2O \longrightarrow ROCO_2H + HCl \qquad (32)$$

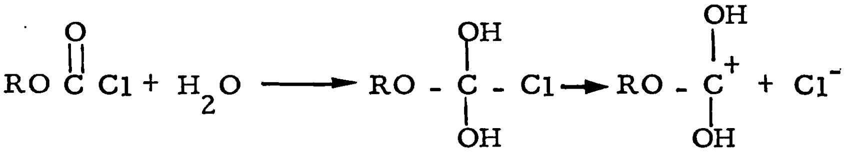


$$ROCO_2H \rightarrow R\overset{+}{\underset{H}{O}}\overline{C}O_2 \longrightarrow ROH + CO_2 \qquad (33)$$

Garner and Lucas (84) suggested that the second step (eqn. 33) proceeds with retention of configuration.

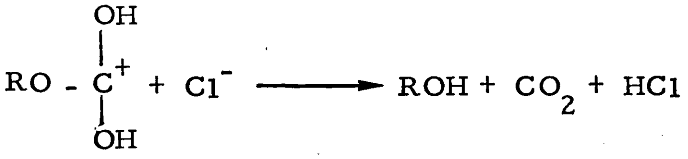
Kivinen (85) has carried out a study of the kinetics of hydrolysis of ethyl chloroformate in deuterium oxide and observed a solvent isotope effect of 1.95 which is similar to that found for other acid chlorides. In a separate study (86) he had examined the hydrolysis of ethyl chloroformate in different solvent (87) composition mixtures of water, methanol and ethanol. The value of the entropy of activation was -100.4, -142.3 and -141.0 J $mol^{-1}K^{-1}$ respectively. On the basis of his results, and comparing the values with those for S_N2 hydrolysis of alkyl halides, he was of the opinion that the hydrolysis of chloroformates proceed by a simple S_N2 reaction. However, these $\Delta S^{\ddagger}$ results are much more negative than for simple S_N2 reaction <u>vide infra</u>.

Queen (88) however, has studied the hydrolysis of methyl, ethyl, propyl, iso-propyl chloroformate and dimethyl carbamyl chloride in water at temperatures ranging from 0°C. to 50°C., and determined the activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and ΔCp . His results, showing more negative values of $\Delta S^{\ddagger}$ (Me ,-79. 5 and Pr, -69.5) than might be expected (89, 90) for S_N2 displacements (-50 J $mol^{-1}K^{-1}$), he said were indicative of the more ordered transition state leading to tetrahedral intermediates (T. 1).



$$RO\overset{O}{\overset{\|}{C}}Cl + H_2O \longrightarrow RO - \underset{OH}{\overset{OH}{C}} - Cl \longrightarrow RO - \underset{OH}{\overset{OH}{C^+}} + Cl^-$$

(T.I.)



$$RO - \underset{OH}{\overset{OH}{C^+}} + Cl^- \longrightarrow ROH + CO_2 + HCl \qquad (34)$$

I. 4. 2 <u>Reactions of alkyl chloroformates with alcohols.</u>

Alkyl chloroformates react with aliphatic alcohols to give disubstituted carbonates and hydrogen chloride(equation 35), but the corresponding reaction with phenols does not occur, even at high temperatures.

A kinetic study of the reaction between aliphatic alcohols and chloroethyl, methyl, ethyl and iso-propyl chloroformates by Leinu (91) has shown the relative reactivity to be $ClCH_2CH_2 > CH_3 > C_2H_5 > i\text{-}C_3H_7$.

$$ROCOCl + MeOH \longrightarrow ROCOOMe + HCl \qquad (35)$$

I. 5 Kinetics and mechanisms of nucleophilic substitution reactions of alkyl chloroformates.

General.

Kinetic studies of chloroformates (5, 56) are often dealt with and viewed from different angles. In this context, perhaps a few examples will show to what extent there has been divarication.

Bimolecular substitution reactions of chloroformates can be summarised by the reaction:

$$\mathrm{ROCOCl} + \mathrm{Y}^- \longrightarrow \mathrm{ROCOY} + \mathrm{Cl}^- \longrightarrow \text{product} \qquad (36)$$

The isolated product depends on the stability of ROCOY. For example, when the nucleophile, Y^- is either fluoride or azide ion, then stable products can be isolated, i. e. fluoroformate and azidoformate. With iodide (92, 93) or nitrate ions the ROCOY formed is less stable and decomposes to give carbon dioxide and RY as products.

The reactivity of anions towards chloroformate esters has been studied by Green and Hudson (94, 95). They obtained the bimolecular rate constants of the reactions of ethyl chloroformate with different ions in aqueous acetone solution at 25.0°C. The following values of $k_2(\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{sec}^{-1})$ were found:

F^-, 0.24; N_3^-, 17.2 ; NO_2^-, 32.2 ; $Ph\bar{O}$, 90.6; acetoxime 506 x 10^3 and OH^-, 169. Their investigations showed that the reaction between ethyl chloroformate and some nucleophiles may proceed through tetrahedral intermediates. Differences in the relative nucleophilicities towards various alkyl and acyl carbon atoms are discussed in terms of the activation parameters leading to the transition states. Later, Hudson and Green (95) concluded that the nucleophilic reactivity varies with the nature of the reaction and with the reaction conditions, but not with the basicity. Many nucleophilic reactions of chloroformates have been carried out using silver salts. In particular considerable attention has been given to the reactions of chloroformates with silver nitrate.

I. 5. 2. Reactions of chloroformates with silver salts.

Boschan (96) in 1959 reported the preparation of aliphatic nitrate esters in high yields by the reaction of silver nitrate with aliphatic chloroformates. The method of synthesis of these nitrate esters consists of the treatment of alkyl chloroformates with silver nitrate in an inert solvent such as acetonitrile, and the overall reaction appears to be:

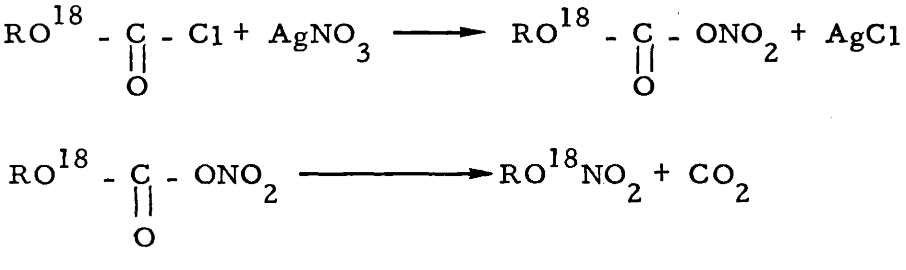
$$ROCOCl + AgNO_3 \longrightarrow RONO_2 + AgCl \qquad (37)$$

An attempt has been made by Boschan to examine the mechanism of this reaction by stereochemical, labelled oxygen and kinetic studies. The stereochemical studies utilised optically active 2-octyl chloroformate which showed that the reaction proceeded mainly with retention of configuration. (70% retention, 30% inversion at the at the 2-octyl group in acetonitrile solution).

For the ^{18}O oxygen studies of n-hexyl chloroformates, a series of transformation of the reaction products degraded these to carbon dioxide. The ^{18}O content was measured by mass spectrometry and compared with the amount of ^{18}O in carbon dioxide obtained from the direct decomposition of hexyl chloroformate.

The results showed that 75% of the n-C_6H_{13}-O bonds in the hexyl chloroformate remained intact during the reaction with silver nitrate. Kinetic studies of n-hexyl chloroformate with silver nitrate in acetonitrile showed that the rate of reaction, which was determined as the rate of evolution of carbon dioxide, obeyed approximately second order kinetics. Deviation from the simple second-order was explained as resulting from the existence of a partially unstable intermediate.

The proposed mechanism is as shown in Scheme (A).

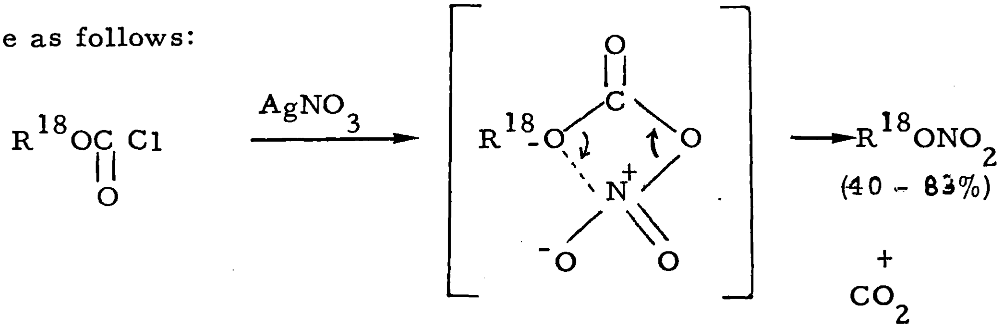


$$RO^{18}-\underset{\underset{O}{\|}}{C}-Cl + AgNO_3 \longrightarrow RO^{18}-\underset{\underset{O}{\|}}{C}-ONO_2 + AgCl \qquad (38)$$

$$RO^{18}-\underset{\underset{O}{\|}}{C}-ONO_2 \longrightarrow RO^{18}NO_2 + CO_2 \qquad (39)$$

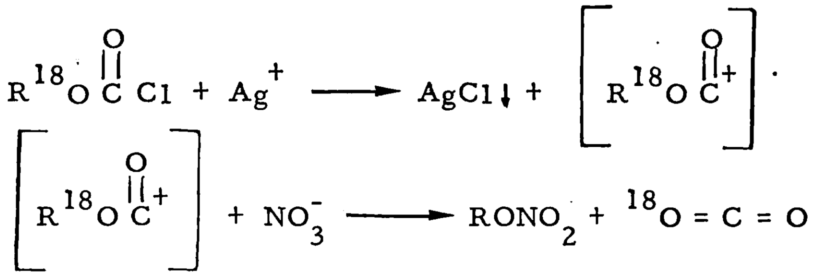
Scheme (A).

Hence, it was postulated that an S_Ni-type of decomposition of this intermediate,to give the nitrate ester and carbon dioxide, was operative. These studies assume a sort of intramolecular cyclic mechanism through a four-centred transition state as follows:



(40)

Alternatively (56), some reactions of chloroformates with silver nitrate were thought to be occurring by an ionic mechanism as shown in the scheme (B) (eqn. 41 and 42).



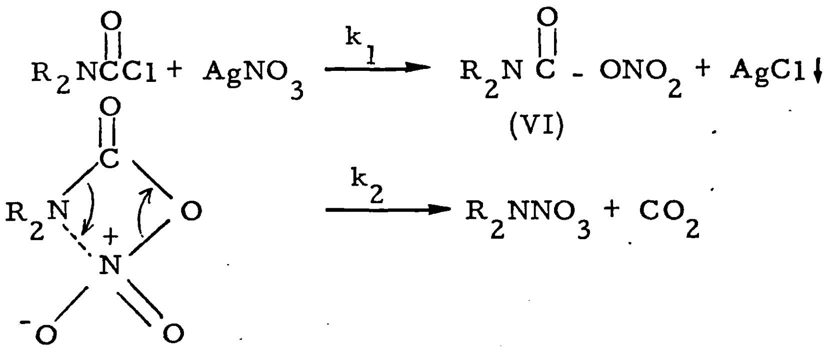
$$R^{18}OC(=O)Cl + Ag^+ \longrightarrow AgCl\downarrow + \left[R^{18}OC^+(=O)\right] \qquad (41)$$

$$\left[R^{18}OC^+(=O)\right] + NO_3^- \longrightarrow RONO_2 + {}^{18}O=C=O \qquad (42)$$

Scheme (B).

This scheme is similar to the mechanism ascribed to the decomposition of optically active alkyl chlorosulfites reported by Boozer and Lewis (97) which suggested that the elimination reaction from secondary alkyl chlorosulphinates is ionic in character.

Further, Boschan has reported a few examples in which compounds similar to chloroformates react with silver salts in line with scheme (A). An example of a similar type of reaction is that reported by Norris (98) in which dialkylcarbamyl chlorides react with silver nitrate in acetonitrile to give dialkylnitramines (14-48%) as a main product. He further determined the rate determining step to be represented by equation 43 with a value of k_1 of $1.5 \times 10^{-2}\ dm^3\ mol^{-1}\ sec^{-1}$ at 38.9°C.



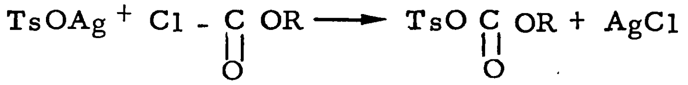
$$R_2NC(=O)Cl + AgNO_3 \xrightarrow{k_1} R_2NC(=O)-ONO_2 + AgCl\downarrow \qquad (43)$$

(VI)

$$\xrightarrow{k_2} R_2NNO_3 + CO_2 \qquad (44)$$

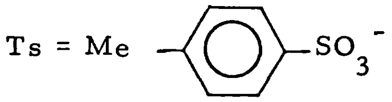
(VI)

In addition to this example, the reaction of silver p-toluene sulphonate (tosylate) with methyl and ethyl chloroformates in acetonitrile has been reinvestigated by Yamamoto (99, 100). It was found that the reaction gives initially carboethoxy p-toluenesulphonate and this may be then decomposed by heating to give the alkyl tosylate as follows:

 (45)

$$TsOAg + Cl - \underset{\underset{O}{\|}}{C}\,OR \longrightarrow TsO\,\underset{\underset{O}{\|}}{C}\,OR + AgCl \qquad (45)$$

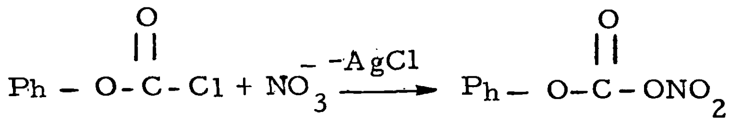
$$TsOC\,OR \longrightarrow T.sOR + CO_2 \qquad (46)$$



In a similar reaction of silver tosylate with iso-butyl chloroformate it led to both iso-butyl and sec-butyl tosylate plus iso-butene.

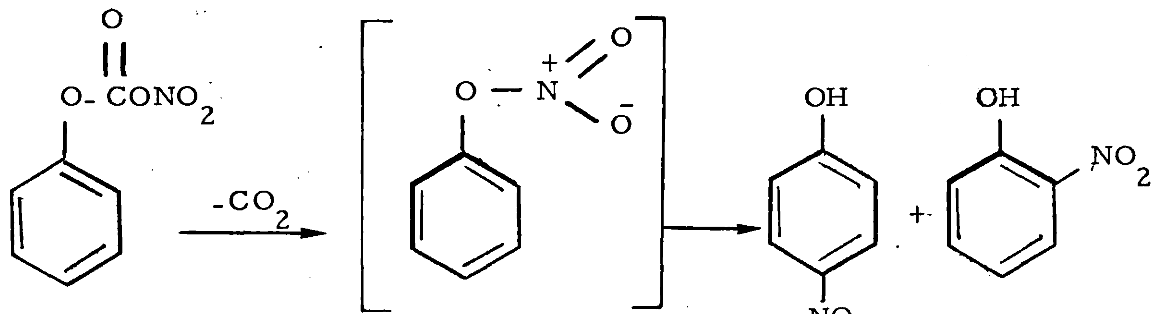
No similar comparison could be made with tert.-butyl chloroformate as this compound is inherently unstable (101).

There have been several investigations of the reaction of alkyl chloroformates with silver nitrate in acetonitrile. This reaction is discussed in Sec. I. 5. 3. Aryl chloroformates however do not react with silver nitrate in acetonitrile to give nitrate esters (e.g. phenyl nitrate), but usually give nitro substituted phenols (102, 103). The mechanism for the rearrangement in this reaction was suggested to be as follows:

 (47)

$$Ph - O-\overset{O}{\overset{\|}{C}}-Cl + NO_3^{-} \xrightarrow{-AgCl} Ph- O-\overset{O}{\overset{\|}{C}}-ONO_2 \qquad (47)$$

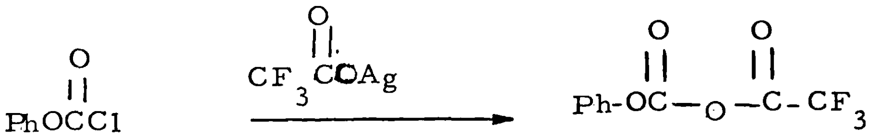
(VIII)



(VIII)

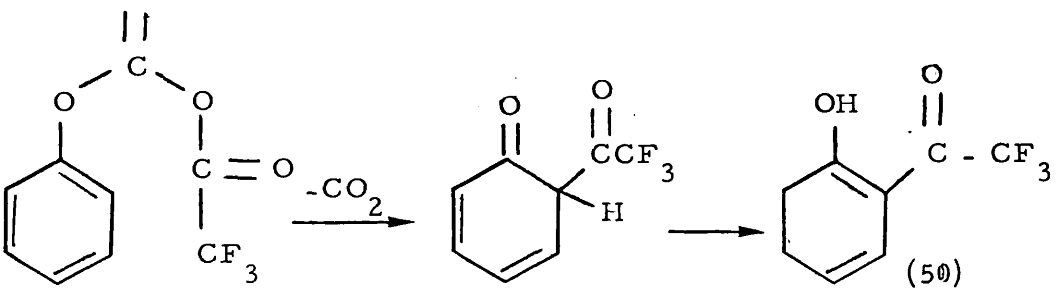
(48)

This mechanism had been suggested before (103) for a similar reaction with silver trifluoroacetate in which 2-hydroxyphenyl, trifluoromethyl ketone was obtained in 95% yield as follows:



$$\mathrm{PhO\overset{O}{\overset{\|}{C}}Cl} \xrightarrow{\mathrm{CF_3\overset{O}{\overset{\|}{C}}OAg}} \mathrm{Ph\text{-}O\overset{O}{\overset{\|}{C}}\text{—}O\text{—}\overset{O}{\overset{\|}{C}}\text{-}CF_3} \qquad (49)$$

(IX)



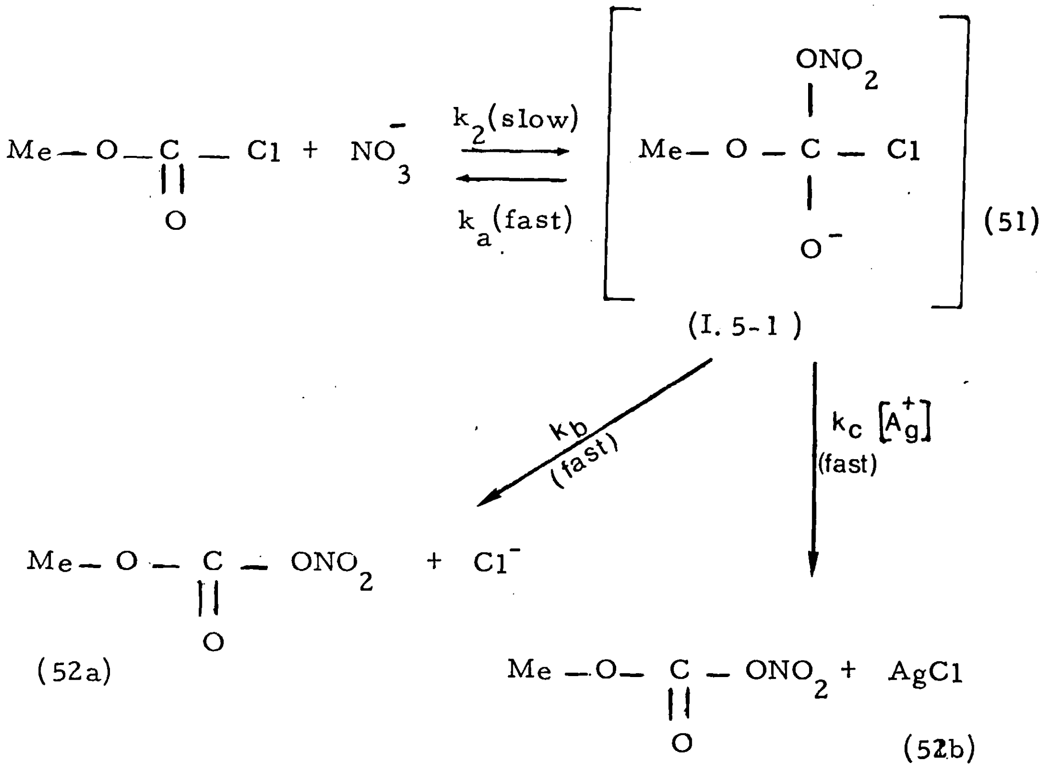
(IX)

(50)

I. 5. 3. Reactions of alkyl chloroformates with nitrate ion:

Several kinetic investigations have been carried out to study the mechanism of the reaction between alkyl chloroformates and silver nitrate in order to prove the existence of tetrahedral intermediates in the replacement reaction at the carbonyl carbon for this reaction.

Much detailed work has been done by Kevill and Johnson (104) to investigate the two mechanisms which were earlier proposed by Boschan (96) (I. 5. 2.). In their investigation of the mechanism (B) they found that while there was a reaction between methyl chloroformate and acetonitrile solutions of silver nitrate, there was no reaction between methyl chloroformate and silver perchlorate. They interpreted this as the lack of any electrophilic assistance to chloride ion removal as shown in scheme (B), (eqn. 42). Accordingly they preferred the formation of methyl nitratocarbonate via a tetrahedral intermediate as in Scheme (C), which is a modified Scheme (A).



Scheme C.

The reaction of methyl chloroformate and silver nitrate in acetonitrile solution at 25°C has been followed quantitatively by the precipitation of silver chloride.

Good second order kinetics during the first 25% of the reaction have been observed with a second order rate coefficient k_2^o, related to the silver nitrate concentration by (eqn. 53).

$$k_2^o = \frac{k_2 k_b\, \alpha/(k_a + k_b) + [k_2 k_c \alpha^2/(k_a + k_b)]\,[\mathrm{AgNO_3}]}{1 + [k_c \alpha / (k_a + k_b)]\,[\mathrm{AgNO_3}]} \qquad (53)$$

where α, is the degree of dissociation (105) of silver nitrate at a concentration of [AgNO$_3$].

An investigation of the reaction of methyl chloroformate (0.0935 M) with various concentrations of silver nitrate (0.001 - 0.16 M at 25°.0C gave a rate coefficient (k_2^o) ranging from 2.23 to 1.08 x 10^{-4} dm^3 mol^{-1} s^{-1}. In addition, the reaction of the same concentration of methyl chloroformate with silver nitrate (0.01M) has been carried out in the presence of silver perchlorate (0.01 M). This rate coefficient was reduced to 1.83 x 10^{-4} from 1.96 x 10^{-4} dm^3 mol^{-1} s^{-1} obtainable in the absence of silver perchlorate.

Moreover (104), the study of the reaction of methyl chloroformate with tetraethylammonium nitrate at 25°C was again followed by the appearance of chloride ion and gave an experimental rate coefficient (k_2^o) 2.00 x 10^{-4} dm^{-3} mol^{-1} s^{-1}. This rate coefficient may be defined by equation 54 .

$$k_2^o = k_2 k_b \,/\, (k_a + k_b)^* \qquad (54)$$

Second order rate coefficients were obtained, and these investigations assumed that the reaction proceeded through a tetrahedral intermediate but with only one of the two mechanisms for the decomposition of that tetrahedral intermediate being applicable. See Scheme (C).

Kevill and Johnson (104) in their investigation have pointed out that in the absence of any silver ion, to assist the removal of chloride ion from the tetrahedral intermediate, the reaction routes occur with 0.42 and 0.58 probabilities by loss of chloride ion and nitrate ion respectively. Also addition of silver perchlorate to the reaction mixture causes a slight decrease in the rate coefficient, but increases the rate of

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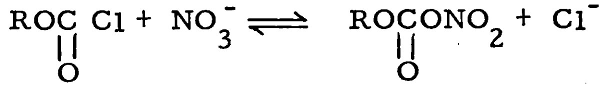
*$[AgNO_3]$ is replaced by $[Et_4NNO_3]$ in equation 42 k_c is = 0 and $\alpha = 1$.

decomposition of the nitratocarbonate to give the final products, nitrate ester and carbon dioxide.

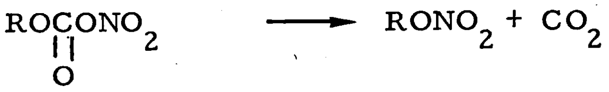
A more detailed kinetic study with methyl (104, 107) ethyl and iso-butyl chloroformates in acetonitrile solution of silver nitrate showed that these chloroformates show similar kinetic characteristics to those expected for the mechanism (C) which has been discussed before.

The reaction between iso-propyl chloroformate and silver nitrate in acetonitrile solution showed an abnormal behaviour compared to those of other alkyl chloroformates previously mentioned. Kevill and Johnson (106) concluded that the reaction follows scheme (B). They also indicated that the reaction of iso-propyl chloroformate with silver nitrate was faster than that with either silver perchlorate or tetra-ethylammonium nitrate and silver perchlorate separately. These results were found to be similar to the corresponding reactions with alkyl halides (108) and allyl halides (109).

The reactions for a series of alkyl chloroformates with tetra-ethylammonium nitrate have been investigated in acetonitrile at temperature 25°C. by Kevill (107). The second-order rate coefficients ($dm^3.mol.^{-1}\ s^{-1}$), were obtained as follows: Me., 20.0 ; Et., 10.6 ; iso-Bu., 11.7 ; and iso-Pr., 3.5×10^{-5}. It was suggested that these reactions proceed via an nitratocarbonate intermediate (eqn. 55 and 56).



$$\mathrm{RO}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\,\mathrm{Cl} + \mathrm{NO_3^-} \rightleftharpoons \mathrm{RO}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{ONO_2} + \mathrm{Cl^-} \qquad (55)$$



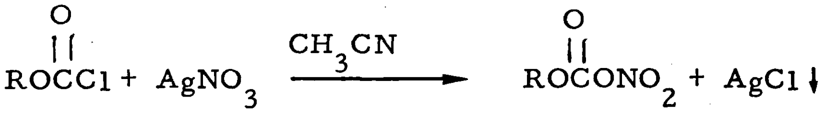
$$\mathrm{RO}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{ONO_2} \longrightarrow \mathrm{RONO_2} + \mathrm{CO_2} \qquad (56)$$

In accordance with the above mentioned study (see Sec. I. 5. 2 and 3) it is reasonable to conclude that, most primary alkyl chloroformates undergo bimolecular reactions with silver nitrate in acetonitrile.

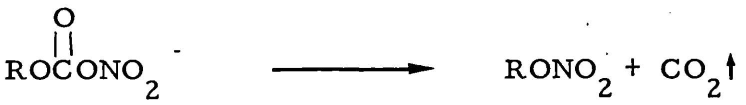
The two step reaction consists of, first the interaction of the nitrate ion with alkyl chloroformates to yield the intermediate nitratocarbonate and silverchloride. This is followed by the second step, the decomposition of that intermediate to yield the nitrate ester and carbon dioxide. This is in line with Scheme (A) rather than Scheme (B). The second step will be further discussed under Sec. I. 6.

I. 6 Decomposition of the intermediate (nitratocarbonate).

Mortimer (110), postulated an alkyl nitratocarbonate as an unstable intermediate formed in the reaction of silver nitrate with an alkyl chloroformate. The synthesis and decomposition of this nitrocarbonate seemed to be as follows:



$$\mathrm{RO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{Cl} + \mathrm{AgNO_3} \xrightarrow{\mathrm{CH_3CN}} \mathrm{RO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{ONO_2} + \mathrm{AgCl}\downarrow \qquad (57)$$



$$\mathrm{RO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{ONO_2} \longrightarrow \mathrm{RONO_2} + \mathrm{CO_2}\uparrow \qquad (58)$$

He further found in his study of this nitratocarbonate that the rates of reaction (eqn. 58) roughly paralleled the rates of reaction (eqn. 57) at moderate temperatures (40°C.), but reaction (eqn. 58) was considerably slower than reaction (eqn. 57) at temperature below 0°C. and accordingly the synthesis of nitrate esters below 0°C., would be of little practical value. In addition Mortimer has reported that pyridine (45, 46) is an excellent catalyst for the metathesis step (eqn. 58) and therefore for the overall reaction triethylamine appears to be even more effective.

When the reaction of alkyl chloroformates with silver nitrate was conducted at -17°C and examined by vapour phase chromatography it was found that only 40% of the alkyl-chloroformate had reacted after two hours and, further, in this time there was no evolution of cabon dioxide. This indicated that reaction (eqn. 57) had taken place, but reaction (eqn. 58) had not. On allowing the reaction temperature to increase, Mortimer found the nitrate ester as 100% product, and thus reaction (58) must have occurred at the higher temperature.

Mortimer investigated the effects of changes in reactants and solvents. The replacement of acetonitrile solution of silver nitrate by ammonium nitrate in N, N-dimethyl formamide solution gave a lower yield of ethyl nitrate with ethyl chloroformate at room temperature. Moreover, the use of pyridinium nitrate instead of silver nitrate and in excess in pyridine for reaction with n-propyl chloroformate at 25°C led to complete decomposition of this chloroformate.

Following these results a patent was taken out by Mortimer (111) regarding the reaction of alkyl chloroformate with nitrate salts which included those metallic cations that precipitate chloride, such as copper, mercury, lead and silver. The latter was the preferred reactant in the presence of an amine catalyst, (e.g. triethylamine, trimethylamine, tripropyl amine, and pyridine in 5-15% by weight of chloroformates) to give the corresponding nitrate esters by using again the preferred solvent, viz., acetonitrile. Mortimer added that, although the first step may be conducted at temperatures as low as -20°C. Temperatures below 15°C., result only in the formation of the nitratocarbonate (as intermediate) without any decomposition to the nitrate ester. The second step can be conducted between 15 and 150°C. to decompose the intermediate.

I. 7. Silver-ion assisted reactions.

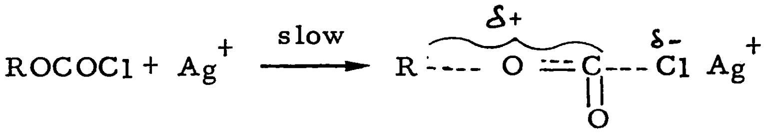
In the foregoing discussion it has become clear that reaction of several alkyl chloroformates with acetonitrile solutions of silver nitrate show that the rate-limiting factor is the direct attack by dissociated nitrate ion at the acyl carbon, to form the tetrahedral intermediate,I.5-1 (see p.38), and that there is some secondary dependence to the rate in the releasing of the chloride-ion from the tetrahedral intermediate in the presence of silver-ion.

However, it is found in the reaction of iso-propyl chloroformate with silver nitrate, that silver ion directly assists the ionization (81). In contrast with these observations, a study of the hydrolysis of n-butyl chloroformate in water with added mercuric ion (112) found that the rate was independent of the concentration of mercuric ion.

Further, the rate of hydrolysis of ethyl chloroformate in acetonitrile-water mixture was unaffected by adding silver-perchlorate (113), see Sec. I.5.2.

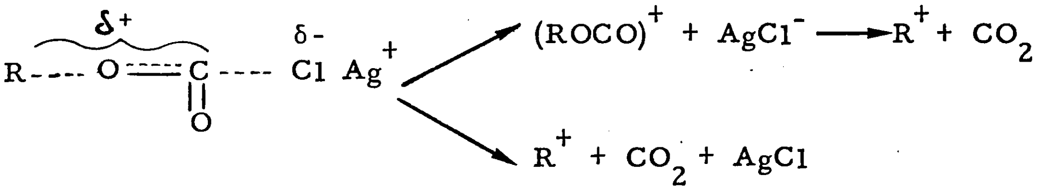
It is appropriate here to emphasise that those silver ion assisted reactions take place with weakly nucleophilic or non-nucleophilic counter-ions, and proceed many orders of magnitude faster than the corresponding reactions in the absence of silver-ion (95). n-Propyl chloroformate reacts with silver tetrafluoroborate or silver hexafluoroantimonate in chlorobenzene at room temperature faster than n-propyl chloride (114, 115) with the same reagents. The high proportion of re-arranged products (iso-propyl chloride and fluoride) together with cyclopropane was considered indicative of a reaction proceeding via a carboxylium ion $(RO - \overset{+}{C} = O)$ (116, 118) by analogy with studies of the products arising from reactions of the corresponding diazonium $(R - \overset{+}{N} \equiv N)$ (119-124) and isocarboxylium ions $(R - \overset{+}{O} = C:)$ (125, 126). Carbonium ion rearrangements have also been observed in a study of the reactions of appropriate alkyl chloroformates with silver perchlorate in benzene solution. The products of this reaction were identified (by addition of toluene) as alkyl-benzene and alkyl perchlorate, whereas a similar reaction of methyl and ethyl halides (127, 129) gave only the perchlorate esters without any benzene alkylation.

The following scheme for the silver assisted pathway therefore has been suggested (56):



$$\mathrm{ROCOCl} + \mathrm{Ag}^{+} \xrightarrow{\text{slow}} \overbrace{\mathrm{R}\text{----}\mathrm{O} \,\text{=:=}\, \underset{\overset{||}{\mathrm{O}}}{\mathrm{C}}}^{\delta+}\text{---}\overset{\delta-}{\mathrm{Cl}}\ \mathrm{Ag}^{+} \qquad (59)$$

(t. s)



$$\overbrace{\mathrm{R}\text{----}\mathrm{O} \,\text{=:=}\, \underset{\overset{||}{\mathrm{O}}}{\mathrm{C}}}^{\delta+}\text{----}\overset{\delta-}{\mathrm{Cl}}\ \mathrm{Ag}^{+} \begin{array}{l} \nearrow (\mathrm{ROCO})^{+} + \mathrm{AgCl}^{-} \longrightarrow \mathrm{R}^{+} + \mathrm{CO}_2 \\ \searrow \mathrm{R}^{+} + \mathrm{CO}_2 + \mathrm{AgCl} \end{array}$$

(t. s)

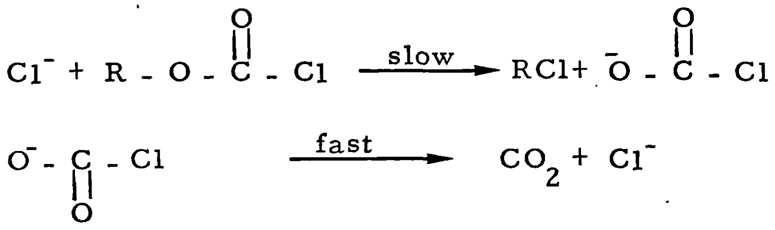
(60)

I.8 Reactions of alkylchloroformates with chloride ion.

The effect upon the rates of hydrolysis and decomposition of alkyl chloroformates in water (32), water/acetone and water/acetonitrile in presence of chloride ions (e.g. tetra ethyl- (130) and tetra-n-butylammonium chlorides (131) have been discussed in Section (I.5).

The impact of the presence of quaternary ammonium chlorides on the reaction of alkyl chloroformates with nitrate ion is discussed under Section (I.5.2)

The following is concerned with the reaction of alkyl chloroformates with chloride ion alone. Kevill and Johnson (107) studied the reaction of chloride ion (tetra ethyl ammonium chloride) with methyl, ethyl, propyl and iso-butyl chloroformates in acetonitrile solution. They reported a rapid chloride ion exchange at the carbonyl carbon and the reaction was found to obey second order kinetics, giving the alkyl chloride and carbon dioxide (S_N2 process)



$$Cl^- + R-O-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{slow} RCl + {}^-O-\overset{O}{\overset{\|}{C}}-Cl$$

$$O^- - \underset{O}{\underset{\|}{C}} - Cl \xrightarrow{fast} CO_2 + Cl^- \qquad (61)$$

The values for the second order rate coefficients they obtained for the reaction between a series of alkyl chloroformates and tetraethylammonium chloride in acetonitrile at 25.0°C are appended:

R = Me, 164; Et 6.2; n-Pr, 5.8; iso-Pr, 0.75 and iso-Bu, 0.26 (10^{-5} dm^3 mol^{-1} s^{-1}).

The extent of any accompanying E_2 reaction was $<1\%$ for ethyl- or n-propyl, $<13\%$ for iso-butyl and $<17\%$ for iso-propylchloroformates.

CHAPTER II

RESULTS AND DISCUSSION

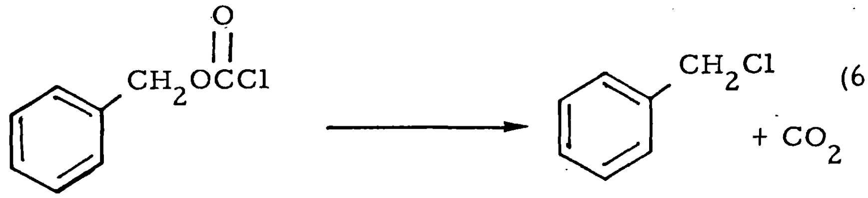
CHAPTER II

RESULTS AND DISCUSSION

II. 1. The reaction of Tetra-n-butylammonium Nitrate with n-Propyl and benzyl Chloroformates in aceonitrile.

II. 1. 1. Stability of solution of n-propyl and benzyl chloroformates in acetonitrile.

The infrared absorption of freshly prepared solutions of n-propyl (0.1) and benzyl (0.37 mol dm^{-3}) chloroformates in acetonitrile were examined between 650 and 4000 cm^{-1} and the absorption bands in the region 1775 to 1780 cm^{-1} were then monitored for several hours. It was found that at temperatures of 25.5 and 35.1 ^{o}C the absorptions of the solution of n-propyl chloroformate do not change over a period of 24 hours, but those of the benzyl chloroformate solution show a slight change due to its decomposition to give benzyl chloride and carbon dioxide as follows:



(61)

The reaction rate for this decomposition was measured at 25.5, 35.1 and 84.0^{o}C and in each case was found to follow a first-order rate law, i.e. similar to that found for the decomposition of iso-Pr chloroformate 1.0 x 10^{-7} s^{-1} at 25^{o}C (106) in acetonitrile. The values of the rate coefficients at these temperatures are given in Table II. 1.

TABLE II.1 FIRST ORDER RATE COEFFICIENTS FOR THE DECOMPOSITION OF BENZYL CHLOROFORMATE IN ACETONITRILE

Temperature ^{o}C	Rate Coefficient $k \times 10^{7}$ / sec^{-1}
25.50	7.01 ± 0.12
35.10	14.40 ± 0.05
84.00	230 ± 0.08

II.1.2 Stability of solutions of tetra-n-butylammonium nitrate in acetonitrile

The decomposition of tetra-n-butylammonium nitrate can occur in two ways, giving either tri-n-butylamine and n-butylnitrate or tri-n-butylammonium nitrate and butene. The latter process does not produce any new nucleophile. However, it will effect the equilibrium concentration of dissociated nitrate ions; but not the overall stoichiometric concentration of nitrate ion.

The extent of tri-butylamine production from a 0.04 mol dm^{-3} solution of tetra-n-butylammonium nitrate in acetonitrile was examined by monitoring its infrared absorption for a period of 48 hours. This showed that the solution remained unchanged throughout that period.

Acetonitrile was the choice of reaction solvent since it dissolves both the chloroformates and tetra-n-butylammonium nitrate resulting in a homogeneous reaction solution.

II. 1. 3. Test for the existence of a reaction between n-propyl and benzyl chloroformates and tetra n-butylammonium nitrate.

The infrared absorptions of solutions of mixtures of n-propyl and benzyl chloroformates with tetra-n-butylammonium nitrate (each component having an initial concentration of 0.34 mol dm^{-3}) were examined between 650 and 4000 cm^{-1}. The solutions were kept in the infrared cells for several hours, and the intensity of the infrared absorption bands were monitored and compared with those of the original solutions. This showed that the absorption peaks for the characteristic chloroformate carbonyl band in the region 1775 to 1780 cm^{-3} almost disappears and is replaced by absorption peaks in the region 1630 to 1635 cm^{-1} which could be attributable to the formation of nitrate esters (18). Figure II. 1 shows typical spectra obtained from this reaction (e.g. with n-propyl chloroformate). For the interpretation of the assignments of the new bands formed see section II. 3.

II. 2 Infrared Spectra and the Determination of Extinction Coefficients.

II. 2. 1. Infrared absorptions of n-propyl and benzyl chloroformates and nitrates.

n-Propyl and benzyl chloroformates, their nitrates, acetonitrile and pyridine were each separately examined between 650 and 4000 cm^{-1}. This showed that the charateristic C=O stretching vibration of the chloroformates and the asymmetric stretching NO_2 vibration of the nitrate esters do not coincide with the main absorption bands of

TABLE II.2 MAIN BANDS IN INFRARED SPECTRA

Compound	Absorption Frequency (cm^{-1}) λ					
Acetonitrile (18)	2260-40(s)		1040-30		910	750-40
Pyridine (18)	3420(s)	1580	1570	1485(m)	1100-1000	750
Chloroformates	$\nu_{C=O}$		ν_{C-O}		ν_{C-O}	
n-Propyl	1780(s)		1180(m)		980(s)	
Benzyl	1775(s)		1265(m)		1150(s)	
Nitrates	ν_{NO_2}		ν_{NO_2}		ν_{C-O}	
n-Propyl	1633(v.s)		1282 (v. s)		973(w)	868(s)
Benzyl	1631(v. s)		1282(v. s)		976(s)	868(s)

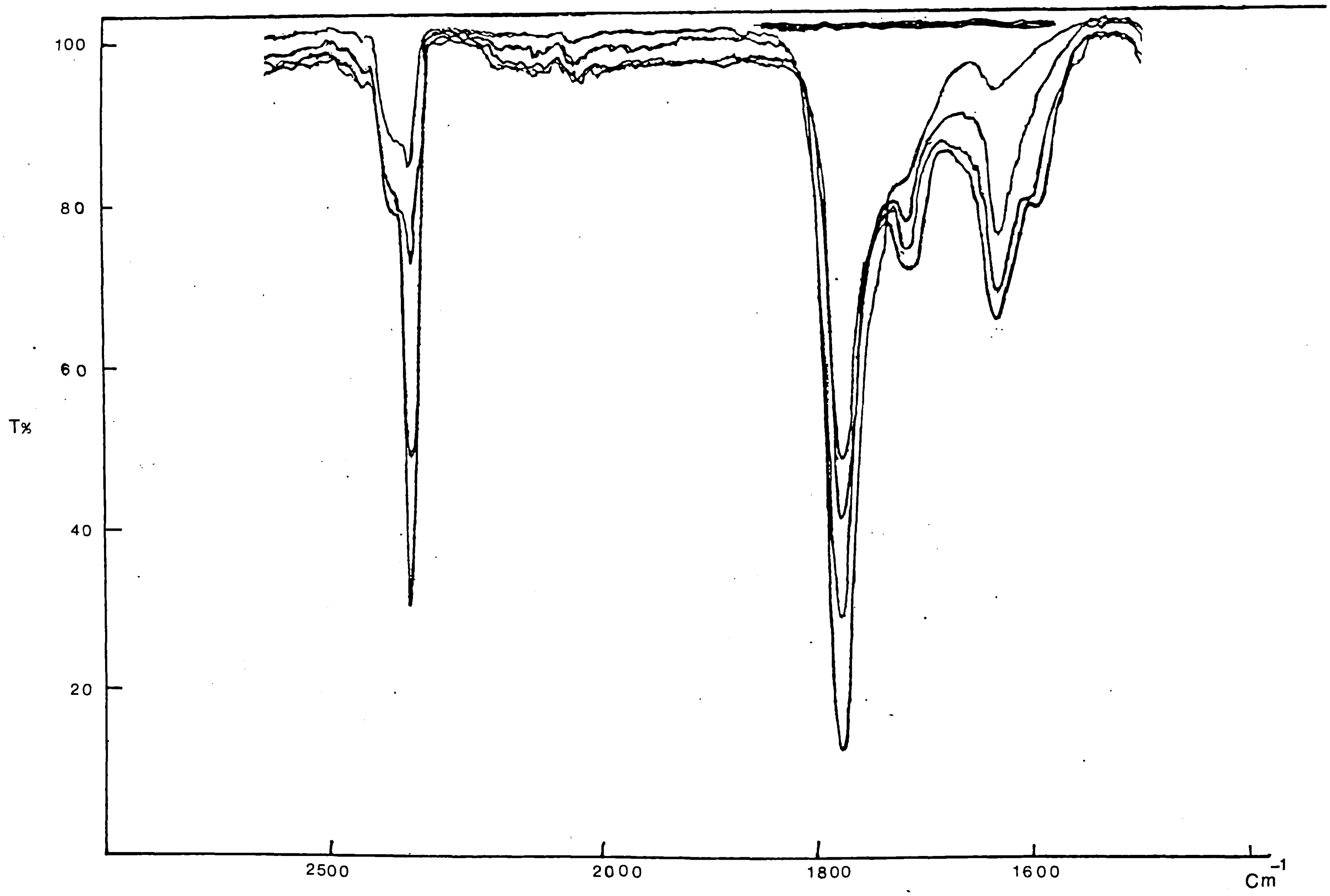


FIG. II. 1 Typical spectra obtained from an analysis of the reaction of n-C_3H_7OCOCl and tetra-Bu_4NNO_3

acetonitrile (the solvent) or of pyridine (included in some catalytic studies). The infrared absorption frequencies are given in Table II. 2.

II. 2. 2. Evaluation of Extinction Coefficients.

The absorption $\log_{10} I_o/I$ for each compound were calculated from measurements of the transmission (I) with the solution in the sample cell, and with acetonitrile contained in both sample and reference cells (I_o).

The absorptions determined in the region 1775 to 1780 cm^{-1} for chloroformates and in the region 1630 to 1635 cm^{-1} for nitrates were plotted against the appropriate concentration for each sample. From this it was established that Beer's Law was obeyed for each solution over the working concentrations. The values of the extinction coefficient for these substances are given in Table II. 3.

II. 3. Products from the reaction of n-propyl chloroformate with tetra-n-butylammonium nitrate.

The reaction of n-propyl chloroformate with tetra-n-butylammonium nitrate was reinvestigated to determine whether n-propyl nitrate was the only product, apart from carbon dioxide and the quaternary ammonium chloride, as reported for the similar reaction with silver nitrate, see section I.5.1 and 2.

The reaction was conducted on a 0.34 mol dm^{-3} scale at 25.5°C, using acetonitrile as the reaction solvent. The infrared spectra of the solution of the products showed, following the disappearance of the chloroformate band at

TABLE II.3 EXTINCTION COEFFICIENTS

Compound	Absorption Frequency λ (cm^{-1})	$10^{-6}\ \mathcal{E}$/mol^{-1} dm^{2}
n-propyl chloroformate	1775-1780	4.439 ± 0.012
n-propyl nitrate	1630-35	4.852 ± 0.03
benzyl chloroformate	1775-1780	3.915 ± 0.10
benzyl nitrate	1630-35	6.052* ± 0.06

[*] The extinction coefficient of benzyl nitrate was found to be in agreement with Brown's result ~6.00 x 10^{6} mol^{-1} dm^{2} (213).

1780 cm^{-1} and the appearance of a band at 1633 cm^{-1} (vide supra), another band in the region 1730 to 1740 cm^{-1} (broad band). This band was similar to the νC=O of ethyl carbamate (urethane) and diethylcarbonate (18). Further, there was also a strong and sharp band at 2350 cm^{-1}, which may be attributed to carbon dioxide (214) in acetonitrile solution.

Attempts were made to determine the yields of n-propyl nitrate by isolation of the reaction products using the distillation experiments described in section III.8.

Experiment 1.

The infrared spectra of the distillate solution (carried out at room temperature (13°) showed only two of the new bands; ν= 1635, related to the corresponding nitrate ester and ν= 1735 cm^{-1}. While the band observed previously at ν= 2350 cm^{-1} was completely absent.

Experiment 2.

The infrared spectra of the distillate, obtained from the reacted solution which had then been refluxed for two hours showed no differences to that in Experiment 1.

Experiment 3.

The experiment was carried out by refluxing the reacted mixture for two hours with pyridine (1 cm^3), followed by the separation of the products. The

The infrared spectra of the distilled part indicated a small increase in the intensity of the band at $\nu = 1635\ cm^{-1}$

Assuming that the absorption at 1633 cm^{-1} is due to only n-propyl nitrate and using the value of its extinction coefficient, the maximum yield of n-propyl nitrate does not exceed 18 ± 1.5%.

G. L. C. Analysis of distillation from Experiment 1.

Using a flame ionization detector (G. L. C.) and, a standard solution of n-propyl nitrate in acetonitrile the amount of n-propyl nitrate produced in experiment 1 was again found to be 18 ± 0.8%.

II. 4. Reaction Kinetics

II. 4. 1 Kinetics of the reaction between n-propyl chloroformate and tetra n-butylammonium nitrate.

Reaction rates were followed by determining the rate of disappearance of n-propyl chloroformate. This was achieved by monitoring the absorption due to the characteristic C=O stretching vibrations at 1778 cm^{-1}.

It was found necessary to use cells fitted with sodium chloride windows since n-propylchloroformate, one of the reactants was observed to react with the windows when they were constructed of potassium bromide. Further, the use of sodium chloride windows had the advantage in that there would be no catalytic effect of bromide ions affecting the rate of the reaction. It was not found possible to monitor the reaction with a sample of the reaction mixture contained in a thermostatted infrared cell owing to the evolution of carbon dioxide.

Accordingly the procedure of removal of aliquots from a reaction vessel supported in a constant temperature bath had to be adopted (see section III. 4). Readings of transmittances were made only after checking the constancy of the "100% transmittance". I_o and most reactions were followed for about three half-times, i. e. about 80% reaction of n-propyl chloroformate.

It was previously ascertained that over a period of about seven hours, no adjustment of the infrared spectrometer for 100% transmission in the region 1950 to 1500 cm^{-1} was necessary with acetonitrile contained in both cells.

The reactions were carried out at temperature of 25. 5, 30. 5, 35. 2, 40. 4 and 45. 1 °C in a constant temperature water-bath controlled to ± 0. 1 °C with equal and different initial molar concentrations of both reactants; n-propyl chloroformate (0. 04 - 0. 34) and tetra-n-butylammonium nitrate (0. 11 - 1. 25 mol dm^{-3}.

II. 4. 1. 1. Kinetics analysis with equal molar concentration of reactants.

Assuming the reaction to follow a second-order rate law equation 62

$$-\frac{d[A]}{dt} = k_2[A]^2 \qquad (62)$$

where [A] is the instantaneous concentration of both n-propyl chloroformate and tetra-n-butylammonium nitrate. Rearrangement and integration of this expression

$$-\int_{A_o}^{A_t} \frac{d[A]}{[A]^2} = \int_o^t k_2 dt \qquad (63)$$

$$kt = 1/[A_t] - 1/[A_o] \qquad (64)$$

Therefore if $1/[A_t] - 1/[A_o]$ is plotted against time t, a straight line should be obtained with a slope equal to the observed rate coefficient (k_2). See Figures II. 2, 3 and 4.

II. 4. 1. 2 Kinetics analysis with different molar concentrations of the reactants.

$$-\frac{[dA]}{dt} = k_2 [A][B] \qquad (65)$$

where [A] and [B] are the instantaneous concentrations of n-propyl chloroformate and tetra-n-butylammonium nitrate respectively. Integration of this equation from time O to t gives:

$$k_2 t = ([A]_o - [B]_o)^{-1} \ln([A_t][B]_o / [B_t][A_o]) \qquad (66)$$

where $[A]_o$ and $[B]_o$ are the initial concentrations of n-propyl chlorformate and tetra-n-butylammonium nitrate at t = O and $[A_t] - [B_t]$ the concentrations at time t. Therefore if $\log([A_t][B]_o / [B_t][A]_o)$ is plotted against time t, a straight line should be obtained, and the observed rate coefficient (k_2) is equal to the slope of that line multiplied by 2. 303 and divided by $[A]_o - [B]_o$. The rate coefficientsfor this reaction were calculated for different initial concentrations for n-propyl chloroformate and tetra-n-butylammonium nitrate and also at different temperatures. The values for the second order rate coefficients according to equation 64 and 66 are given in Table II. 4 and have been shown to be constant at each temperature.

Some kinetic plots for this reaction are shown in Figures II. 5 and II. 6.

II. 4. 1. 3 Kinetics analysis for reactions with tetra-n-butylammonium nitrate in excess.

Some reactions between n-propyl chloroformate and tetra-n-butylammonium nitrate were carried out with about a five-fold excess of tetra-n-butylammonium nitrate at the temperatures of 25. 5, 30. 5, 35. 2, 40. 4 and 45. 1° ± 0. 1°C and with about ten-fold excess at temperatures 35. 2 and 45. 1°C. In these cases also the reactions were followed until 80% of the initial n-propyl chloroformate concentration had reacted. These reactions were expected to obey a pseudo first-order rate law, equation 67.

$$-\frac{d[A]}{dt} = k_1' [A] \qquad (67)$$

where [A] is the instantaneous concentration of n-propyl chloroformate. Integration gives equation 68.

$$k_1' t = \ln([A]_0 \ / \ [A]_t) \qquad (68)$$

By plotting ln $[A_t]$ against time t, a good straight line should be obtained with a slope equal to the rate constant and the intercept equal to ln $[A_0]$, where $[A_0]$ is the initial concentration of n-propyl chloroformate. An example of this behaviour is illustrated in Figure II. 7. The value of the observed first-order rate coefficients (k_1') are given in Table II. 5, and also the observed second order rate coefficients (k_2), calculated from $k_1'/[B_o]$ where $[B_o]$ represents the initial concentrations of tetra-n-butylammonium nitrate.

II. 4. 2. Kinetics of the reaction between benzyl chloroformate and tetra-n-butylammonium nitrate in acetonitrile.

The reaction of benzyl chloroformate with tetra-n-butylammonium nitrate was carried out similarly to that of n-propyl chloroformate (see section III. 3. 1) Aliquots were removed after convenient time intervals and analysed separately (owing to the evolution of carbon dioxide) as described above. It was found necessary to use longer pathlength cells (1 mm) owing to the smaller absorption of the carbonyl group at 1778 cm^{-1} than that of n-propyl chloroformate. The cells were again fitted with sodium chloride windows.

This reaction has been investigated at temperatures of 25.1, 30.5, 35.1, 40 and 45.2 $\pm$ 0.1 °C, with equal and different molar concentrations of both reactants, varying between 0.02 and 0.025 mol dm^{-3} for benzyl chloroformate and between 0.025 and 0.150 mol dm^{-3} for tetra-n-butylammonium nitrate. The reaction was followed by the rate of disappearance of the characteristic C=O vibration band at 1780 cm^{-1}, of benzyl chloroformate. Using similar calculations as in Sec. II. 4. 1. 1 and 2 at each temperature, it was found that the kinetics were consistent with the equation 64 and 66 for equal and different molar concentrations of the reactants giving observed second order rate coefficients, k_2. Consistent values were observed at each temperature. The values for these rate coefficients are given in Table II.6, and kinetic plots are shown in Figures II.8 and 9.

Similar experiments (as in Sec. II.4.1.3) were carried out under pseudo first-order reaction conditions with benzyl chloroformate and about a seven-fold excess of tetra-n-butylammonium nitrate. Similar features were observed as in Sec.II.3.1.3, and resulted in pseudo first-order rate coefficient being obtained for at least 80% of the benzyl chloroformate.

The results of this reaction are given in Table II.7, and a graph for a typical pseudo first-order reaction is shown in Figure II.10. The observed second order rate coefficients were calculated from pseudo first-order rate coefficients as described for n-propyl chloroformate.

II.4.3 Discussion of the kinetics of the reaction of tetra-n-butylammonium nitrate with chloroformates.

There are a number of conclusions that can be drawn from the kinetics studies of the reactions between n-propyl and benzyl chloroformates with tetra-n-butylammonium nitrate in acetonitrile solution. These reactions showed second-order behaviour at each given temperature.

The kinetics determinations for different molar concentration of the reactants with nitrate to chloroformate ratio 5:1 were examined up to ≃ 80% of disappearance of the two chloroformates. Between 0 and 80 percentage reaction the second-order rate plots are good straight lines showing the following of the second-order rate law.

However, it is observed that in similar reactions with equimolar concentrations of the reactants at ca. 25, 30 and 35^{o} (see Figures II. 3 and 4) the observed second-order rate coefficients appear to increase after 60% disappearance of the chloroformates. This same observation begins after 50% of disappearance of chloroformates at the higher temperatures ca. 40 and 45.

Possibly these deviations were due to the auto-catalytic effects of one of the products formed during the reaction. To examine these possibilities experimentally, kinetic determinations were conducted with the tetra-n-butylammonium chloride product. (see Section II. 7).

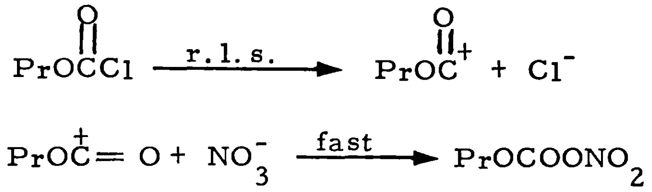
Accordingly all of the data for the kinetics studies with equimolar concentrations of the reactants were determined from the initial 40 to 50% decrease of the chloroformates. All subsequent discussion of rate coefficients are related to initial rates (40 - 50 completion) and are not related to overall rates of reaction. This approach is followed even in the case of the reactions between n-propyl chloroformate and tetra-n-butylammonium nitrate at 25. C, for which the second-order rate law was followed up to 70% completion. Many workers have found similar results for the reactions between alkyl and aryl chloroformates. Boschan (96) pointed out that for the reactions between alkyl chloroformates and silver nitrate in acetonitrile, the kinetics were shown to be approximately second-order as measured by the rate of evolution of carbon dioxide (reaction followed only during the initial 25% reaction). Kevill and Johnson (107) obtained also second-order rate coefficients for the reactions of a series of primary and secondary alkyl chloroformates reacting with tetra ethylammonium nitrate. The values of the rate coefficient were in the order of Me > Et ~ iso-Bu > iso-Pr. In their investigation they indicated complications of the reaction due to S_N2 attack by the developing chloride ion. In a similar reaction but in which methyl chloroformate was reacted with silver nitrate, Kevill and Johnson (104) obtained good second-order kinetics during at least the first 25% change, the reaction being followed by titration of the soluble silver ion.

For the reaction between phenyl and substituted phenyl chloroformates, with silver nitrate, Zabik and Schuetz (103) obtained second-order rate coefficients, and found them to hold only for the initial 20% reaction. These reactions were followed by the rate of disappearance of the aryl chloroformates by the decrease in the infrared absorptions in the region 1775-1880 cm^{-1} (i.e. the same technique as used in this work).

In the present studies pseudo first-order rate coefficients for the reactions between n-propyl and benzyl chloroformates with excess tetra-n-butylammonium nitrate were obtained with the latter in considerable excess the first-order plots gave good straight lines holding for at least 95% of the reaction; the values of these first-order rate coefficients were proportional to the conentration of the tetra-n-butylammonium nitrate (see Figure II.11), indicating that the tetra-n-butylammonium nitrate was taking part in the rate limiting steps of these reactions. Consistent with the above formulations Kevill and Johnson (107) observed that the reactions between a series of chloroformates and tetra ethyl ammonium chloride and nitrate had pseudo first-order rate coefficients which were proportional to the chloride and nitrate ion concentrations. Reactions of silver nitrate with phenyl and p-substituted phenyl chloroformates have been also found to follow the pseudo first-order behaviour up to 80% of the disappearance of these chloroformates.

It was observed that when the observed pseudo first-order rate coefficients obtained in this study were converted to second-order rate coefficients, there was good agreement with the values obtained from the second-order plots.

On the basis of the second-order behaviour it is possible to eliminate mechanistic schemes in which the nitrate ion plays no part in the rate limiting step, e.g.



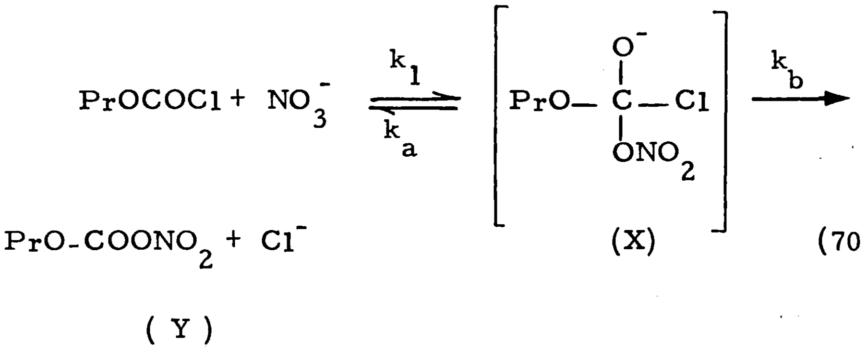
$$\mathrm{PrO}\overset{\overset{O}{\|}}{\mathrm{C}}\mathrm{Cl} \xrightarrow{\text{r.l.s.}} \mathrm{PrO}\overset{\overset{O}{\|}}{\mathrm{C}}{}^{+} + \mathrm{Cl}^-$$

$$\mathrm{PrO}\overset{+}{\mathrm{C}}{=}\mathrm{O} + \mathrm{NO}_3^- \xrightarrow{\text{fast}} \mathrm{PrOCOONO}_2 \qquad (69)$$

In deciding between the simple S_N2 pathway (Scheme A p. 34) and that involving a tetrahedral intermediate (Scheme C p. 38) it is necessary to consider observations of other workers. The relative order of reactivity of alkyl groups in a series of chloroformate reactions with tetraethylammonium nitrate Me > Et ~ iso-Bu > iso-Pr shows that the nucleophilic attack by NO_3^- is impaired by the increasing electron donating ability of the alkyl groups. This would be expected to be a common observation in mechanisms that have either simultaneous or subsequent loss of the chloride ion from the chloroformate if the attack by nitrate is slow.

Kevill (104) has shown that by comparing the rates of reaction of methyl chloroformate with tetraethylammonium nitrate, having an observed second-order rate coefficient of $k_2k_b / (k_a + k_b)$ (see equation 54 p. 39), with that of a large excess of silver nitrate (when the degree of dissociation $\alpha \longrightarrow 0$ and the limiting value of $(k_2^o / \alpha) \longrightarrow k_2$ (see equation 53 p. 38); $k_b / (k_a + k_b)$ has a value of 0.42. This represents the proportion of the intermediate (I. 5-1), to which both chloride and nitrate are attached, that loses chloride ion. This process holds in the absence of silver ion and $k_a/(k_a + k_b)$ similarly represents the proportion of (I. 5-1) that loses the nitrate ion viz., 0.58. The structure of such an intermediate derived from n-propyl chloroformate is given below.

A reaction scheme for both its formation and decomposition to n-propyl nitratocarbonate is as follows:



$$PrOCOCl + NO_3^- \underset{k_a}{\overset{k_1}{\rightleftharpoons}} \left[PrO-\overset{\overset{O^-}{|}}{\underset{\underset{ONO_2}{|}}{C}}-Cl \right] \xrightarrow{k_b} PrO\text{-}COONO_2 + Cl^- \qquad (70)$$

(X)

(Y)

Application of the steady state hypothesis to the intermediate (X) gives:-

$$\frac{d[X]}{dt} = k_1[A][B] - k_b[X] - k_\alpha[X] = 0 \qquad (71)$$

$$\therefore \frac{d[Y]}{dt} = k_b[X] = \frac{k_1 k_b [A][B]}{k_a + k_b} \qquad (72)$$

If the observed second-order rate coefficient (k_2) is given by:

$$\text{rate} = \frac{d[Y]}{dt} = k_2 [A][B] \qquad (73)$$

then

$$k_2 = \frac{k_1 k_b}{k_a + k_b} \qquad (74)$$

Limiting conditions can be applied so that

$$k_2 = k_1 \qquad \text{when} \quad k_b \gg k_a \qquad (75)$$

and

$$k_2 = k_b \times \left(\frac{k_1}{k_a}\right) = k_b \times K \qquad \text{when } k_b \ll k_a \qquad (76)$$

It is unlikely that the rate coefficient k_a and k_b will be very different in magnitude if this reaction parallels the reaction of methyl chloroformate with nitrate ion and so the limiting conditions may not be applied and the observed rate constant is then a composite term. The true second-order rate coefficient k_1 is reduced by a factor of $(1 + (k_a/k_b))$.

TABLE II.4 SECOND-ORDER RATE COEFFICIENTS FOR THE REACTION BETWEEN n-PROPYL CHLOROFORMATE AND TETRA-n-BUTYLAMMONIUM NITRATE

Temperature °C	$[PrOCOCl]^a$ mol dm^{-3}	$[Bu_4NNO_3]^a$ mol dm^{-3}	10^5k_2/ dm^3 mol^{-1} s^{-1}	Mean 10^5k_2/ dm^3 mol^{-1} s^{-1}
25.5	0.120	0.510	8.701	
	0.250	0.250	8.671	8.658 ± 0.126
	0.340	0.340	8.602	
30.5	0.120	0.510	14.792	
	0.250	0.250	14.821	14.838 ± 0.142
	0.340	0.340	14.902	
35.2	0.115	0.115	22.921	
	0.115	0.400	22.461	
	0.123	0.510	22.452	22.650 ± 0.208
	0.200	0.200	22.802	
	0.210	0.115	22.404	
	0.340	0.340	22.911	
40.4	0.120	0.510	39.752	
	0.200	0.200	39.801	39.788 ± 0.078
	0.340	0.340	39.811	
45.1	0.100	0.401	60.992	
	0.110	0.110	61.320	61.108 ± 0.311
	0.233	0.233	60.900	
	0.340	0.340	61.221	

a) Solutions were prepared at room temperature so the concentrations are uncorrected for thermal expansion of nitronitrile when used at higher temperatures.

TABLE II. 5 PSEUDO FIRST-ORDER AND SECOND-ORDER RATE COEFFICIENTS FOR THE REACTION BETWEEN n-PROPYL CHLOROFORMATE AND TETRA-n-BUTYLAMMONIUM NITRATE

Temperature °C	PrOCOCl $[A_o]^a$ mol dm^{-3}	$Bu_4NNO_3[B_o]^a$ mol dm^{-3}	$10^5k_1'$/ s^{-1}	$10^5k_2^*$/ dm^3 mol^{-1} s^{-1}
25.5	0.100	0.512	4.450	8.700 ± 0.010
30.5	0.120	0.840	12.310	14.650 ± 0.020
35.2	0.123	1.130	25.120	
	0.123	1.250	28.080	22.280
	0.120	1.520	33.671	± 0.158
40.4	0.120	0.750	29.851	39.800 ± 0.051
45.1	0.100	0.500	30.46	60.910 ± 0.022
	0.045	0.500	30.232	60.451 ± 0.210
45.5	0.045	0.500	32.099	64.198 ± 0.010

$^* k_2 = k_1' / [B_o]$

Also each rate coefficient is the mean of three determinations.

a) See footnote page 66

TABLE II. 6 SECOND-ORDER RATE COEFFICIENTS FOR THE REACTION BETWEEN BENZYL CHLOROFORMATE AND TETRA n-BUTYLAMMONIUM NITRATE

Temperature °C	$[BzOCOCl]^a$ mol dm^{-3}	$[Bu_4NNO_3]^a$ mol dm^{-3}	10^4k_2/ $dm^3 mol^{-1} s^{-1}$	Mean 10^4k_2/ $dm^3 mol^{-1} s^{-1}$
25.1	0.025	0.050	10.170*	9.812 ± 0.217
	0.020	0.050	9.900	
	0.02	0.100	9.811	
	0.02	0.15	9.725	
30.5	0.025	0.025	22.940*	19.768 ± 0.469
	0.025	0.050	19.801	
	0.020	0.100	19.902	
	0.020	0.025	19.601	
35.1	0.025	0.025	31.701*	30.308 ± 0.300
	0.020	0.025	30.020	
	0.025	0.050	30.220	
	0.020	0.100	30.030	
40.0	0.025	0.025	56.080	56.055 ± 0.071
	0.020	0.025	56.061	
	0.020	0.050	56.024	
45.2	0.025	0.025	87.096	87.089 ± 0.020
	0.020	0.025	87.080	
	0.020	0.050	87.091	

* Reactions were normally followed to 50 % except in those cases when the reactions were allowed to proceed to 70 % - competition of reaction with Cl^- ion becoming more pronounced in the later stages.

a) See footnote page 66

TABLE II. 7 PSEUDO FIRST-ORDER AND SECOND-ORDER RATE COEFFICIENTS FOR THE REACTION OF BENZYL CHLOROFORMATE AND TETRA-n-BUTYLAMMONIUM NITRATE

Temperature °C	BzOCOCl[A_o]^a mol dm^{-3}	Bu_4NNO_3[B_o]^a mol dm^{-3}	$10^4k_1'$/ s^{-1}	$10^4k_2^*$/ dm^3 mol^{-1} s^{-1}
25.1	0.020	0.150	1.473	9.820 ± 0.210
30.5	0.020	0.150	2.971	19.800 ± 0.152
35.1	0.020	0.200	6.022	30.11 ± 0.112
40.0	0.020	0.200	11.208	56.040 ± 0.120
45.2	0.020	0.150	13.062	87.080 ± 0.091

* $k_2 = k_1' / [B_o]$

Also each rate coefficient is the mean of three determinations.

a) See footnote page 66

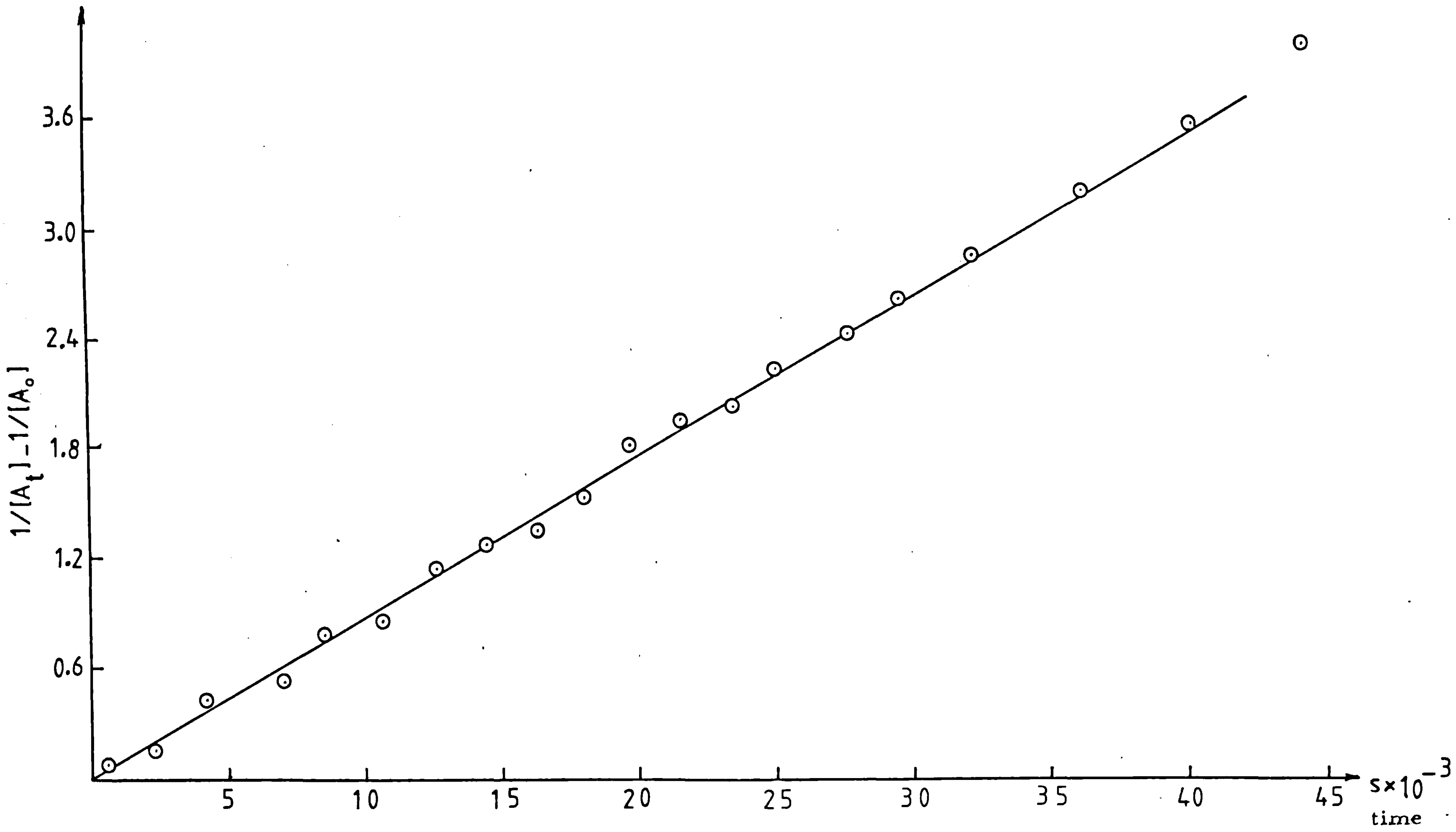


FIG. II. 2 Second-order rate plot for the reaction between n-C_3H_7OCOCl (0.340) with n-Bu_4NNO_3 (0.340 mol dm^{-3}) at 25.5^{o}C.

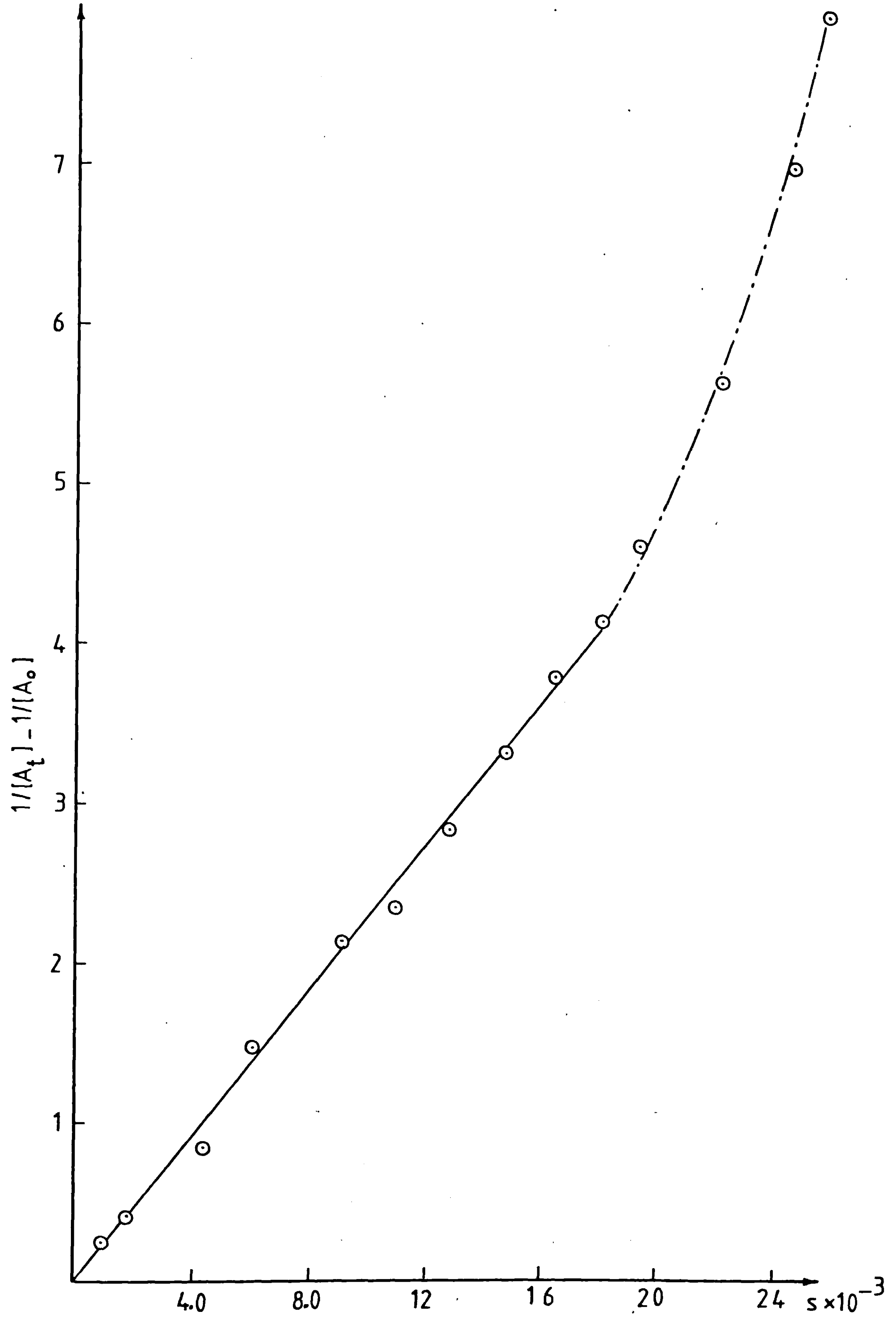


FIG II. 3 Second-order rate plot for the reaction of n-C_3H_7OCOCl (0.34) with n-Bu_4NNO_3(0.34 mol dm^{-3}) at 35.2°C

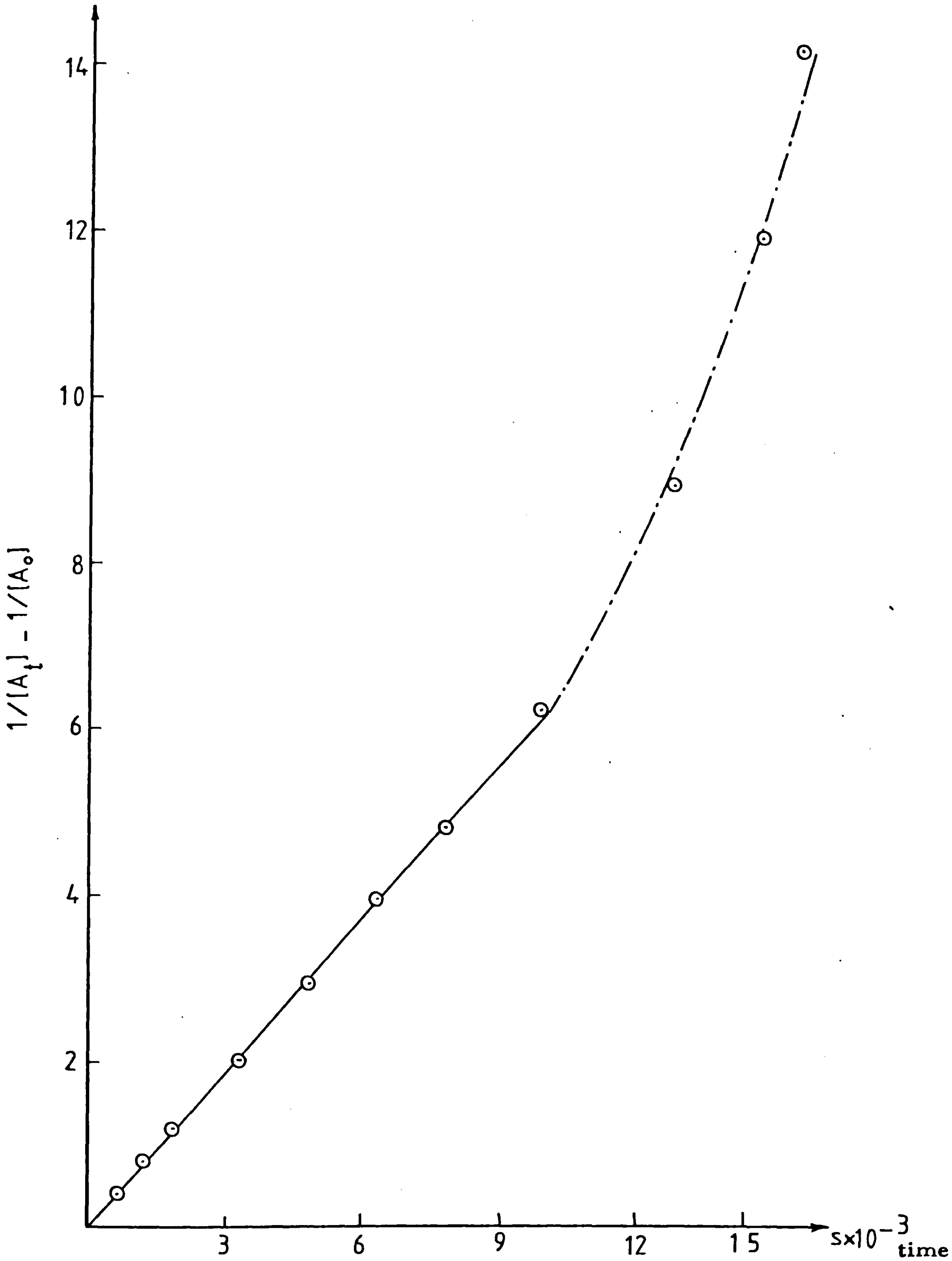


FIG. II. 4 Second-order rate plot for the reaction of n-C_3H_7OCOCl (0.34) with n-Bu_4NNO_3 (0.34 mol dm^{-3}) at 45.1°C.

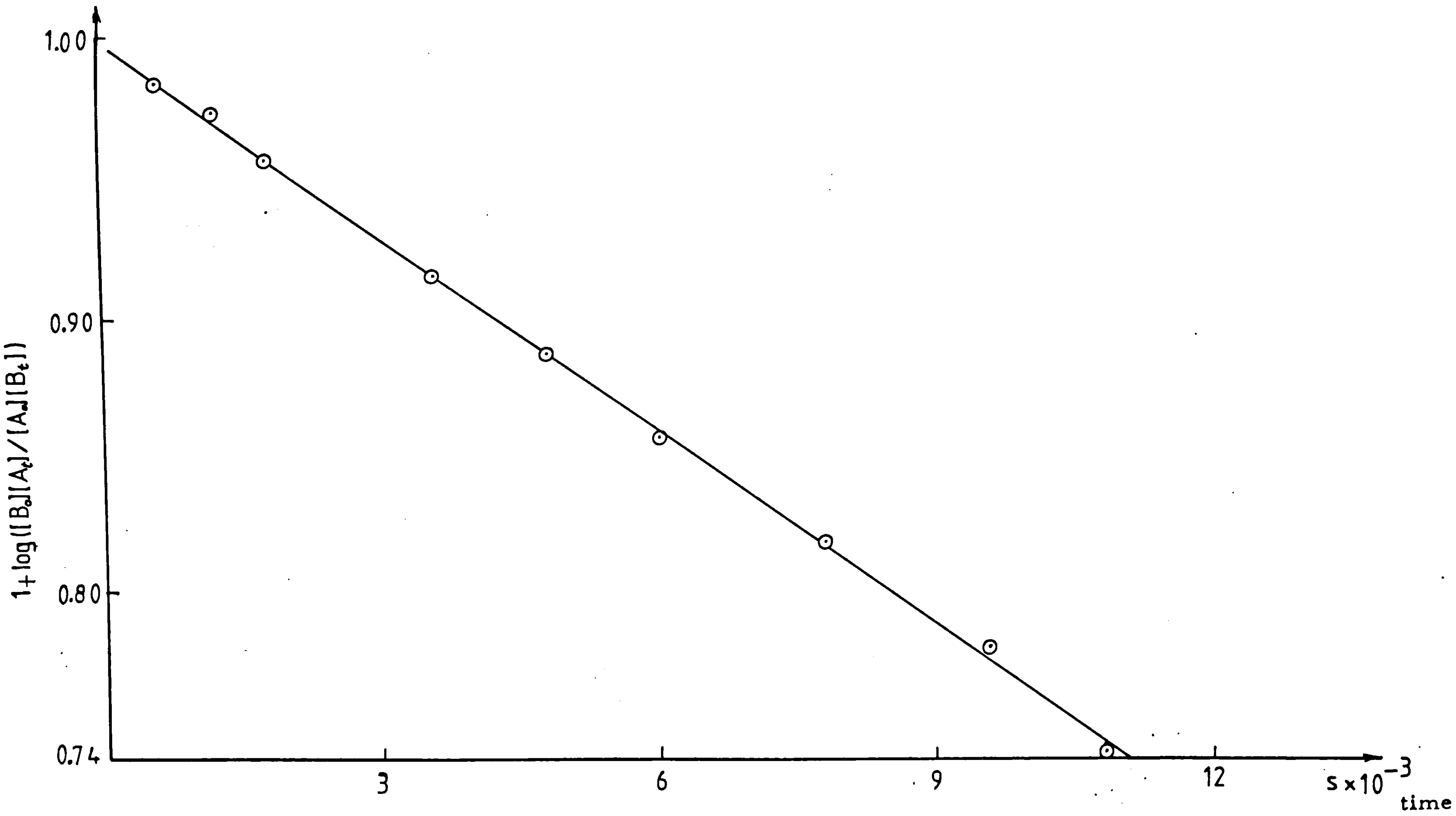


FIG. II.5 Second-order plot for the reaction of n-C_3H_7OCOCl (0.29) with n-Bu_4NNO_3 (0.51 mol dm^{-3}) at 35.2 ± 0.1°C

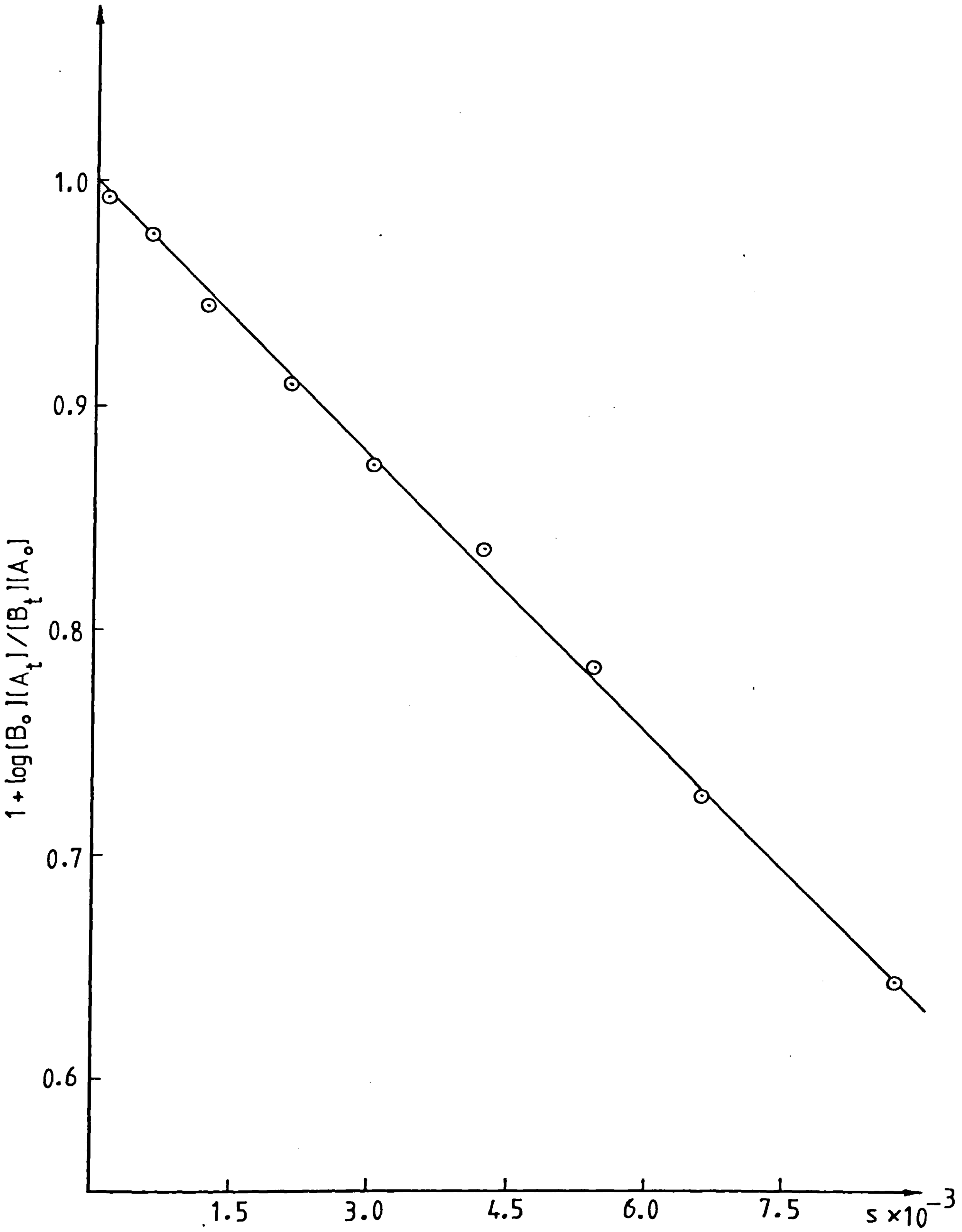


FIG. II. 6 Second-order rate plot for the reaction of n-C_3H_7OCOCl (0.123) with n-Bu_4NNO_3 (0.510 mol dm^{-3}) at 35.2 ± 0.1 °C

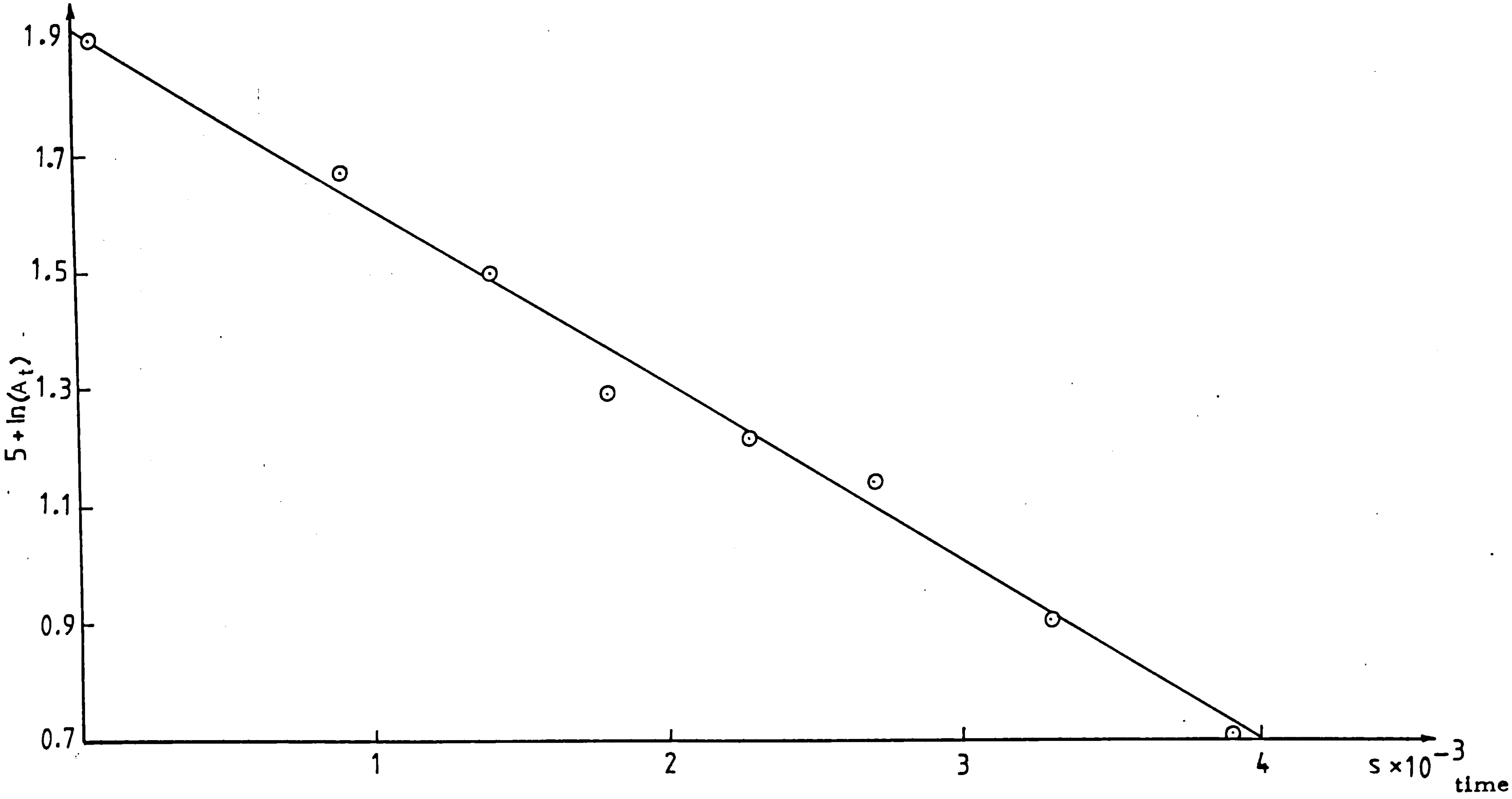


FIG. II. 7 Pseudo first-order rate plot for the reaction of n-C_3H_7OCOCl (0.045) with n-Bu_4NNO_3 (0.500 mol dm^{-3}) at 45.1 C^o.

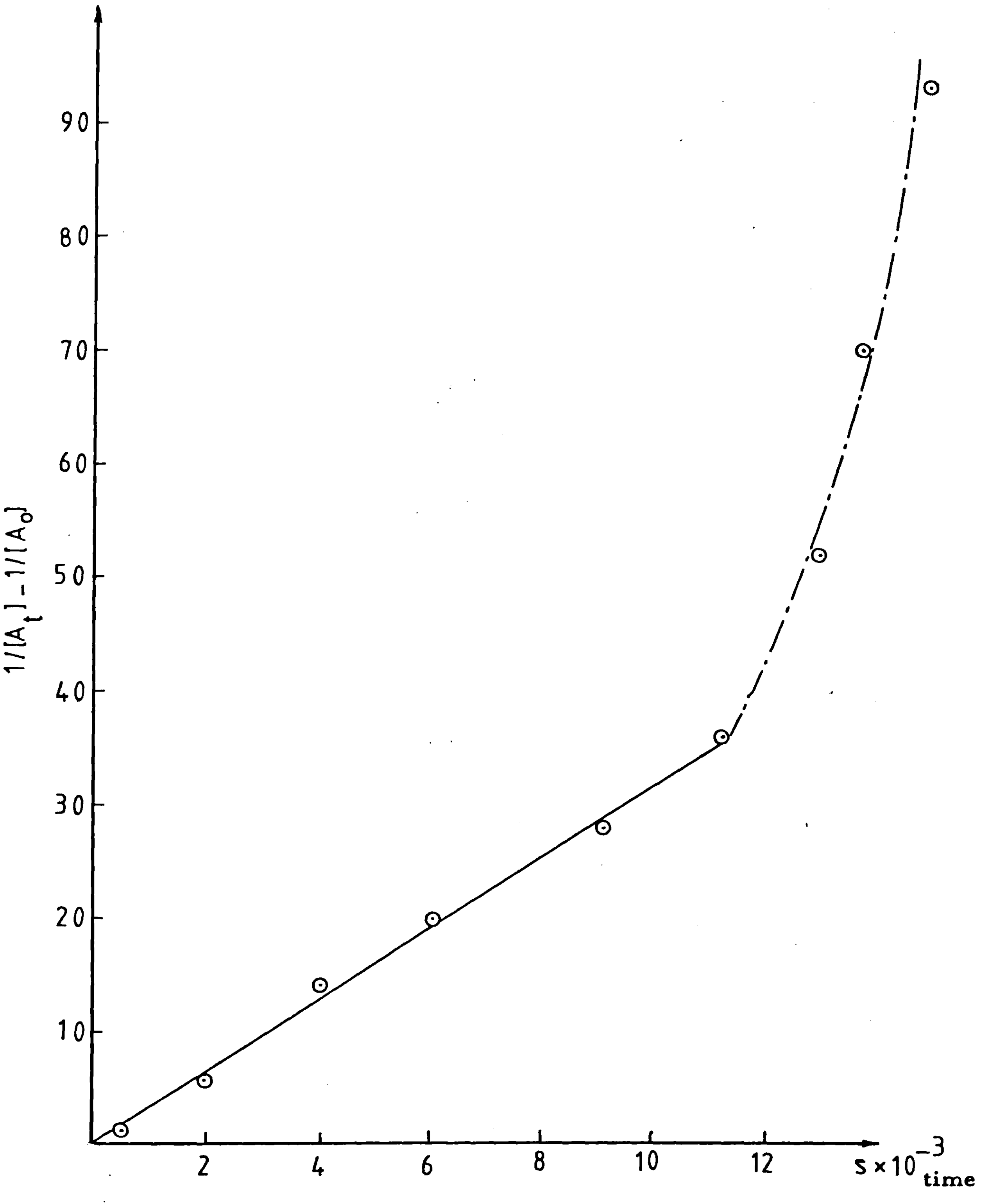


FIG. II. 8 Second-order rate plot for the reaction between $PhCH_2$ OCOCl (0.025) with n-Bu_4NNO_3 (0.025 mol dm^{-3}) at 35.2°C.

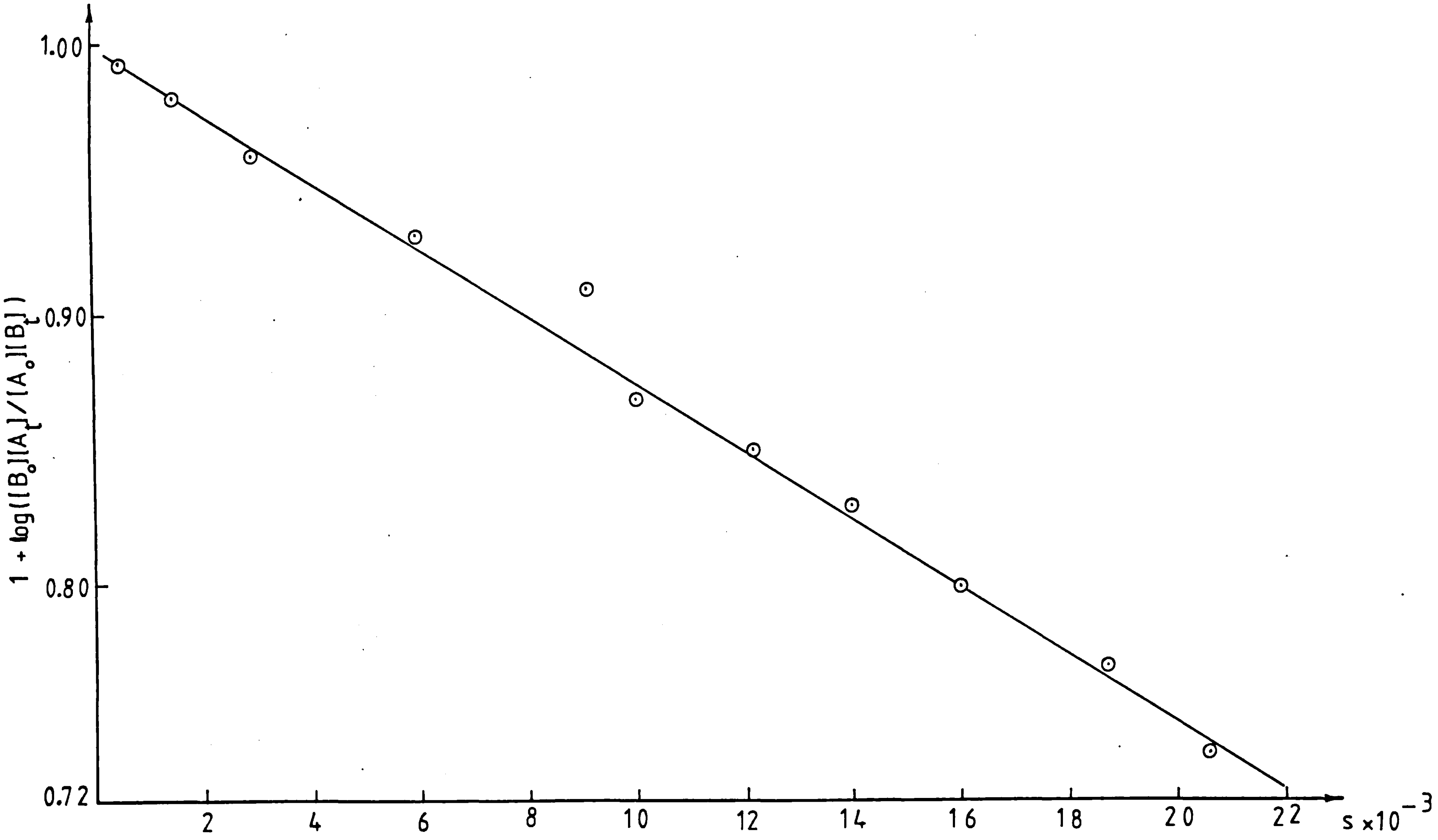


FIG. II. 9 Second-order rate plot for the reaction of $PhCH_2OCOCl$ (0.02) with n-Bu_4NNO_3 (0.05 mol dm^{-3}) at 25.5°C.

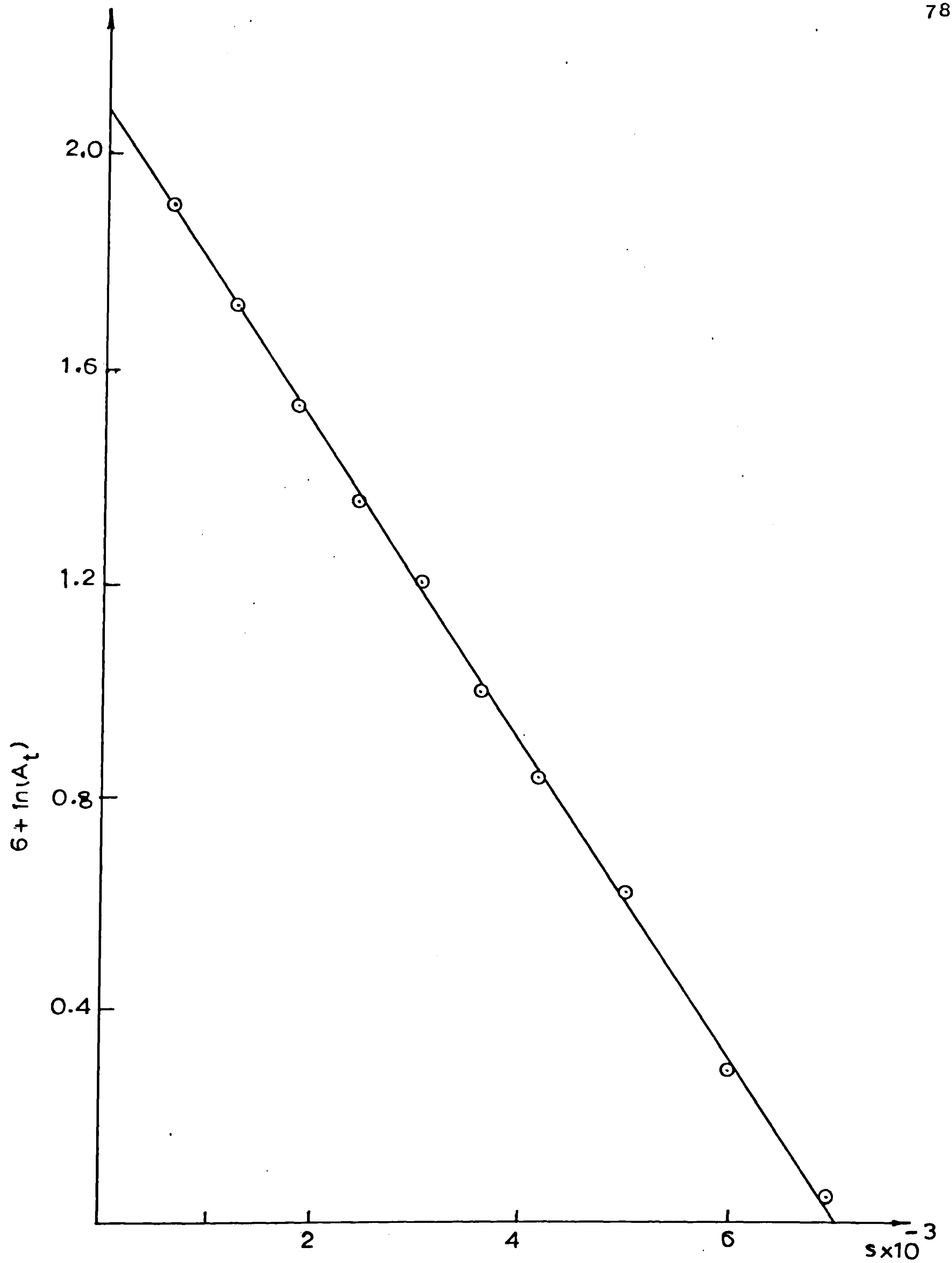


FIG. II. 10. Pseudo first-order plot for the reaction of $C_6H_5CH_2OCOCl$ (0. 02) with n-Bu_4NNO_3(0. 15 mol dm^{-3}) at 30. 2°C.

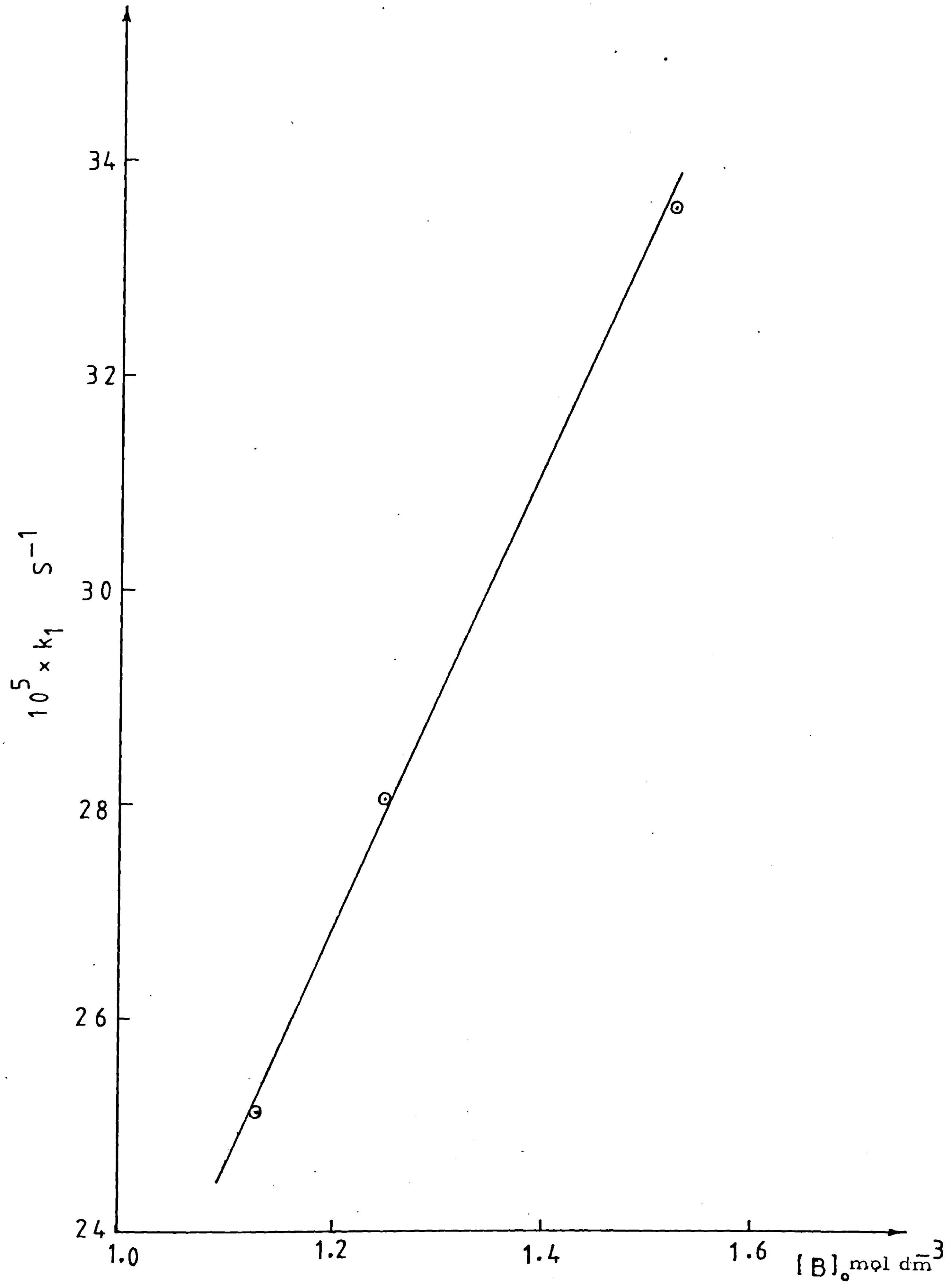


FIG. II. 11. Variation of first-order rate coefficient n-C_3H_7OCOCl and n-Bu_4NNO_3 with the concentration of n-Bu_4NNO_3 $[B_o]$.

II. 5 Arrhenius plots and the discussion of activation parameters.

The energies of activation, $E_a^{\ddagger}$, of the bimolecular reactions between n-propyl and benzyl chloroformates and tetra-n-butylammonium nitrate ion were calculated using equation 77.

$$k_1 = A\, e^{-E_a^{\ddagger} / RT} \tag{77}$$

where k_1 is the true second order rate coefficient for the attack of nitrate ion upon the chloroformate. Now k_1 is related to the observed second-order rate coefficient (k_2) as follows:

$$k_1 = k_2 \left(1 + \frac{k_a}{k_b}\right) \tag{78}$$

where k_a and k_b are the first order rate coefficient for the loss of nitrate ion and chloride ion respectively (see Section II. 4. 3) from the tetrahedral intermediate.

Accordingly k_1 may be expressed as follows:

$$\log k_1 = \log k_2 + \log \left(1 + \frac{k_a}{k_b}\right) = \log A - (E_a^{\ddagger} / 2.303\, R) \tag{79}$$

If it is assumed that the ratio of k_a / k_b is not very temperature dependent, i. e. the activation energies for those first-order reaction are comparable, then $E_a^{\ddagger}$ is obtainable from a least squares plot of the logarithm of the mean values for the observed second-order rate coefficients log (k_2) versus the reciprocal of the absolute temperature (1 / T). The energy of activation was obtained (slope equal to ($E_a^{\ddagger}$ / 2. 303 R), and the enthalpies of activation $\Delta H^{\ddagger}$ were calculated for the reactions with both chloroformates using equation 80.

$$\Delta H^{\ddagger} = E_a^{\ddagger} - RT \tag{80}$$

by substituting the appropriate values for $E_a^{\ddagger}$, R and T.

The corresponding entropies of activation $\Delta S^{\ddagger}$

are defined using the Eyring equation 81 (214)

$$k_1 = \frac{KT}{h} e^{\Delta S^{\ddagger}/R} e^{-(E_a^{\ddagger} - RT)/RT} \qquad (81)$$

where K is Boltzmann's constant, T is the absolute temperature and h is the Planck's constant.

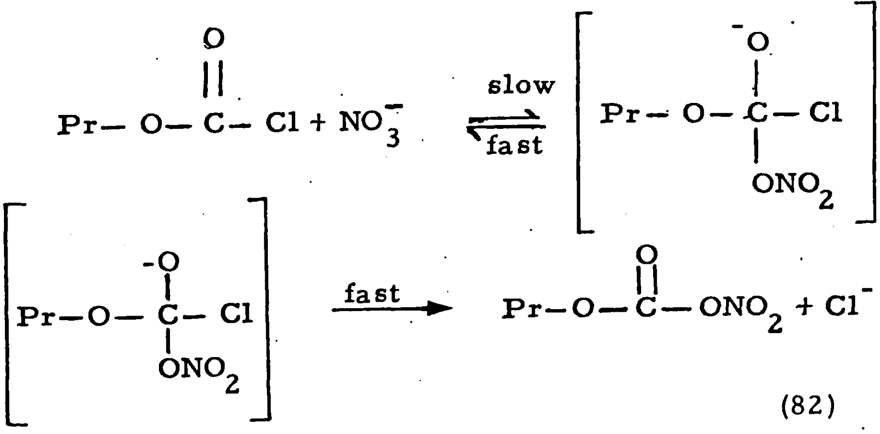
If it is supposed that the relative losses of Cl^- and NO_3^- from the tetrahedral intermediate X (see equation 70) lie between (i) 20% Cl^- and 80% NO_3^- and (ii) 80% Cl^- and 20% NO_3^-, then the following treatment can be adopted.

When (i) $4k_a = k_b$, and (ii) $k_a = 4k_b$ then $k_1 = 5k_2$ and $k_1 = 5k_2/4$ respectively, then the values of $\Delta S^{\ddagger}$ lie between -54 ± 2 and -65 ± 2 J mol^{-1} K^{-1} for n-propyl chloroformate and between -20 ± 3 and -9 ± 3 J mol^{-1} K^{-1} for benzyl chloroformate.

The values of the activation parameters for both the reaction between n-propyl and benzyl chloroformates and tetra-n-butylammonium nitrate are given in Table II. 8. Figures II. 12 and 13 show Arrhenius plot of log k_2 values versus $(1/T)$.

To use the Eyring equation for second order rate coefficients the units of these rate coefficients must be dm^3 mol^{-1} s^{-1} and the standard state for the entropy of activation is then 1 mol dm^{-3}. This is the accepted approach for making comparisons with other reactions both unimolecular and bimolecular (217) e. g. the acid catalysed hydrolysis of simple aliphatic esters have substantial negative entropies of activation $\Delta S^{\ddagger} = -96$ J mol^{-1} K^{-1} when proceeding through tetrahedral intermediates.

The results of this study show that the values of $\Delta S^{\ddagger}$ for the reaction between n-propyl chloroformate and tetra-n-butyl ammonium nitrate supports a mechanism having a tetrahedral intermediate. The hydrolysis of a series of chloroformates have been studied by Queen (88) who observed values of $\Delta S^{\ddagger}$ as follows, Me - 79.9, Et - 71.1 and n-Pr -69.5 J mol^{-1} K^{-1}. He favoured a reaction pathway involving the reversible formation of a tetrahedral intermediate rather than a direct S_N2 displacement of chloride. His values of enthalpies of activation for the above chloroformates were ~ 71 kJ mol^{-1} which he noted were somewhat less than those associated with S_N2 displacements of chloride from primary alkyl chlorides in water viz., ~ 104 kJ mol^{-1} (218) but more like those observed for hydrolysis of carboxylic acid derivatives; e.g. a value of $\Delta H^{\ddagger} = 72$ kJ mol^{-1} has been found by Moelwyn-Hughes (219) for the hydrolysis of methyl acetate and a value of $\Delta H^{\ddagger} = 67$ kJ mol^{-1} has been found by Hudson (220) for the hydrolysis of benzoyl chloride. The measurement of a value of $\Delta H^{\ddagger} = 76$ kJ mol^{-1} for the reaction of propyl chloroformate with tetra-n-butylammonium nitrate seems to be more in keeping with those found for the hydrolysis of chloroformates and the hydrolysis of acid derivatives. It is supposed therefore, that the reaction proceeds as follows, i.e. analogously to that proposed by Kevill (107) for the reaction between methyl chloroformate and the nitrate ion, derived in this case from tetra ethylammonium nitrate:-



$$\mathrm{Pr-O-\overset{O}{\overset{\|}{C}}-Cl + NO_3^-} \underset{fast}{\overset{slow}{\rightleftharpoons}} \left[\mathrm{Pr-O-\underset{ONO_2}{\underset{|}{\overset{^-O}{\overset{|}{C}}}}-Cl}\right]$$

$$\left[\mathrm{Pr-O-\underset{ONO_2}{\underset{|}{\overset{-O}{\overset{|}{C}}}}-Cl}\right] \xrightarrow{fast} \mathrm{Pr-O-\overset{O}{\overset{\|}{C}}-ONO_2 + Cl^-}$$

(82)

With benzyl chloroformate, the increase in electron donation by the benzyl group might be expected to retard the approach of the nitrate ion (the effect of which should be to increase $\Delta H^{\ddagger}$) and to facilitate the heterolysis of the carbon-chlorine bond (the effect of which would be to make $\Delta S^{\ddagger}$ less negative). Queen (88) noted in his hydrolysis studies a large value of $\Delta H^{\ddagger}$ for iso-propyl chloroformate viz., 100 kJ mol^{-1} and a positive value for $\Delta S^{\ddagger} = 42$ J mol^{-1} K^{-1}.

The only measurement of an entropy of activation for reactions between a chloroformate and nitrate ion has been in the work of Zabik and Schultz (103) in their study of aryl chloroformates. They reported $\Delta S^{\ddagger}$ values - 21.3 for p-methoxyphenyl, -28.0 for phenyl and -87.5 J K^{-1} mol^{-1} for p-chlorophenyl chloroformates. The values of $\Delta H^{\ddagger} = 84$ kJ mol^{-1} and $\Delta S^{\ddagger}$ lying between -21 and -9 J mol^{-1} K^{-1} for the reaction between benzyl chloroformate and tetra-n-butylammonium nitrate seem to support similar schemes like those of Boschan (56) and Kevill (104) in which there is more carbon-chlorine bond breaking accompanying the nitrate ion attack and less involvement of a tetrahedral intermediate, Scheme D, (see p. 87).

TABLE II.8 ACTIVATION PARAMETERS OF THE REACTIONS BETWEEN n-PROPYL AND BENZYL CHLOROFORMATES WITH TETRA-n-BUTYLAMMONIUM NITRATE at THE MEAN TEMPERATURE*
(ca 35°C.)

Compound	Activation Parameters[a]		
	$E_a^\ddagger$ /kJ mol^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J mol^{-1}K^{-1}
n-C_3H_7OCOCl	78.8 ± 1.4	76.2 ± 1.4	-65 ± 2[b] -54 ± 2[c]
$C_6H_5CH_2OCOCl$	86.1 ± 0.1	83.5 ± 0.1	-9 ± 3[b] -20 ± 3[c]

*n - C_3H_7OCOCl at 35.34°C

*$C_6H_5CH_2OCOCl$ at 35.18°C

a) See Appendix III for the determination of errors in the activation parameters.

$\Delta S^\ddagger$ Determined taking $k_2 = k_b \times \left(\frac{k_1}{k_a+k_b}\right)$ See page (65 and 81).

when

b) $k_a = 4\ k_b$

c) $4\ k_a = k_b$

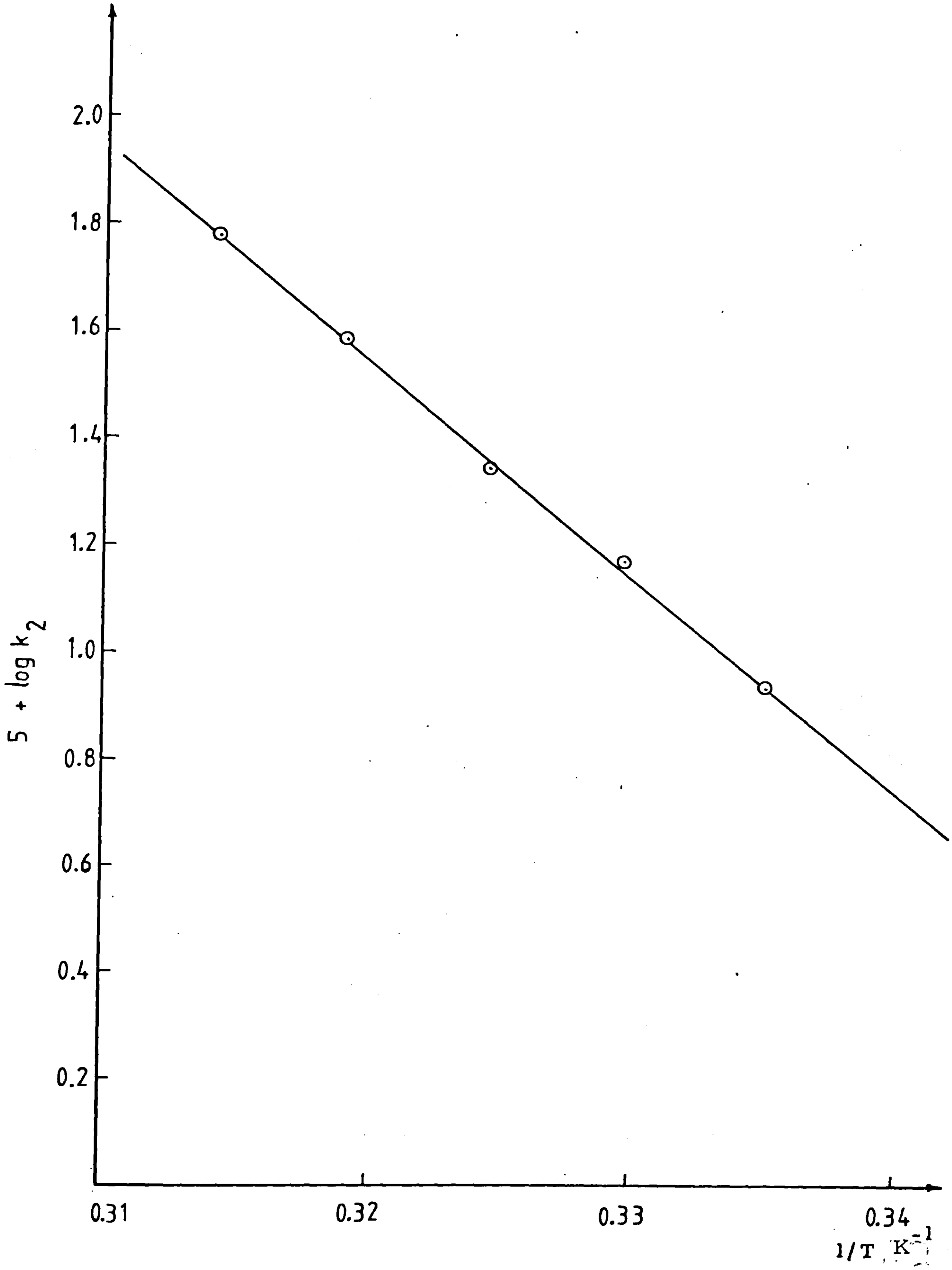


FIG. II. 12 Arrhenius plot of the limiting values of the second-order rate coefficient for the reaction between n-C_3H_7OCOCl and n-Bu_4NNO_3.

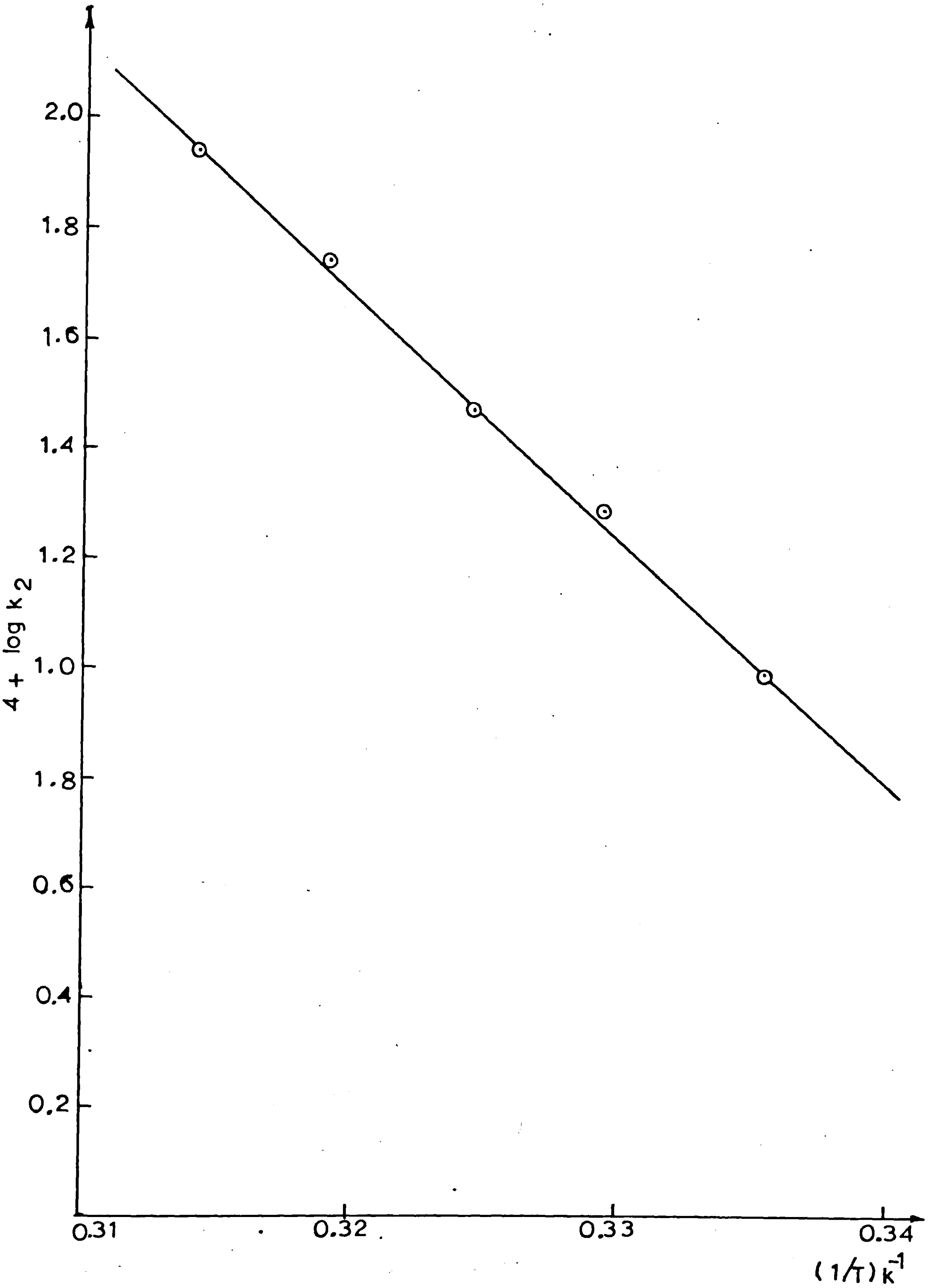
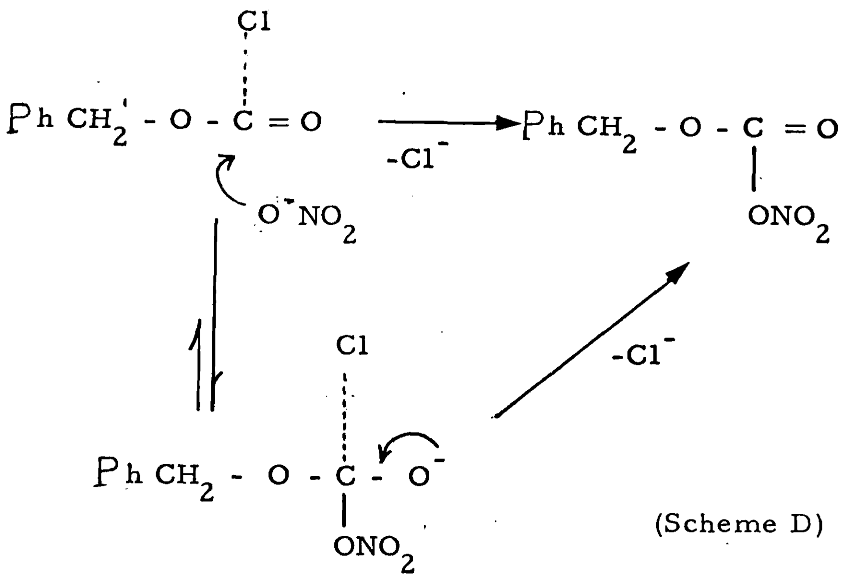
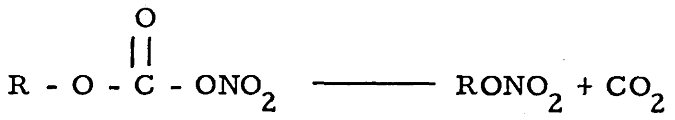


FIG. II. 13 Arrhenius plot of the limiting value of the second-order rate coefficient for the reaction between PhOCOCl and n-Bu_4NNO_3.



(Scheme D)

The decomposition of benzyl and propyl nitrato-carbonates complete the scheme for the transformation of chloroformates to nitrate esters thus:



$$R - O - \overset{\overset{O}{||}}{C} - ONO_2 \longrightarrow RONO_2 + CO_2$$

In the experimental conditions used in this work the latter reaction appears not to proceed very rapidly.

II. 6 Results of carbon dioxide analysis.

The quantitative determination of carbon dioxide evolved during the course of the reaction between n-propyl chloroformate and tetra-n-butylammonium nitrate was carried out as described in Section III. 8 and the corresponding amount of n-propyl nitrate product was measured as described in Section III. 3. 2.

Although the infrared analysis showed that all of the n-propyl chloroformate had reacted, the amount of n-propyl nitrate produced corresponded to only 18% reaction assuming that the band at 1635 cm^{-1} was due solely to the asymmetric stretching of the nitro group in this compound. However, the evolution of carbon dioxide corresponded to 61% reaction leaving 39% still involved in some possible intermediate viz., $n\text{-}C_3H_7OCOONO_2$. An additional route for the production of carbon dioxide, over and above the decomposition of this intermediate, must have operated giving the extra 43% i.e. (61-18%). This could have arisen by the competitive reaction of chloride ions with the n-propyl chloroformate once sufficient tetra-n-butylammonium nitrate had reacted.

$$Cl^- + PrOCOCl \longrightarrow PrCl + {}^-OCOCl$$

$${}^-OCOCl \longrightarrow Cl^- + CO_2$$

II. 7 Investigation of the existence of a competitive reaction with chloride ion.

The reaction between benzyl chloroformate and tetra-n-butylammonium chloride in acetonitrile.

This reaction was carried out at 25.1°C., as other typical kinetic determinations in Section II.4. 2. A second-order rate law was obeyed having an observed rate coefficient much higher than that corresponding reaction with tetra-n-butylammonium nitrate. The second-order rate coefficients are given in Table II. 9, and a kinetic plot is shown in Figure II. 14.

TABLE II.9 SECOND-ORDER RATE COEFFICIENTS OF THE REACTION BETWEEN BENZYL CHLOROFORMATE AND TETRA-n-BUTYLAMMONIUM NITRATE AND CHLORIDE AT 25.1°C.

$PhCH_2OCOCl[A_o]$ / mol dm^{-3}	n-$Bu_4NNO_3[B_o]$ / mol dm^{-3}	n-BuNCl / mol dm^{-3}	$10^4 \times k_2$/ dm^3 mol^{-1} s^{-1}
0.025	0.050	-	10.170
0.025	-	0.05	109.605

The observation of the second-order rate coefficient for the reaction between benzyl chloroformate and tetra-n-butylammonium chloride being larger than that for the corresponding reaction with tetra-n-butylammonium nitrate by one order of magnitude, explains the existence of the "auto catalytic effect upon the disappearance of benzyl chloroformate."

The build up of chloride ion is most significant in reactions were there is a low nitrate to chloroformate ratio.

The products of this reaction were investigated and it was found that the products were benzyl chloride and carbon dioxide.

Kevill and Johnson (107) obtained second-order rate coefficients for the reaction between tetra ethylammonium chloride and a series of alkyl chloroformates and

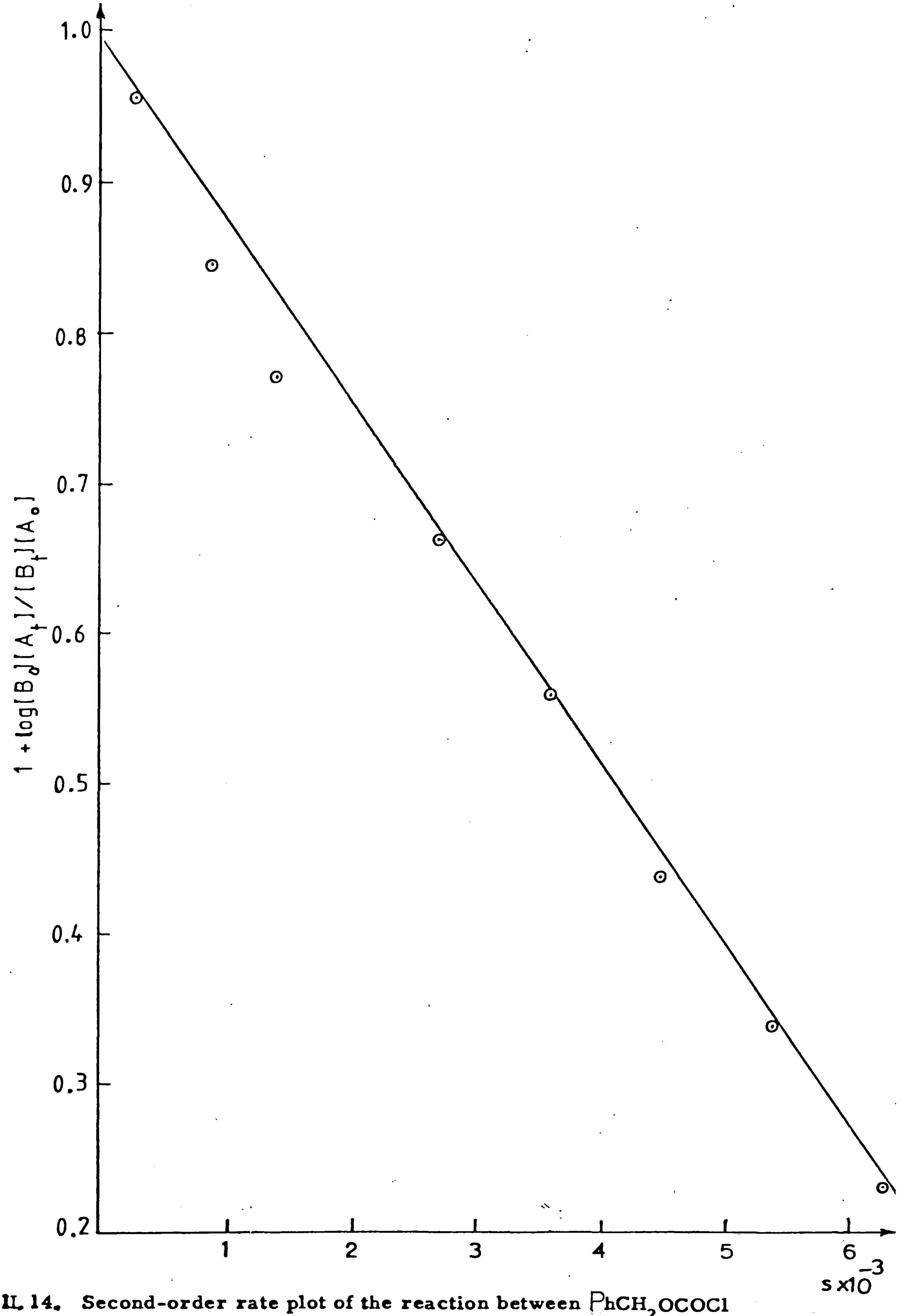
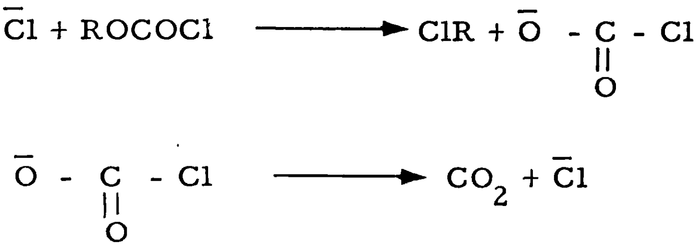


FIG. II. 14. Second-order rate plot of the reaction between $PhCH_2OCOCl$ (0. 025) and n-Bu_4NCl (0. 050 mol dm^{-3}) at 25. 1°C.

proposed a bimolecular mechanism as follows:



$$\bar{Cl} + ROCOCl \longrightarrow ClR + \bar{O} - \underset{\underset{O}{\|}}{C} - Cl$$

$$\bar{O} - \underset{\underset{O}{\|}}{C} - Cl \longrightarrow CO_2 + \bar{Cl}$$

The order of reactivity of the alkyl chloroformates was consistent with a bimolecular nucleophilic attack upon the alkyl group, the largest rate being shown by methylchloroformate viz.:-

$$Me \gg Et \sim n\text{-}Pr > iso\text{-}Pr$$

The inductive release in the alkyl group ($X_2 X_1$ CH) in $X_2X_1CHOCOCl$ is least with $X_1 = X_2 = H$ and increases with $X_2 = X_1 = CH_3$.

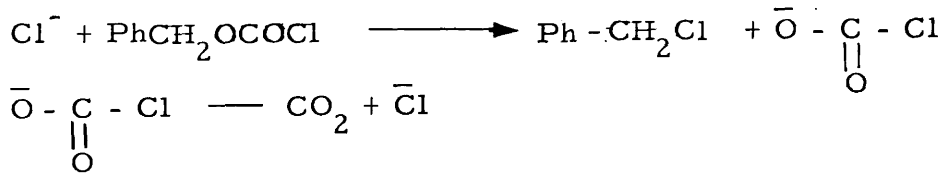
The electron withdrawing phenyl group on the other hand would be expected to aid attack by chloride ion and also to stabilise the pentacoordinate transition state. With benzyl chloroformate

($X_1 = Ph$, $X_2 = H$) ($k_2 = 109.6 \times 10^{-4} dm^3 mol^{-1} s^{-1}$)

The corresponding rate coefficient for the reaction of methyl chloroformate with tetraethylammonium chloride was

$16.4 \times 10^{-4}\ dm^3 mol^{-1} s^{-1}$.

It is expected therefore that the above mechanism should hold for benzyl chloroformate.



$$\mathrm{Cl^- + PhCH_2OCOCl \longrightarrow Ph\text{-}CH_2Cl + \bar{O}\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl}$$

$$\mathrm{\bar{O}\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl \;—\; CO_2 + \bar{Cl}}$$

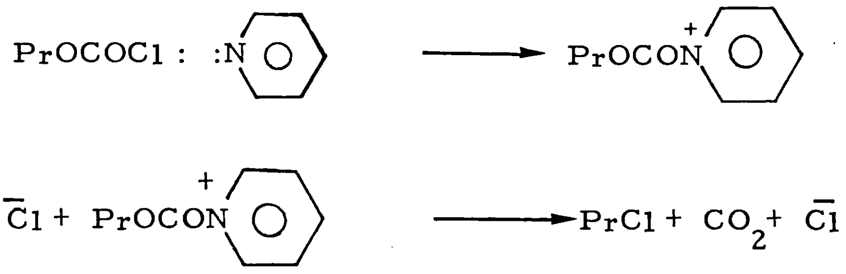
II. 8 Catalysis and Related Kinetic Study.

II. 8. 1 Reaction of n-propyl chloroformate with tetra-n-butyl ammonium nitrate in the presence of pyridine.

The reaction of n-propyl chloroformate (0. 34 mol dm^{-3}) with tetra-n-butylammonium nitrate (0. 34 mol dm^{-3}) was carried out in the presence of pyridine (0. 5 cm^3) in acetonitrile at 25. 5°C. Pyridine in acetonitrile solution (of the same concentration) was used in the reference cell for the infrared determination of the unreacted n-propyl chloroformate.

The second-order coefficient was calculated according to the equation 64 and its value is given in Table II. 10. Brief investigations have been made in order to investigate whether the presence of pyridine affects the formation of n-propylnitrate product or catalyses the reaction of nitrate ion with n-propyl chloroformate. It was concluded that the presence of pyridine increases the rate-coefficient for the disappearance of the chloroformate but provides no assistance for the formation of n-propyl nitrate. The major product in the presence of pyridine was n-propyl chloride.

This observation has been found before in which the tertiary amine catalysis the decomposition of alkyl chloroformates (48). This mechanism is considered to be as follows:



Support for this mechanism comes from the observation in which $\bar{\mathrm{Cl}}$ catalyses the decomposition of chloroformates in acetonitrile solutions.

II. 8. 2 The effect of added tetra-n-butylammonium perchlorate on the reaction between benzyl chloroformate and tetra-n-butylammonium nitrate.

Previous studies have been concerned with the reaction of benzyl chloroformate with tetra-n-butylammonium nitrate at several temperatures. At each temperature the kinetics have been found to be second-order, first order in each reactant.

Following the investigation of Kevill (104 and 105) of the effect of the presence of perchlorate salts in the reactions of methyl chloroformate with nitrate ions in the presence of a perchlorate salt a related study was carried out with the reaction between benzyl chloroformate and tetra-n-butylammonium nitrate in the presence of tetra-n-butylammonium perchlorate.

The effect of perchlorate salts upon reacting systems are often examined (104) as the perchlorate anion is not a nucleophile and so cannot enter directly into reaction but the salt ion affects the rate of reaction and the rate of formation of products.

Kevill's investigation into the reaction between methyl chloroformate solution (0.0935) and silver nitrate (0.0100 mol dm^{-3}) reported second-order rate coefficient with value = 1.93×10^{-4} dm^3 mol^{-1} s^{-1}. When silver perchlorate solution (0.01 mol dm^{-3}) was added to this reaction the second-order rate coefficient fell in value to 1.83×10^{-4} dm^3 mol^{-1} s^{-1}.

The absence of any increase in rate showed that the additional silver ions did not assist the removal of chloride whether from the methyl chloroformate or from the intermediate that leads to methyl nitratocarbonate. However, under these conditions more of this intermediate was partitioned to the nitratocarbonate rather than returned to the reactants.

To the reaction between benzyl chloroformate (0.02) and tetra-n-butylammonium nitrate (0.10) a solution of tetra-n-butylammonium perchlorate (0.02 mol dm^{-3}) was added at 25.5°C; the reaction was followed as previously until the concentration of benzyl chloroformate was reduced to 10% of its initial value. The second-order rate coefficient so obtained, is given in Table II.10 and Figure II.15 displays the kinetic plot.

It was found that addition of tetra-n-butylammonium perchlorate depressed the reaction rate, whilst increasing only slightly (ca. 1.5%) conversion to the product benzyl nitrate above that in the absence of perchlorate.

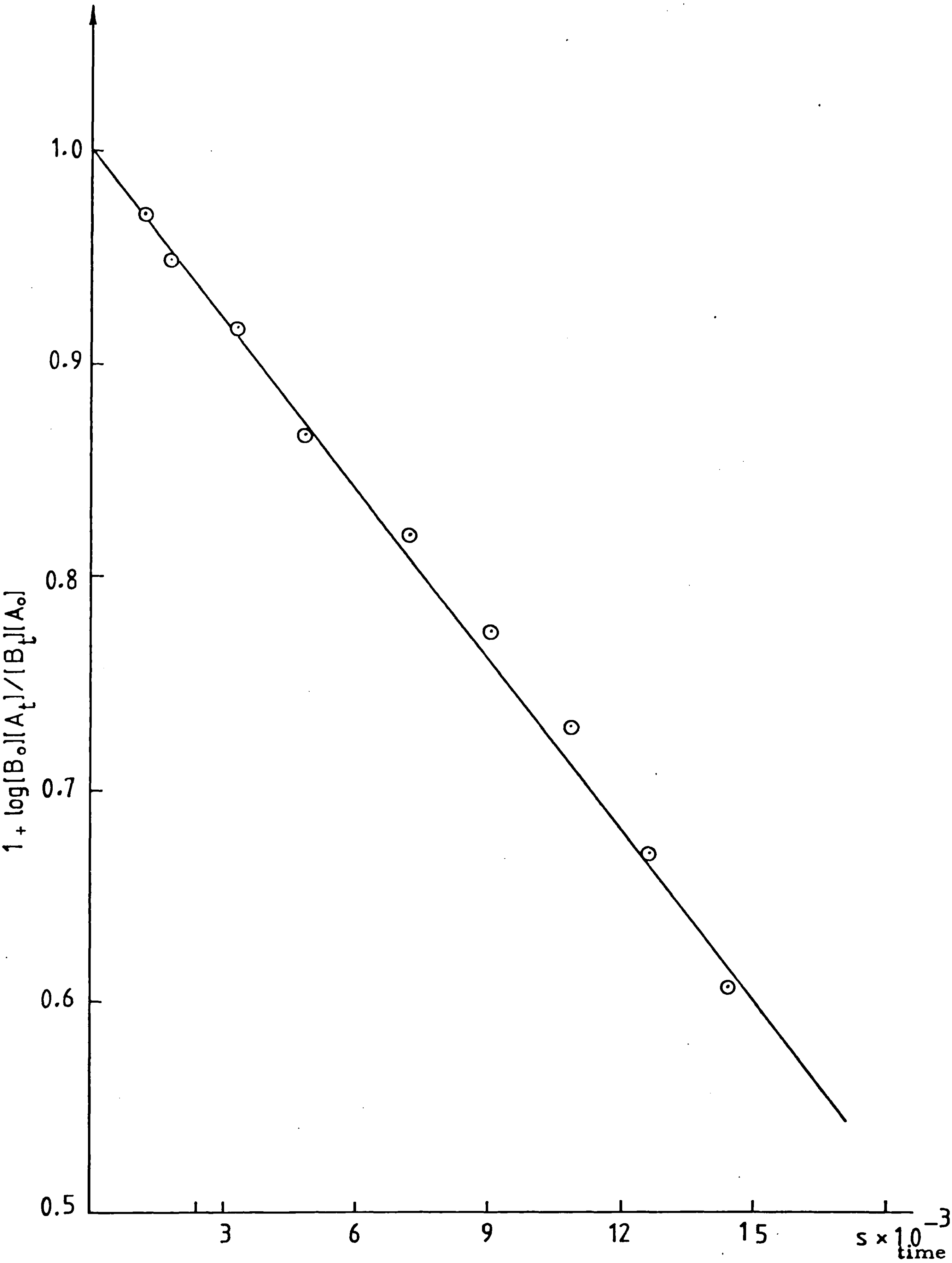


FIG II. 15 Second-order rate plot for the reaction between $PhCH_2OCOCl$ (0. 02) $n\text{-}Bu_4NNO_3$ (0. 1 0) in the presence of $n\text{-}Bu_4NClO_4$ (0. 02 mol dm^{-3}).

TABLE II. 10 THE SECOND-ORDER RATE COEFFICIENT OF THE REACTION BETWEEN $PhCH_2OCOCl$ AND $n\text{-}Bu_4NNO_3$ IN THE PRESENCE OF $n\text{-}Bu_4NClO_4$.

$[PhCH_2OCOCl]$ / mol dm^{-3}	$Bu_4NNO_3[B_o]$/ mol dm^{-3}	$[Bu_4NClO_4]$/ mol dm^{-3}	$10^4 \times k_2$/ $dm^3 mol^{-1} s^{-1}$
0.02	0.100	0.020	7.677
0.02	0.100	-	9.811
0.34	0.340		107.211*

In a study with iso-propyl chloroformate Kevill and Johnson (106) did observe a reaction with silver perchlorate alone and also that the experimental second-order rate constant for a similar reaction with silver nitrate equalled the sum of contribution from silver perchlorate and tetraethylammonium nitrate separately. The benzyl chloroformate could have been expected to behave analogously to the iso-propyl chloroformate with the tetra-n-butylammonium ion perhaps assisting the ionisation of the chloride ion (electrophilic assistance).

$$PhHCH_2OCOCl + Bu_4\overset{+}{N}Cl^-O_4 \longrightarrow PhCH_2O\overset{+}{C}O + Bu_4\overset{+}{N}\overset{-}{Cl} + Cl\overset{-}{O}_4$$

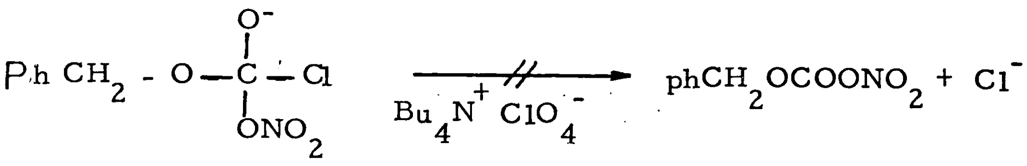
$$PhHCH_2O\overset{+}{C}O + Bu_4\overset{+}{N}\,\bar{N}NO_3 + Cl^-O_4 \xrightarrow{fast} PhCH_2OCOONO_2 + Bu_4\overset{+}{N}ClO_4^-$$

---

*Reaction carried out in the presence of pyridine (see Section III. 7).

The decrease in the second order rate constant precluded this involvement of the tetra-n-butylammonium perchlorate.

The lack of any sizeable increase in concentration of nitrate product suggests that the perchlorate was not acting to assist chloride removal from the intermediate (X)



$$PhCH_2-O-\overset{O^-}{\underset{ONO_2}{C}}-Cl \xrightarrow[Bu_4N^+\,ClO_4^-]{/\!/} phCH_2OCOONO_2 + Cl^-$$

(X)

The retardation must be explained by the common ion effect upon the dissociation of the tetra-n-butylammonium nitrate reducing the amount of free nitrate ion

$$Bu_4N^+\,NO_3^- \underset{Bu_4N^+\,ClO_4^-}{\rightleftharpoons} Bu_4N^+ + NO_3^-$$

General conclusions

The experimental evidence determined in the investigation of the reaction of n-propyl and benzyl chloroformates with tetra-n-butylammonium nitrate in acetonitrile has shown:

(i) The reactions are second-order for various concentrations of tetra-n-butylammonium nitrate and these chloroformates.

(ii) The entropy change, $\Delta S^{\ddagger}$, is negative which is indicative that the reaction proceeds by a bimolecular mechanism.

(iii) The corresponding nitrate ester products are produced in only 18 - 20%.

(iv) The reaction rate is increased by the addition of pyridine to the reaction media and decreased by addition of tetra-n-butylammonium perchlorate but both have no effect on the percentage of the nitrate ester product

(v) Competition of reaction with the tetra-n-butylammonium chloride product, becomes more pronounced in the later stages of reactions of tetra-n-butylammonium nitrate.

(vi) The reaction between tetra-n-butylammonium chloride and benzyl chloroformate is ten times faster than the corresponding reaction with tetra-n-butylammonium nitrate.

(vii) These results support a mechanism for the formation of nitratocarbonates from the chloroformates via a tetrahedral intermediate. The nitratocarbonates are only slowly decomposed to nitrate esters.

CHAPTER III

EXPERIMENTAL TECHNIQUES

CHAPTER III

EXPERIMENTAL TECHNIQUES

III. 1 Purification, preparation and storage of materials

III. 1. 1 Solvent

III. 1. 1. 1. Acetonitrile

B.D.H "Spectrograde" acetonitrile, dried with calcium hydride was fractionally distilled through a 50 cm column packed with fine glass helices. The middle fraction, b p 81.2 - 81.4°C, was collected. and stored over "4A" molecular sieve in a dark bottle until required.

III. 1. 1. 2 Pyridine

B.D.H."Laboratory Reagent" was refluxed over potassium hydroxide, distilled at 113-114°C and stored over "4A" molecular sieve.

III. 1. 2 Tetra-n-butylammonium salts

These materials were prepared according to the neutralisation method described by Burgess and Chorrles (132).

Aqueous solutions of(B.D.H)tetra-n-butylammonium hydroxide (60%) were neutralised by adding the appropriate acids with stirring (nitric, hydrochloric and perchloric) from a dropping burette. The solutions were evaporated at reduced pressure using a rotary evaporator and temperatures ranging between 30 to 35°C to leave the products. The materials were then recrystallised as follows:

III. 1. 2. 1. Tetra-n-butylammonium nitrate

This salt was dissolved in methyl alcohol, charcoal (0.5 w/w) was added and the methanol was refluxed for 30 minutes. The charcoal was then filtered off and the filtrate evaporated. Tetra-n-butylammonium nitrate was recrystallised from benzene, and the solid was collected using a sintered glass funnel (G_3) in a "dry bag", and then kept in a vacuum dessicator over phosphorus pentoxide. Its melting point was found to be 117.5°C; literature values 118.00 (133).

III. 1.2.2. Tetra-n-butylammonium chloride

The salt was repeatedly crystallised from ethyl alcohol containing ether (134) and then maintained at a temperature above its m p with continued pumping to remove solvents of crystallisation. After this treatment its melting point was found to be 69.5°C which is lower than that previously recorded in literature 75°C (135, 136). A Volhard's method of determination of chloride showed that this sample of tetra-n-butylammonium chloride had a purity of 95.5%. All handling of the tetra-n-butylammonium chloride was carried out under nitrogen in "glove bag" owing to its hygroscopic nature.

III. 1.2.3. Tetra-n-butylammonium perchlorate.

Several methods for crystallisation of this salt have been reported i.e. from nitrobenzene (137) and ethyl acetate (138), however the salt was recrystallised from conductivity water. The salt was further purified by precipitation from ethyl acetate solution by the addition of benzene, its m p 212.0°C (Lit. (139) 213°C).

Owing to the explosive properties of perchlorates (140), all necessary precautions were taken into account in the preparation and crystallisation processes.

III. 1.3. Alkyl chloroformates

III. 1.3.1 n-Propyl chloroformate

Koch-Light (pure) n-proply chlorformate was purified by distillation, through a 60 cm fractionating column in an atmosphere of dry nitrogen. The first and last 5 cm^3 of distillate were discarded and the middle fraction, b p 114.2°C, was collected. Lit (1) b p 114.4-5°C).

Since n-propyl chloroformate hydrolyses in aqueous solution to give propyl alcohol, hydrogen chloride and carbon dioxide (56), it was possible to assess the chlorine content by using aqueous sodium hydroxide for the hydrolysis followed by Volhard's method. The results showed that n-propyl chloroformate had a purity of 99.8%. The N.M.R. spectrum showed that the distillation had removed some contaminants.

III. 1.3.2. Benzyl chloroformate

Eastman benzyl chloroformate was purified by fractionation under reduced pressure, its boiling point was found to be 75°C at 1-2 mm.Hg pressure (Lit. (142) b p 76-78 °C at 1-2 mm Hg pressure.

Benzyl chloroformate was analysed, using the method described by Kalika (143) which is based on saponification in ethanolic alkali and determination of free Cl^-.

Refluxing five samples of 0.2 gm benzyl chloroformate each with 25 cm^3 ethyl alcohol and 15 cm^3 of sodium hydroxide solution(1 mole)at temperature of 100°C for 2 hours followed by the analysis of the free Cl^- yields 99.4% purity.

III. 1.4 Nitrate esters

The preparation of nitrate esters is generally accomplished by one or two methods: either esterification with nitric acid of the appropriate alcohols (144) or by reacting the halides with silver nitrate. The second method (145 or 146) proved to be applicable here.

III. 1.4.1. Benzyl nitrate (147)

This was prepared by adding B D H benzyl chloride (8 g) over a period of 30 minutes to B D H silver nitrate (13 g) in acetonitrile (50 cm^3). The mixture was heated for

1 hour with refluxing of the solvent, cooled and the silver chloride formed removed by filtration. After removal of the acetonitrile, the residue on distillation yielded 4.60 gm benzyl nitrate. The product was purified by fractional distillation from silver nitrate. The boiling point found was 44.6°C at 0.5 mm.Hg. pressure and the refractive index n_D^{20} 1.5185. Literature value (146) b p 45.0°C at 0.5 mm.Hg pressure and the refractive index n_D^{20} 1.5180 (149)

III.1.4.2 n-Propyl nitrate

Eastman reagent grade n-propyl nitrate was purified by fractional distillation (3 X) at 30°C and 35 mm Hg. pressure. The analysis of this compound using g.l.c. Pye Series 104 at 75°C and 3% O.V. 17 column (2 m.) showed only a single peak corresponding to n-propyl nitrate instead of three peaks prior to the purification. The infrared spectrum of an acetonitrile solution of n-propyl nitrate showed only the bands characteristic of n-propyl nitrate in addition to the solvent. Further distillation showed no change in these spectra.

The purified n-propyl and benzyl nitrate were kept in a dark bottle contained in a desiccator at −4°C until use.

III.2. Method of determination of reactants and products in kinetic systems.

III.2.1. Infrared spectra.

All spectra reported in this thesis for n-propyl chloroformate, and nitrate have been recorded using a Perkin-Elmer 177 grating infrared spectrophotometer and matched 0.75 mm infrared cells. Spectra recorded for the reactions involving benzyl chloroformate and nitrate employed a

Perkin-Elmer 257 infrared spectrometer in conjunction with 1 mm infrared cells.

Infrared cells were fitted with sodium chloride windows. Before use the cells were rinsed with dry acetone and this removed completely with dry nitrogen. The cells were kept in a vacuum desiccator containing calcium chloride.

Infrared spectrophotometers, that had previously been balanced for 100% tansmission with acetonitrile contained in both reference and sample cells were used to record the absorption spectrum of benzyl, n-propyl chloroformates and nitrate solutions in acetonitrile between 650 and 4000 cm^{1}. It was observed the absorption peaks of the solvent do not interfere with either the characteristic peaks of the reactants (benzyl and n-propyl chloroformates) or the products (benzyl and n-propyl nitrates). The infrared absorptions of the above materials are given in Table II.2.

III.2.2. The calibration curves and extinction coefficients.

The extinction coefficients of n-propyl, benzyl chloroformates and nitrates were determined by measuring the infrared absorptions for a series of concentrations of each pure sample in acetonitrile: for n-propyl (0.02 - 0.2), for benzyl chloroformates and nitrates (0.002 - 0.02 mol. dm^{-3}). The values of the transmissions (I) of the characteristic C=O stretching vibrations of the chloroformates in the region 1775-1780 cm^{-1} and the characteristic assymetric stretching NO_2 vibration in the region 1630 - 1635 cm^{-1} for nitrate esters (150) were recorded for each concentration. The absorbances ($\log_{10} {}^{I}0/_{I}$ were then calculated and plotted against concentrations

It was then established that Beer's Law was obeyed for each compound over the working concentration range stated above. Determinations of the extinction coefficients ($\mathcal{E}$) for n-propyl, benzyl chloroformates and nitrates were obtained in duplicate, i.e. by weighing out the compounds for two different stock solutions before dilution to test Beer's Law. The values of the extinction coefficients for these substances are given in Table II. 3.

III. 3. Procedure for examining the reaction of n-propyl and benzyl-chloroformates with tetra n-butylammonium nitrate and analysis of the products.

The following experimental procedures were used to investigate the reactions of n-propyl and benzyl chloroformates with tetra n-butylammonium nitrate and analysis of the products in the presence and absence of pyridine.

III. 3.1. Reaction of n-propyl and benzyl chloroformates with tetra n-butylammonium nitrate.

A solution in acetonitrile of n-propyl- and benzyl chloroformates (20 cm^3, 0.68 mol dm^{-3}) was added to a reaction flask and magnetically stirred, with tetra n-butylammonium nitrate (20 cm^3, 0.68 mol dm^{-3}) in acetonitrile.

After the reaction mixtures have been allowed to react at a temperature of 25.5°C for 48 hours, the infrared spectra of the resulting solutions were examined between 650 and 4000 cm^{-1} using 0.5 mm matching infrared cells (see Section II. 3, also Fig. II. 1).

III. 3.2. Product analysis.

Product isolation was attempted by distilling the resulting solution at 35 mm Hg. pressure, and room temperature using an all-glass apparatus consisting of a Claisen distillation head, modified to include a Jackson condenser. The temperature of the condenser was maintained at -55 to -60°C with an acetone/solid carbon dioxide mixture.

In a second experiment, at the conclusion of reaction period (48 hours) the resulting mixture was refluxed for 2 hours and cooled to room temperature before the distillation process (repeated as above).

In a third experiment the resulting mixture was refluxed for two hours with pyridine (1 cm^3) present, followed by distillation at room temperature in the same way as above.

The infrared of the separated products have been examined between 650 - 4000 cm^{-1}. The results of these experiments are given in Section II. 3.

III. 4 Procedure for examining the kinetics of the reaction of n-propyl and benzyl chloroformates with tetra n-butylammonium nitrate.

Stock solutions of the following concentrations: n-propyl chloroformate 0.246, 1.36, tetra n-butylammonium nitrate 1.36 and 2.0 mol dm^{-3} were prepared and diluted as appropriate to give solutions of n-propyl chloroformate in the range 0.04 - 0.5 and tetra n-butylammonium nitrate 0.11 - 1.25 mol dm^{-3}. Solution of benzyl chloroformate in acetonitrile was freshly prepared to avoid the decomposition of this compound in the solvent (see Section II. 1. 1 and Table II. 1).

All solutions for kinetic experiments were prepared at room temperature, in "the dry-box", so the concentrations are uncorrected for thermal expansion of acetonitrile when used at higher temperatures. The solutions were used immediately after preparation.

The kinetic determinations were conducted by placing solutions containing known concentrations of n-propyl or benzyl chloroformate (15 cm^3), and tetra n-butyl ammonium nitrate (15 cm^3) and immersing in a constant temperature water bath and allowed to reach the bath temperature. The temperature of which was maintained constant to within 0.1°C. The matched infrared cells were removed from the desiccator within a "glove bag", one cell filled with acetonitrile as reference and the other cell made ready for the reaction solution to be analysed. Prior to the analysis of reaction solution, a value for the initial transmittance of the chloroformate was determined by the appropriate dilution of the stock solution and examining this solution in the sample cell.

After allowing thermal equilibration of the reactant solutions a given volume of the solution of n-propyl or benzyl chloroformates was added to a given volume of the solution of tetra n-butylammonium nitrate. After convenient time intervals an aliquot was withdrawn from the reaction vessel with a syringe and transferred to the sample infrared cell located in a "glove bag" near to the water bath. Both cells were transferred to the infrared spectrometer and the spectrum recorded. In preparation for each determination the previous sample that had been tested was withdrawn from the cell, the cell washed out with acetonitrile and dried by forcing dry air or nitrogen through it. The absorptions of the carbonyl group for n-propyl and benzyl chloroformates in the region 1775-1780 cm^{-1} were monitored against time until no further change occurred.

Since the reaction mixture could contain the corresponding nitrate as well as the chloroformate, the infrared absorption spectra of the reaction mixture were recorded between 1600 - 1900 cm^{-1}. The values of the absorption at 1778 cm^{-1} together with the value of the extinction coefficient were subsequently used to estimate the concentration of n-propyl and benzyl chloroformates present in the reaction mixture at each time.

The rate of these reactions were studied at various temperatures ranging from 25 to 45°C and with several different initial concentrations of the reactants. Rate constants were calculated and recorded for each temperature, and are given in Table II. 4, 5, 6 and 7, Figs. II. 2 - II.10.

Moreover, the absorptions of n-propyl and benzyl nitrates were recorded and used to determine the amounts of those nitrates present in the kinetic experiment (see Sections II. 3. 1, 2, 3 and 4.

III. 5. The kinetic salt effect upon the reaction of benzyl chloroformate with tetra n-butyl ammonium nitrate at 25. 5°C using tetra n-butylammonium perchlorate.

In a typical kinetic determination a solution of benzyl chloroformate (0.02 mol dm^{-3}) was added to the reaction flask containing tetra n-butyl ammonium nitrate (0.1 mol dm^{-3}) and tetra n-butylammonium perchlorate (0.2 mol dm^{-3}) at 25.1°C. At predetermined time intervals samples were withdrawn from the reaction flask and injected into the sample cell contained in a "glove bag", and the infrared spectra recorded as previously between 1600 and 1900 cm^{-1}.

By this procedure, as before, the rate of the disappearance of the chloroformate carbonyl band and the appearance of nitrate band could be accurately followed. The value of the second order rate constant is given in Table II.10.

III. 6 Competitive reaction with chloride ion reaction of benzyl chloroformate with tetra n-butylammonium chloride.

An acetonitrile solution of benzyl chloroformate (0.025 mol dm^{-3}) and the reaction flask containing the tetra n-butylammonium chloride (0.05 mol dm^{-3}) were placed in a constant temperature water bath at 25.5 ± 0.1 °C. The solutions were left for 15 minutes to reach the temperature of the bath. After this period the solution of benzyl chloroformate was added to the reaction flask and the mixture was shaken.

Samples (0.5 cm^3) were removed after convenient time intervals and the infrared absorption spectra between 650 - 1800 cm^{-1} range recorded using (1 mm) cells. By this method the reaction was followed as the rate of disappearance of benzyl chloroformate. The results are given in Table II.9.

III. 7 Reaction of n-propyl chloroformate and tetra n-butylammonium nitrate in the presence of pyridine.

To a solution containing n-propyl chloroformate in acetonitrile (20 cm^3, 0.68 mol dm^{-3}) was added an equimolar concentration of tetra n-butylammonium nitrate (20 cm^3) and of pyridine (0.5 cm^3). The reaction mixture was kept at 25.5°C and a rapid evolution of carbon dioxide occurred after approximately 10 minutes. An aliquot was transferred to an infrared sample cell after 30 minutes and the absorption examined between 650 and 400 cm^{-1}. The reaction was left for 48 hours at that temperature and then the product was isolated in the manner already described (Section III.3.2).

The above experiment was also repeated under the same conditions except that the resulting mixture was refluxed for 2 hours before the isolation procedure was attempted.

Infrared absorption spectra in all cases have been examined before and after isolation of the product between 650 and 4000 cm^{-1} using matched 0.5 mm infrared cell equipment with sodium chloride windows; the one cell containing acetonitrile/ pyridine mixture as a reference, the other the solution to be examined.

The absorption peaks of pyridine were found not to interfere with the absorption of the reactants and the products in this experiment. The value of the second-order rate constant is given in Table II.10.

III.8 Estimation of carbon dioxide evolved in the reaction between n-propyl chloroformate and tetra n-butylammonium nitrate.

In a two necked flask an acetonitrile solution 20 cm^3 of n-propyl nitrate (0.34 mol dm^{-3}) and tetra n-butylammonium nitrate (0.34 mol dm^{-3}) was maintained at 25.5^{o}C in a water bath. Dry nitrogen was allowed to enter through one neck and the other was connected to a trap containing sodium hydroxide solution (40 cm^3, 0.20 mol dm^{-3}) for any carbon dioxide evolved. The chloroformate was allowed to interact for 48 hours under a slow flow rate of dry nitrogen gas.

The carbon dioxide evolved during the reaction was then determined as sodium carbonate in the sodium hydroxide solution by titration of the mixture with hydrochloric acid (0.20 mol dm^{-3}) using methyl orange and a mixture of thymol blue/ cresol red indicators (151).

Following the usual product isolation procedure of the mother liquid, the amount of n-propyl nitrate formed was obtained. The results for the carbon dioxide evolved and the nitrate formed are given in Section II. 6

THERMODYNAMIC WORK

CHAPTER IV

INTRODUCTION

CHAPTER IV

IV. Introduction

Thermodynamics are concerned with heat and temperature specifically, and deals with the laws governing the conversion of heat into other forms of energy (e.g. mechanical, electrical etc.). Thermodynamics have important applications in chemistry, physics, biology (152), and engineering. An important characteristic of thermodynamics is that it permits the derivation of relationships between different laws of nature. It is also a phenomenological theory, concerning macroscopic quantities such as pressure, temperature, or volume, and can be used also as a guide in the development of microscopic theories.

IV. 1 Thermodynamics and thermochemistry

The thermodynamic approach to various problems in the field of chemical reaction of organic (153) organometallic(154) transition metal(155) and inorganic compounds have been discussed; the most important review of this subject can be found in the Bulletin of Thermodynamics and Thermochemistry (156).

A specific application of thermodynamics in thermochemistry is a study of heat changes, absorbed or given out, in chemical reactions and the relationships between them. The subject has great immediate practical importance. Thermochemistry also provides the data from which the relative energy or enthalpy contents of chemical compounds can be deduced. This aspect implies that thermochemistry is basic to the study of chemical bonding, and also provides data necessary for the thermodynamic study of chemical equilibria.

Since there are various types of chemical reactions which may take place in the gaseous state, or in solution, or involve solids, the definition of the heat of reaction must be quite clear. Reactions can take place at constant volume or constant pressure and the relationship between these will be considered.

IV.2. Techniques of measurements.

Energy changes feature in all chemical and physical processes. Calorimetry is used for the measurement of the changes in thermal energy content in chemical processes, which are accompanied by changing the system from one state to another under specified conditions. Careful consideration must therefore be taken in defining the initial and final states. However, this introduction is confined to that area of techniques of measurement which deal with the enthalpy of formation and upon which the work described in this thesis was mainly based. The most widely calorimetric method used in determining enthalpies of formation of organic compounds is by measuring the enthalpy of combustion, by static-bomb calorimetry, for compounds containing C, H, O, N, and by rotating-bomb calorimetry for compounds containing sulphur, halogen and for organometallic compounds. A review of the literature concerning the use of these methods for measurement of the heat change has been made (157 and 158).

Any other method of determining the enthalpy of formation is reaction calorimetry, which is considered to be applicable to the measurement of heats of reaction other than combustion reactions.

IV.3 Reaction calorimetry

Reaction calorimetry in solution is relatively straightforward if the reaction is well defined, complete within a few minutes and there is no interference from side reactions. Variables such as temperature, concentration and catalyst must be chosen.

The most common types of reaction studied calorimetrically may be classified as hydrogenation, halogenation, hydrolysis and polymerization. In this method of reaction calorimetry calibration must be made. The electrical method is the preferred calibration method for reaction calorimeters, and is internationally recognized.

The enthalpy change for the reaction

$$\text{Tris.}^{*}_{(c)} + \text{HCl}_{(g)} \longrightarrow \text{Tris.HCl}_{(c)}$$

was derived (i) from reaction calorimetry using the LKB reaction calorimeter by measuring the enthalpies of solution of Tris.$_{(c)}$ and Tris.HCl$_{(c)}$ in aqueous HCl, and (ii) from rotating-bomb calorimetry of Tris$_{(c)}$ and Tris. HCl$_{(c)}$ (159). The results from the two methods,

(i) viz, $\underline{-29.96 \times 4. \pm 0.01}$ and

(ii) viz, $\underline{-30.29 \times 4. \pm 0.46}$ k J mol^{-1},

agree within the limits of experimental error. Irving and Wadsö (66) proposed the enthalpy of solution of Tris.$_{(c)}$ in 0.1 mol dm^{3} HCl as a suitable test reaction for solution calorimetry.

The thermodynamic and thermochemistry data concerning many chemical compounds have been reported (160). Nevertheless, the enthalpies of formation of n-propyl and benzyl chloroformates are not available in the literature.

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[*] Tris-(hydroxymethyl)-methylamine (THAM).

IV.4 Enthalpy of formation

Determinations of the enthalpy of formation of other organochlorine, or in general organo halogen compounds have been attempted (e.g. phosgene and acyl halides).

The enthalpy of formation of gaseous phosgene by calorimetric study of the alkaline hydrolysis reaction has been made by Davies and Pritchard (161).

$$\Delta H_f^\ominus = \underline{-220.12 \pm 0.23 \text{ kJ mol}^{-1}}$$

which is much closer to that obtained from equilibrium measurements (160), than any other previous calorimetric study

$$\Delta H_f^\ominus = \underline{-219.12 \pm 0.20 \text{ kJ mol}^{-1}}$$

Enthalpies of formation data of acyl halides in the gaseous state are available. These data have been used to determine other quantities such as the enthalpy of formation of acyl radical (RCO), C - X bond dissociation energy and CO double bond energy.

It is convenient, before illustrating the results obtained for the bond strength of acyl halides, to give a brief definition and a review of the importance of bond strengths.

IV.5 The bond energies and the bond strengths.

It is a great help in understanding some aspects of chemical reactions and compounds to have some idea of the energies of the chemical bonds.

The structural formula of a molecule may be looked at in several ways, such as an indication of the chemical reactivity, or as a representation of the physical properties of the compound. The treatment of molecules in terms of bonds implies the existence of properties which can be associated with these bonds, such as bond length and bond strength.

Regarding the chemical reactivity, the bond strength determines how much energy is required to break the bond; the bond dissociation energy is a measure of bond strength. Regarding the physical properties of the compound, the bond strength as a bond energy term is characteristic of each bond, which when summed over all the bonds in the molecule gives the heat of formation from the gaseous elements.

From the heat of formation of gaseous acetyl chloride (161, 2, 3 and 4) the C-X bond dissociation energy was calculated from the following reactions:

$$(CH_3COX)_g \longrightarrow 2C + 3/2\,H_2 + \tfrac{1}{2}\,O_2 + \tfrac{1}{2}\,X_2$$

$$2C + 3/2\,H_2 + \tfrac{1}{2}\,O_2 \longrightarrow (CH_3CO\ )_g$$

$$\tfrac{1}{2}\,X_2 \longrightarrow (X\ )_g$$

$$(CH_3COX)_g \longrightarrow (CH_3CO\ )_g + (X\ )_g$$

The result obtained for D_{C-Cl} is 318.82 kJ mol^{-1}. A similar calculation for gaseous benzoyl halides (164) gave a slightly different result, viz. D_{C-Cl} = 305.43 kJ mol^{-1}. There is good agreement between these results and the bond energy terms for C-Cl bonds discussed by Cottrell (165). Also the C-Cl bond dissociation energy of benzoyl chloride has been measured by the kinetic method (166) giving 307.94 kJ mol^{-1}, in good agreement with that obtained from the heats of formation.

Using the heats of formation of carbonyl and acetyl halides and the bond energy terms for C-C, C-H and C-X single bonds, the value of C=O double bond energy was found to be 794.96 kJ mol^{-1}; the CO bond is hence strong. Results obtained from solution calorimetry of chloroformates used in determining the enthalpy of formation of chloroformates in the liquid state See: section V.2.

In order to measure the bond energies of these compounds the enthalpies of vaporization of n-propyl and benzyl chloroformates have been measured. These enthalpies of vaporization have been used for the determination of the enthalpies of formation of the n-propyl and benzyl chloroformates in the gaseous state (see Section V.3 and 4).

IV.6 Enthalpies of vaporization, importance and measurements.

As we have seen, reaction thermochemistry is particularly important in determining the enthalpy of formation of organic compounds containing elements in addition to C, H and O. Earlier work of this reaction thermochemistry was concerned to establish enthalpies of formation of chlorine - containing organic compounds by measuring enthalpies of hydrolysis (167 , 168 , and 169).

For discussion of energy term it is necessary to refer to the gas state. Therefore, for substances whose standard enthalpies of formation in the liquid state are available, the standard enthalpies of vaporization at the appropriate temperature are required.

$$\Delta H_f^\ominus \text{ (ideal gas)} = \Delta H_{f\ (1)}^\ominus + \Delta H_v^\ominus$$

For those compounds whose standard enthalpies of formation in the solid state ($\Delta H_f^\ominus$ (c)) are known, standard enthalpies of sublimation ($\Delta H_{sub}^\ominus$) are required.

$$\Delta H_f^\ominus \text{ (ideal gas)} = \Delta H_f^\ominus \text{ (c)} + \Delta H_{sub}^\ominus$$

Enthalpies of vaporization are usually obtained either by calculation from the change of vapour pressure with temperature, or by direct calorimetric methods.

Some empirical relationships are also available.

IV.6.1. Method of estimation of ΔH_v.

One of the many methods proposed for the estimation of the enthalpy of vaporization, is that of Trouton (170).

$$\Delta H_v = 21\ Tbp \qquad \text{(Trouton's equation)}$$

where ΔH_v is the enthalpy of vaporization in cal mol^{-1} and Tbp is the boiling point (^{o}K). It has been found that the ratio $(\Delta H_v / T_{bp})$ is not exact, increasing with increasing the boiling point. Several modifications of Trouton's equation have been proposed and tested over wide ranges of boiling point. An equation proposed by Nerst (170)

$$\Delta H_v = Tbp\,(17 + 0.011\ Tbp)$$

and Bingham (170) in which

$$\Delta H_v = Tbp\,(\,9.5 \log Tbp - 0.007\ Tbp).$$

have resulted in high values of ΔH_v at the higher boiling point (172).

Kistiakowsky (171) deduced an equation from the third law of thermodynamics:

$$\Delta H_v = T_{bp}\ (8.75 + 4.57 \log T_{bp})$$

This equation agrees with the entire range of experimentally observed values with high accuracy.

The above equations have been used to estimate values of the enthalpies of vaporization (ΔH_v) at the boiling point. In order to measure the values of ΔH_v at any given temperature Watson (172) proposed the following expression

$$\Delta H_{v_1} / \Delta H_{v_2} = (1 - Tr_1 / 1 - Tr_2)^{0.38}$$

CHAPTER V

THERMODYNAMICS RESULTS AND DISCUSSIONS

where T_{r_1} and T_{r_2} are the reduced temperature corresponding to T_1 and T_2.

Meissner and Redding (173) proposed equations for the estimation of the critical temperature (Tc).

$$Tc = 1.70\ Tbp - 2.0$$

where Tbp $<$ 235°K.

$$Tc = 1.027\ Tbp + 159$$

where Tbp $>$ 235°K

IV.6.2 Calorimetric methods

Regarding the direct calorimetric methods for measurement of the enthalpy of vaporization, several types of the vaporization calorimeters have been described in the literature These include:

i) Osborne and Ginning calorimeter (174), used to obtain ΔH_v values for about 50 hydrocarbons. The observed values are confirmed by the results of other calorimetric determinations. As an example, the ΔH_v of n-hexane has been measured by Douslin (175), viz $\Delta H_v(298.15\ K) = \underline{31.55\ kJ\ mol^{-1}}$, which is in excellent agreement with that derived from vapour pressure measurements (176), viz $\Delta H_v = \underline{31.55\ kJ\ mol^{-1}}$.

ii) The Wadso calorimeter (177 and 178) which is very effective for use with small quantities of liquids (100 mg) having vapour pressures between 0.1 and 27.0 kPa at 25°C. The results obtained for water, viz., ΔH_v (298.15 K) = $\underline{10.52\ kJ\ mol^{-1}}$ compares well with the result obtained by Osborne and Ginning, viz.

$$\Delta H_v\ (298.15\ K) = \underline{10.51\ kJ\ mol^{-1}}.$$

Arnett (179) reported a simple calorimeter for determining accurate enthalpy of vaporization data ΔH_v. The principle and description are given elsewhere (179 and 180). This calorimeter has been used to measure ΔH_v for many compounds at 25°C. The result obtained for CH_3OH viz., $\Delta H_v = \underline{37.28}$ kJ mol is in excellent agreement with that obtained by Wadsö (181), viz., $\Delta H_v = \underline{37.28}$ kJ mol^{-1}.

It is interesting to know that Arnett (179) has used his calorimeter to determine ΔH_v at temperatures higher than 25°C; results obtained for $(CH_2)_3COH$ viz., ΔH_v (50°C) = $\underline{43.26}$ kJ mol^{-1}; similar results were obtained by Bevnon and McKetta (182) viz., $\Delta H_v(50°C) = \underline{43.37}$ kJ mol^{-1}.

IV.6.3. Calculations from the variation of the vapour pressure with temperature.

The change with temperature of the vapour pressure, P, is related to ΔH_v by the Clapeyron expression (197)

$$\frac{d \ln(P_{vp})}{d(\frac{1}{T})} = - \Delta H_v / R \Delta Z_v$$

where P_{vp} is the vapour pressure at temperature T, R is the gas constant, ΔH_v is the enthalpy of vaporization and $\Delta Z_v = P(V_{vap} - V_{liq})/RT$; where V_{vap} and V_{liq} are the molar volumes of the vapour and liquid respectively. The liquid volume V_{liq} can be neglected compared with the vapour volume V_{vap} (for liquid-vapour equilibria) at temperatures below the critical temperature. The integrated form of Clapeyron equation can be written as follows:

$$\ln p = - \frac{\Delta H_v}{RT} + \text{const.}$$

The preceding derivation indicates that a plot of ln P vs. 1/T should give a straight line, and that the slope of such a line is to be identified with $-\Delta H_v/R$.

Different methods for measuring the vapour pressure are available (184 and 185); these methods have been applied over temperature and pressure ranges as wide as possible and over the largest possible number of compounds. Using these values of the vapour pressures, the enthalpies of vaporization ΔH_v can be derived by applying Clapeyron equation. No vapour pressure data for n-propyl and benzyl chloroformates are available in the literature.

CHAPTER V.

Thermodynamics Results and Discussions

V.1. Solution Calorimetry

The standard enthalpies of formation for n-propyl and benzyl chloroformates reported in this section were derived from experimentally determined enthalpies of aqueous hydrolysis of n-propyl and benzyl chloroformates and appropriate ancillary data. The LKB-8700 precision calorimetric system was used for these measurements. Electrical calibration, performed after each enthalpy of reaction or solution measurement, was used to determine the mean energy equivalent of the calorimetric system.

The reaction chosen for these calorimetric studies was the hydrolysis of n-propyl and benzyl chloroformates in 1 mol dm^{-3} sodium hydroxide solution at 298.15 K. These reactions are rapid and have well-established products (see: section I.4). However, it was found during preliminary experiments that the rates of these reactions were too low to be of use for direct calorimetric measurement.

A major reason for the inability to observe reaction completion within an acceptable time-period is the low solubility of n-propyl and benzyl chloroformates in aqueous solution; in addition, the relatively high densities (1.09 and 1.20 g cm^{3} respectively at 20°C) for n-propyl and benzyl chloroformates render less efficient the stirring in the calorimeter vessel. This problem was overcome by pre-dissolving a known quantity of chloroformate ester in 1,4 dioxan, to ensure rapid dissolution. This aqueous dioxan solution contained in a sealed glass ampoule, was introduced into a calorimetric liquid in the normal manner.

Products of the main reaction can be simply described by (equation 1)

$$[\ ROCOCl.\ x\ C_4H_8O_2]_{\ solution} + (y + 3)\ NaOH_{(aq)} \longrightarrow$$
$$[ROH + NaCl + Na_2CO_3 + H_2O + \ x\ C_4H_8O_2 + y\ NaOH\ ]_{aq} \qquad (1)$$

($R = n\text{-}C_3H_7$-and $phCH_2$-)

The time of ampoule-breaking has been considered to be negligible. The error limits assigned to the experimental and derived results and ancillary data are discussed in Appendix II.

No standard enthalpy of formation data for the n-propyl and benzyl chloroformate compound are reported in the literature.

V.2 Experimental Results of Solution Calorimetry.

V.2.1. n-Propyl Chloroformate.

Details of five measurements of the enthalpy change of alkaline hydrolysis of n-propyl chloroformate in sodium hydroxide (1 mol dm^{-3}) solution are given in Table V.1. where Q_h is the quantity of heat produced during the isothermal reaction, and n_1 and n_2 are the mole ratios of water to n-propyl chloroformate and 1, 4 dioxan.

Since the enthalpy of solution of 1, 4-dioxan in sodium hydroxide solution is not known, the enthalpy of solution of 1, 4 dioxan was measured in 1 mol dm^{-3} sodium hydroxide solution. The data are given in Table IV.2 and the process is written as

$$1,4\ \text{dioxan}_{(1)} + n\ NaOH_{(aq)} \xrightarrow{\Delta H_2} (1,4,\ \text{dioxan} + n\ NaOH)_{aq} \qquad (2)$$

The equation for the hydrolysis reaction may be written as follows:

$$Q_h = n'\Delta H_1 + n''\Delta H_2 \qquad (3)$$

where n' and n'' are the numbers of moles of n-propyl chloroformate and 1, 4 dioxan respectively and ΔH_1 and ΔH_2 are the molar enthalpy changes for their hydrolysis and solution in sodium hydroxide (1 mol dm^{-3}).

The data given in Table V.3 represent the values of enthalpy of hydrolysis of a dioxan solution of n-propyl chloroformate in sodium hydroxide.

TABLE V.1 ENTHALPY CHANGE DURING THE HYDROLYSIS OF DIOXAN SOLUTION OF n-PROPYL CHLOROFORMATE in 100 dm^3 NaOH (1 mol dm^{-3}) at 298.15 K.

m / g (C_3H_7OCOCl)	m/ g ($C_4H_5O_2$)	dilution n_1	dilution n_2	$-Q_h$/J
0.09685	0.61016	7031	803	246.3698
0.07385	0.40028	9222	1223	181.0254
0.11761	0.34370	5791	847	127.2448
0.08401	0.64526	8106	759	219.1502

n_1 and n_2 are the mole ratios of water to n-propyl chloroformate and 1,4 dioxan and Q_h is the observed enthalpy change in J.

TABLE V.2 ENTHALPY OF SOLUTION OF 1,4-DIOXAN

1 mol dm^{-3} NaOH at 298.15 K.

$$(1,4\text{ dioxan})_{l} + (n\text{ NaOH})_{aq} \xrightarrow{\Delta H_2} (1,4\text{-dioxan} + n\text{ NaOH})_{aq}$$

m/g	dilution, n	$-\Delta H_2$/kJ mol^{-1}
0.72134	679	9.4781
0.53641	913	9.4750
0.47499	1031	9.4731
0.48350	1013	9.4752

The enthalpies of solution (Table V.2) show no significant dilution effect in the ΔH_2 values, and hence

$$\text{Mean: } \Delta H_2 = \underline{-9.475 \pm 0.003}\text{ kJ mol}^{-1}$$

TABLE V.3 CALCULATED VALUES FOR THE ENTHALPY OF HYDROYLSIS OF (n-C_3H_7 OCOCl)$_{(D)}$ in 100 cm^3 of SODIUM HYDROXIDE 1 mol dm^{-3}

m/g (C_3H_7OCOCl)	m/g ($C_4H_8O_2$)	dilution n_1	dilution n_2	$-\Delta H_1$ kJ mol^{-1}
0.09685	0.61016	7031	803	228.622
0.07385	0.40028	9222	1223	228.881
0.11761	0.34370	5791	1425	228.746
0.03476	0.57829	19593	847	229.280
0.08401	0.64526	8106	759	228.955

The values for the enthalpies of hydrolysis which are given in Table V.3 show no significant dilution effects, and therefore the mean value is reported as:

Mean: $\Delta H_1 = -228.890 \pm 0.310$ kJ mol^{-1}

The reaction occuring in the calorimeter was assumed to follow the equation:

$$\left(n\text{-}C_3H_7OCOCl + m\ \text{dioxan}\right)_{(s)} + \ (n+3)\ NaOH_{\ (aq)} \xrightarrow{Q_h}$$

$$\left(n\text{-}C_3H_7OH + NaCl + NaCO_3 + H_2O + m\ \text{dioxan} + n\ NaOH\right)_{(aq)}$$

$$(4\ )$$

Various ancillary measurements were made. They were:

(i) the enthalpy of solution of sodium carbonate in 1 mol dm^{-3} sodium hydroxide solution Table V.4;

(ii) the enthalpy of solution of sodium chloride in 1 mol dm^{-3} sodium hydroxide solution Table V.5;

(iii) the enthalpy of solution of n-propyl alcohol in 1 mol dm^{-3} sodium hydroxide solution Table V.6;

(iv) the enthalpy of solution of a n-propyl chloroformate in 1,4 dioxan Table V.7.

The results of these measurements are presented in Tables V.4-7; in all cases n is the mole ratio of solvent to solute and (l) = liquid, (c) = crystal, (s) = solution and (D) = in dioxan.

TABLE V.4 ENTHALPY OF SOLUTION OF $Na_2CO_{3\,(c)}$ in I mol dm^{-3} $NaOH_{(aq)}$ at 298.15 K.

$$Na_2CO_{3\,(c)} + n\,NaOH_{(aq)} \xrightarrow{\Delta H_3} (NaCO_3 + n\,NaOH)_{(aq)} \quad (5)$$

m/g	dilution, n	$-\Delta H_3$ / kJ mol^{-1}
0.26084	2258	27.990
0.14720	4001	27.574
0.18120	3250	27.965
0.28960	2034	27.903

The enthalpies of solution (Table V.4) show no significant dilution effect in ΔH_3 values, and hence:

$$\text{Mean: } \Delta H_3 = \underline{-27.858 \pm 0.307 \text{ kJ mol}^{-1}}$$

TABLE V.5 ENTHALPY DATA FOR SOLUTION OF $NaCl_{(c)}$ in 1 mol dm^{-3} $NaOH_{(aq)}$ at 298.25 K.

$$NaCl_{(c)} + (n\ NaOH)_{aq} \xrightarrow{\Delta H_4} (Na_2CO_3 + n\ NaOH)_{aq} \qquad (6)$$

m/g	n	ΔH_4 / kJ mol^{-1}
0.52450	619	2.718
0.27386	1186	2.730
0.29641	1096	2.729

Mean: $\Delta H_4 = 2.726 \pm 0.017$ kJ mol^{-1}

TABLE V.6 ENTHALPY OF SOLUTION OF n-PROPYL ALCOHOL$_{(l)}$ in 100 cm^3 1 mol dm^{-3} NaOH$_{(aq)}$ at 298.15 K

$$n\text{-}C_3H_7OH_{(l)} + n\ NaOH_{(aq)} \xrightarrow{\Delta H_5} (n\text{-}C_3H_7OH + n\ NaOH)_{(aq)} \qquad (7)$$

m/g	n	ΔH_5/ kJ mol^{-1}
0.23210	1439	8.327
0.21089	1584	8.406
0.16058	2080	8.508
0.32006	1044	8.320
0.04356	7669	8.486
0.17070	1957	8.620

The values for the enthalpies of solution show no significant dilution effects, and therefore the mean value is reported as:

Mean: $\Delta H_5 = \underline{-8.446 \pm 0.133}$ kJ mol^{-1}

TABLE V. 7 ENTHALPY OF SOLUTION OF n-PROPYL CHLOROFORMATE in 1, 4-DIOXAN (ΔH_6)

$$n\text{-}C_3H_7OCOCl_{(l)} + m\ 1,4\ \text{dioxan}_{(l)} \xrightarrow{\Delta H_6}$$

$$[\,n\text{-}C_3H_7OCOCl + m\ 1,4\ \text{dioxan}\,]_{(l)} \qquad (8)$$

m.(C_3H_7OCOCl/g	n	ΔH_6/ kJ mol^{-1}
0.47319	304	0.9486
0.19886	723	0.8730
0.67982	211	0.8854
0.21350	673	0.8759

The enthalpy of solution (Table V. 7) shows no significant dilution effect in the ΔH_6 values, and hence:

Mean: ΔH_6 = 0.896 ± 0.056 kJ mol^{-1}

Combination of hydrolysis and solution processes gives equation 9.

$$n\text{-}C_3H_7OCOCl_{(l)} + 3\,NaOH_{(c)} \xrightarrow{\Delta H_h^{\ominus}} n\text{-}C_3H_7OH_{(l)} + Na_2CO_{3(c)} + NaCl_{(c)} + H_2O \qquad (9)$$

where $\Delta H_h^{\ominus}$ is the standard enthalpy change for the reaction (equation 9).

$$\Delta H_h^{\ominus} = \Delta H_1 - \Delta H_3 - \Delta H_4 - \Delta H_5 + \Delta H_6 + 3\,\Delta H_7 \qquad (10)$$

ΔH_7 is the molar enthalpy of solution of sodium hydroxide$_{(c)}$ in water to a concentration of 1 mol dm^{-3} (186)

$$\Delta H_7 = -42.480 \pm 0.010 \quad \text{kJ mol}^{-1}$$

$$NaOH_{(c)} + NaOH_{(aq)} \xrightarrow{\Delta H_7} NaOH_{(aq)} \qquad (11)$$

The value of $\Delta H_7^{\ominus}$ was found to be = $\underline{-321.855 \pm 0.460\ \text{kJ mol}^{-1}}$ for $5791 < n < 19593$

V.2.2. Benzyl Chloroformate

The enthalpy of hydrolysis of benzyl chloroformate has been determined at 298.15 K in 100 cm^3 sodium hydroxide solution having a concentration of 1 mol dm^{-3}.

Details of five measurements of the enthalpy change for the alkaline hydrolysis of benzyl chloroformate/ dioxan are given in Table V.8 where Q_h is the observed enthalpy change in J. Using these values of Q_h in conjunction with values for the enthalpy of solution of 1.4 dioxan in sodium hydroxide 1 mol dm^{-3} (see Table V.2) and the hydrolysis reaction, we may write

$$Q = n' \Delta H_1' + n'' \Delta H_2' \qquad (13)$$

where n' and n'' are the numbers of moles of benzyl chloroformate and 1, 4 dioxan $\Delta H_1'$ and $\Delta H_2'$ are the molar enthalpy changes for their hydrolysis and solution in sodium hydroxide (1 mol dm^{-3}). Related data are given in Table V.9.

The reaction occurring in the calorimeter is represented by the equation:

$$C_6H_5 - CH_2OCOCl_{(D)} + X\,H_2O + Y\,NaOH_{(s)} \xrightarrow{Q_h}$$

$$NaOH + Na_2CO_3 + C_6H_5 - CH_2OH + d.\text{dioxan} + (X+1)H_2O +$$

$$(y - 3)\,NaOH_{(s)} \qquad (14)$$

Additional ancillary measurements were:

(i) the enthalpy of solution of benzyl alcohol in sodium hydroxide 1 mol dm^{-3}.

(ii) the enthalpy of solution of benzyl chloroformate in 1, 4 dioxan.

The results of these measurements are tabulated in Tables V.10 and 11.

TABLE V.8 ENTHALPY CHANGE DURING THE HYDROLYSIS OF BENZYL CHLOROFORMATE at 298.15 K.

$$(\mathrm{Ph-CH_2OCOCl + m\ dioxan})_{soln} + (n+3)\,\mathrm{NaOH}_{(aq)} \xrightarrow{Q_h}$$

$$(\mathrm{Ph-CH_2OH + NaCl + Na_2CO_3 + H_2O + m\ dioxan + n\ NaOH})_{(aq)} \quad (12)$$

$m(C_6H_5CH_2OCOCl)/g$	$m(C_4H_8O_2)/g$	dilution n_1	dilution n_2	$-Q_h/J$
0.02562	0.58219	37004	841	89.328
0.01806	0.53555	52495	914	76.551
0.02347	0.63918	40398	766	93.342
0.01927	0.52110	49207	940	76.242
0.02576	0.66299	36804	739	98.360

where n_1 and n_2 are the mole ratios of water to benzyl chloroformate and 1, 4 dioxan and Q_h is the observed enthalpy change in J.

TABLE V.9 CALCULATED VALUES FOR THE ENTHALPY OF HYDROLYSIS OF A DIOXAN SOLUTION OF BENZYL CHLOROFORMATE IN NaOH 1 mol dm^{-3} at 298.15 K.

$n_1(C_6H_5CH_2OCOCl)$	$n_2(C_4H_8O_2)$	$-Q_h$/J	$-\Delta H_1'$ / kJ mol^{-1}
37004	841	89.3276	177.902
52495	914	76.5511	179.126
40398	766	93.3415	178.910
49207	940	76.2423	178.909
36804	739	98.3599	179.125

The values for the enthalpies of hydrolysis which are given in Table IV.9 show no significant dilution effects, and therefore the mean value is reported as

Mean: $\Delta H_1' = -178.794 \pm 0.709$ kJ mol^{-1}

TABLE V.10 ENTHALPY OF SOLUTION OF BENZYL ALCOHOL$_{(l)}$ in NaOH 1 mol dm^{-3} at 298.15 K

$$C_6H_5-CH_2OH_{(l)} + n\,NaOH_{(aq)} \xrightarrow{\Delta H_5'} (C_6H_5-CH_2OH + n\,NaOH)_{aq} \qquad (15)$$

m/g ($C_6H_5CH_2OH$)	n	$\Delta H_5'$/ kJ mol^{-1}
0.29575	2032	0.480
0.32151	1869	0.488
0.28310	2123	0.490
0.35612	1688	0.492

Mean: $\Delta H_5'$ = 0.487 ± 0.006 kJ mol^{-1}

TABLE V.11 ENTHALPY OF SOLUTION OF BENZYL CHLOROFORMATE$_{(l)}$ in 1, 4 DIOXAN

$$(C_6H_5 - CH_2OCOCl)_{(l)} + m\ 1,4\ \text{dioxan}_{(l)} \xrightarrow{\Delta H_6'}$$

$$(C_6H_5 - CH_2OCOCl + m\ 1,4\ \text{dioxan})_{(l)} \qquad (16)$$

m / g (C_6H_5-CH_2OCOCl)	n	-$\Delta H_6'$ kJ mol^{-1}
0.60120	211	1.523
0.59348	214	1.514
0.62150	204	1.521
0.58211	218	1.518

Mean: $\Delta H_6' = -1.519 \pm 0.008$ kJ mol^{-1}

Combination of the hydrolysis and solution processes gives equation 17

$$C_6H_5CH_2OCOCl_{(l)} + 3NaOH_{(c)} \xrightarrow{\Delta H_h^{\ominus}}$$

$$C_6H_5 - CH_2OH_{(l)} + Na_{2\,(c)} + NaCl_{(c)} + H_2O \qquad (17)$$

and

$$\Delta H_h^{\ominus} = \Delta H_1' - \Delta H_3 - \Delta H_4 - \Delta H_5' + \Delta H_6' + 3\Delta H_7 \qquad (18)$$

where $\Delta H_h^{\ominus}$ is the standard enthalpy change of the reaction 17:

$\Delta H_1'$ is the enthalpy of hydrolysis of benzyl chloroformate

$\Delta H_3 = -27.858 \pm 0.307$ k J mol^{-1} (Table V.3)

$\Delta H_4 = 2.726 \pm 0.017$ k J mol^{-1} (Table V.3)

$\Delta H_7 = -42.48 \pm 0.01$ kJ mol^{-1} (equation 11)

ΔH_5 is the enthalpy of hydrolysis of benzyl chloroformate in 1, 4 dioxan.

$$\Delta H_h^{\ominus}\,(298.15\text{ K}) = \underset{52495 > n > 36804}{\underline{-\,283.108 \pm 0.773\ \text{kJ mol}^{-1}}}$$

V.2.3. Standard Enthalpies of Formation of Liquid n-Propyl and Benzyl Chloroformates.

The standard enthalpies change of the hydrolysis reaction of n-propyl and benzyl chloroformates were used in connexion with the known literature values for the standard enthalpies of formation of sodium chloride (187), sodium carbonate (188, 89), n-propyl alcohol (190), benzyl alcohol (191), sodium hydroxide (192, 193) and water (189), tabulated in Table V.12, giving values of the enthalpies heat of formation of liquid n-propyl chloroformate via equation 19.

$$
\begin{aligned}
\Delta H_f^{\ominus}[\text{ n-ProCOCl, l }] = {} & \Delta H_f^{\ominus}[\text{Na}_2\text{CO}_3\text{, c}] + \Delta H_f^{\ominus}[\text{ NaCl, c}] \\
& + \Delta H_f^{\ominus}[\text{ n-ProCOCl, l }] + \Delta H_f^{\ominus}[\text{H}_2\text{O, l}] \\
& - 3\Delta H_f^{\ominus}[\text{ NaOH, c}] - \Delta H_h^{\ominus}
\end{aligned} \tag{19}
$$

Using the corresponding values of $\Delta H_f^{\ominus}[C_6H_5CH_2OCOCl, l]$ $\Delta H_f^{\ominus}[C_6H_5CH_2OH]$ and $\Delta H_h^{\ominus}$ for benzyl chloroformate, a value for the standard enthalpy of formation of benzyl chloroformate was calculated.

The values of the standard enthalpies of reactions and formations of n-propyl and benzyl chloroformates are given in Table V.13.

TABLE V.12 ANCILLARY THERMODYNAMIC DATA at 298.15 K

Compound	$-\Delta H_f^\ominus$ / kJ mol^{-1}
$NaCl_{(c)}$	411.270 ± 0.109
$Na_2CO_{3\ (c)}$	1129.180 ± 0.230
$NaOH_{(c)}$	427.576 ± 0.079
$H_2O_{\ (1)}$	285.830 ± 0.042
$n\text{-}C_3H_7OH_{(1)}$	302.700 ± 0.600
$C_6H_5CH_2OH_{(1)}$	114.800 ± 0.700

The values of the standard enthalpies of reactions and formations of n-propyl and benzyl chloroformates are given in Table V.13.

TABLE V. 13 STANDARD ENTHALPIES OF FORMATION FOR n-PROPYL$_{(l)}$ AND BENZYL CHLOROFORMATES at 298.15 K

Compound	$-\Delta H^{\ominus}_{h}$ / J mol^{-1}	$-\Delta H^{\ominus}_{f}$ / kJ mol^{-1}
n-$C_3H_7OCOCl_{(l)}$	321.855 + 0.460	524.396 ± 0.761
$-CH_2OCOCl_{(l)}$	283.108 ± 0.773	375.244 ± 1.088

The statistical method used in determining confidence limits for $\Delta H^{\ominus}_{h}$ and $\Delta H^{\ominus}_{f}$ shown in Table V.13 is described in Appendix II.

V.3 Vapour Pressure Measurements of chloroformates.

The enthalpies of vaporization of n-propyl and benzyl chloroformates were derived from a series of measurements of vapour pressure in the temperature range 293.17 to 303.66 K for benzyl- and 293.40 to 303.40 for n-propyl chloroformates.

Pressures were measured using a Texas quartz gauge and trial experiments showed that the practical temperature range was from 291.35 to 305.20 K. Selected temperatures in this range were maintained using a well stirred water-bath.

The pressure gauge readings may be considered to be proportional to the pressure, and are related to absolute pressures by the gauge factor. This varies non-linearly with increasing gauge reading, but was found to be constant over the narrow pressure range.

The gauge factor was determined by calibrating the spiral with benzene over the temperature range 293.77 K to 302.34 K. The results are presented in Table VI.1, section VI 3.1. The gauge factor which was derived from measurements of benzene calibration experiments, does not vary over the pressure range studied (see Table VI.1). The high precision of the pressure reading reflected the temperature stability of the lagged water bath. Vapour pressure data for benzene were calculated, applying equation 20 described by Ambrose (194)

$$\log_{10}(P/Pa) = 11.56868 - 2338.888\,(K/T) - 1.12859 \times 10^{-2}(T/K) + 8.3738 \times 10^{-6}\,(T/K)^2 \qquad (20)$$

The following relation was found between the observed gauge reading (G) and the pressure P (Pascal).

$$P/Pa = G\,[\,114.531 \pm 0.099\,] + 0.255 \pm 0.041 \qquad (21)$$

Heat of vaporization of benzene at 298.15 K, thus found, ΔH_v = 33.939 ± 0.421 kJ mol^{-1}, is in very good agreement with the accepted literature value (195) ΔH_v = 33.856 ± 0.417 kJ mol^{-1}.

The vapour pressure data for n-propyl and benzyl chloroformates, presented in the next section, were calculated using a gauge factor 114.531 to convert pressure gauge readings (G) to absolute pressures. The plot of ln (P/Pa) vs. [(I/T) K^{-1}] for either n-propyl or benzyl chloroformates is of the form

$$\ln(P/Pa) = A + \frac{B}{(T/K)} \qquad (22)$$

where A is the intercept and B is the gradient, the values of A and B for either benzyl or n-propyl chloroformates are given in equations 24 and 25 respectively.

From the Clapeyron equation (183) the gradient in the above equation (22) is $\Delta H_v / \Delta Z R$, where ΔH_v is the molar enthalpy of vaporization and $\Delta Z = P(V_g - V_l)/RT$ where V_g and V_l are the molar volumes of the vapour and liquid respectively and R is the gas constant in Joule. The deviation of ΔZ from unity was estimated (196) and the correction found to be negligible.

Correction to 298.15 K was also made using Watson's equation 23 (172).

$$\Delta H_{v_2} = \Delta H_{v_1} \; [\; (1 - Tr_2) \; / \; (\; 1 - Tr_1) \;]^{n^*} \qquad (23)$$

where ΔH_{v_1}, ΔH_{v_2} are the enthalpies of vaporization, and Tr_1 and Tr_2 are the reduced temperatures T_1 and T_2. Values of Tr_1 and Tr_2 were calculated by estimating the critical temperature from Lydersen's increments (197).

V.3.1 Vapour pressure measurements of benzyl chloroformate.

The pressure data for five runs of benzyl chloroformate are presented in Tables 14, 15, 16, 17 and 18. A plot of ln P/Pa against (1/T K) Figure V.1, gives an acceptable least-squares line having a slope corresponding to the heat of vaporization of benzyl chloroformate. The results from these runs for benzyl chloroformate, Tables 14 - 18, were fitted to equation 24.

$$\ln P/Pa = 22.977 \pm 0.037 - \frac{4633.991 \pm 1.325}{T/K} \qquad (24)$$

where the gradient is equal to (enthalpy heat of vaporization/R)

---

[*] generally $0.3 < n < 0.4$, the best results were obtained when $n = 0.38$.

TABLE V.14 VAPOUR PRESSURES (P) FOR BENZYL CHLOROFORMATE at VARIOUS TEMPERATURES T (K)

T/K	G	P/Pa
293.61	11.270	1291
294.56	11.884	1361
295.13	12.345	1414
295.57	12.606	1444
296.65	13.335	1527
297.33	13.804	1581
298.33	14.538	1665
299.05	15.092	1729
299.49	15.474	1772
300.40	16.217	1857
301.65	17.230	1973
302.27	17.888	2049
303.57	18.938	2170

ΔH_v (298.278 K) = 38.611 kJ mol^{-1}

TABLE V.15 VAPOUR PRESSURES P (Pascal) FOR $C_6H_5CH_2OCOCl$ at VARIOUS TEMPERATURES T (K)

T/K	G	P/Pa
294.09	11.602	1329
294.85	12.079	1383
295.25	12.369	1417
296.13	12.972	1486
297.00	13.592	1557
297.63	14.109	1616
298.77	15.038	1722
299.70	15.614	1788
301.11	16.847	1930
301.66	16.960	1943
302.30	17.835	2043
303.66	19.205	2120

ΔH_v (298.512 K) = 38.535 kJ mol^{-1}

TABLE V.16 VAPOUR PRESSURES P (Pascal) FOR $C_6H_5CH_2OCOCl$ at VARIOUS TEMPERATURES T (K)

T/K	G	P/Pa
293.17	11.147	1277
294.16	11.743	1345
295.21	12.443	1425
296.40	13.124	1503
298.07	14.371	1646
298.63	14.699	1684
299.31	15.311	1754
300.06	15.897	1821
300.75	16.482	1888
301.35	16.940	1940
301.99	17.622	2018
302.21	17.888	2049
303.11	18.600	2130

ΔH_v (298.512 K) = $\underline{38.509 \text{ kJ mol}^{-1}}$

TABLE V.17 VAPOUR PRESSURES P (Pascal) FOR
$C_6H_5CH_2OCOCl$ at VARIOUS
TEMPERATURES T (K)

T/K	G	P/Pa
294.06	11.648	1334
295.05	12.301	1409
295.96	12.848	1472
296.56	13.279	1521
297.73	14.008	1604
298.65	15.629	1790
299.36	15.332	1756
300.66	16.406	1879
301.74	17.396	1992
302.30	17.894	2049
302.67	18.252	2090
302.06	17.575	2013

ΔH_v (298.900 K) = $\underline{38.387 \text{ kJ mol}^{-1}}$

TABLE V.18 VAPOUR PRESSURES P (Pascal) FOR $C_6H_5CH_2OCOCl$ at VARIOUS TEMPERATURES T (K)

T/K	G	P/Pa
293.13	11.022	1262
293.71	11.378	1303
294.38	11.800	1352
295.21	12.356	1415
295.63	12.608	1444
295.94	12.844	1471
296.56	13.177	1509
296.74	13.419	1537
297.34	13.834	1584
298.14	14.430	1653
298.27	14.573	1669
299.46	15.474	1772
300.70	16.398	1878
301.27	16.974	1944
302.07	17.663	2023
302.38	17.978	2059
302.86	18.259	2091
303.36	19.090	2186
304.65	20.271	2322
306.30	22.277	2551

ΔH_v (298.338 K) = $\underline{38.593 \text{ kJ mol}^{-1}}$

The boiling point of benzyl chloroformate has been estimated (197) as 523.30 **K**; this in turn was used to estimate the values of the critical and reduced temperatures in order to correct values of the standard enthalpy of vaporization for benzyl chloroformate to 298.15 K by applying Watson's equation 23. However, this correction was considered to be negligible.

Results from the vapour pressure measurements are summarized in Table V.19 each value reported is the mean from thirteen or more determinations.

TABLE V.19 THE MEAN VALUES FOR THE ENTHALPY OF VAPORISATION OF BENZYL CHLOROFORMATE

Experiment	ΔH_v kJ mol^{-1}	Mean temperature T/K
1	38.611	298.278
2	38.535	298.512
3	38.509	298.840
4	38.387	298.900
5	38.593	298.338

$$\Delta H_v\ C_6H_5CH_2OCOCl\ (298.574 \pm 0.354\ K)$$

$$= 38.527 \pm 0.110\ \text{kJ mol}^{-1}$$

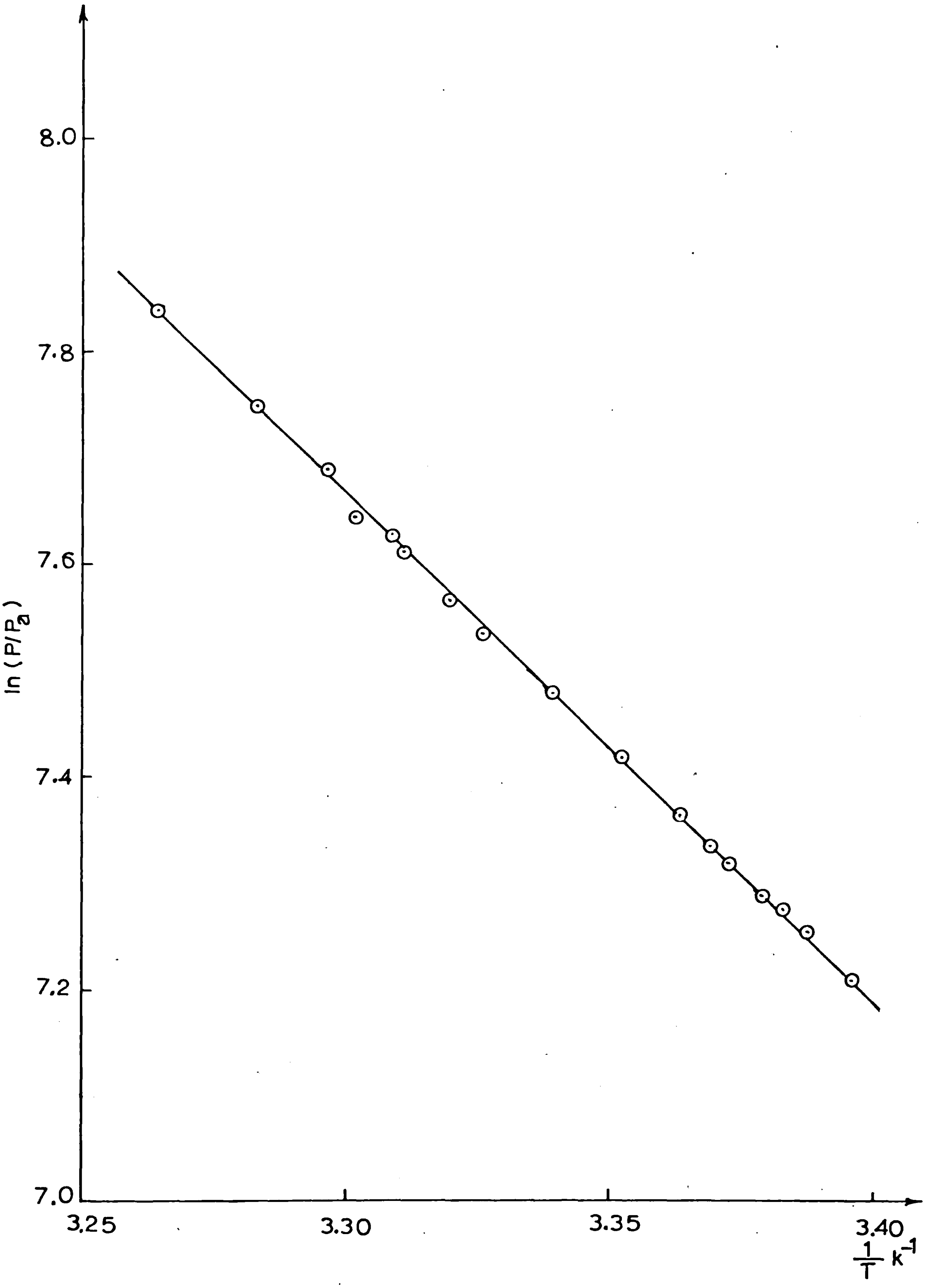

FIG. V. 1. Plot of the vapour pressure (ln/p/pa) for $C_6H_5CH_2OCOCl$ at various temperatures ((1/T K).

V. 3. 2 Vapour pressure measurements of n-propyl chloroformate.

The vapour pressure of n-propyl chloroformate was measured at about sixty temperatures ranging from 293.17 to 303.66 K and the results obtained are listed in Tables V 20, 21, 22 and 23. The results from these tables can be fitted to equation 25.

$$\ln (P/Pa) = 24.424 \pm 0.159 - \frac{4886.208 + 52.869}{T/K} \qquad (25)$$

Table IV. 24 shows the values obtained from four different runs of n-propyl chloroformate, and the mean temperature for each run. Also the values of enthalpies of vaporization corrected to 298.15 K were made using equation 23 and a critical temperature of (574.802 K) was estimated from Lydersen's increments (192). The results of the correct values of the enthalpies of vaporization of n-propyl chloroformate are tabulated in Table V. 24.

Figure V. 2 illustrates a plot of ln p/pa against ($^{1}/T$)K^{-1} which gives an acceptable least squares line.

TABLE V.20 VAPOUR PRESSURES P/Pa (Pascal) FOR $n\text{-}C_3H_7OCOCl$ at VARIOUS TEMPERATURE T/K

T/K	G	P/Pa
294.00	21.036	2409
294.72	21.877	2506
295.35	22.647	2594
296.21	23.788	2725
296.37	24.026	2752
296.95	24.659	2824
297.85	26.132	2993
298.45	26.887	3080
299.15	27.973	3204
299.70	28.765	3295
300.45	30.089	3446
301.15	31.105	3562
302.27	33.190	3801
303.40	34.905	3998

ΔH_v (298.287 K) = 40.4003 kJ mol^{-1}

TABLE V.21 VAPOUR PRESSURES P/Pa (Pascal) FOR n-C_3H_7OCOCl at VARIOUS TEMPERATURES T/K

T/K	G	P/Pa
293.71	20.608	2360
294.30	21.310	2441
294.80	21.959	2515
295.21	22.458	2572
296.13	23.645	2708
296.75	24.487	2805
297.34	25.314	2899
298.63	27.204	3116
299.35	28.252	3236
299.65	28.771	3295
300.56	30.255	3465
301.20	31.223	3576
302.07	32.7582	3752
303.07	34.628	3966

ΔH_v (298.055 K) = 40.9552 kJ mol^{-1}

TABLE V.22 VAPOUR PRESSURES P/Pa (Pascal) FOR $n\text{-}C_3H_7OCOCl$ at VARIOUS TEMPERATURES T/K

T/K	G	P/Pa
293.89	20.888	2392
294.05	21.013	2407
294.47	21.524	2465
295.95	23.410	2681
296.15	24.820	2843
297.45	25.410	2910
298.25	26.607	3047
299.50	28.479	3262
300.45	30.089	3446
300.90	30.820	3530
301.27	31.442	3601
301.91	32.592	3733
302.60	33.722	3862
302.67	33.857	3878

ΔH_v (298.844 K) = 40.3916 kJ mol^{-1}

TABLE V.23 VAPOUR PRESSURES P/Pa (Pascal) FOR $n\text{-}C_3H_7OCOCl$ at VARIOUS TEMPERATURES T/K

T/K	G	P/Pa
293.40	20.276	2322
294.75	21.871	2505
295.65	23.038	2639
296.35	23.931	2749
297.10	24.610	2819
297.90	26.106	2990
298.60	27.144	3109
299.27	28.167	3226
300.00	29.287	3354
301.01	31.005	3551
301.70	32.045	3670
302.10	32.857	3763
302.69	33.857	3878
303.17	34.645	3968

ΔH_v (298.835 K) = 40.7487 kJ mol^{-1}

TABLE V.24 THE MEAN VALUES FOR THE ENTHALPY OF VAPORIZATION OF n-PROPYL CLOROFORMATE.

ΔH_v(obs)	Mean T/K	ΔH_v(298.15 K)
40.7487	298.835	40.8491
40.3916	298.844	40.4932
40.9552	298.055	40.9412
40.4003	298.287	40.4200

Mean: $\Delta H_v(298.15\ K) = 40.6758 \pm 0.4096\ kJ\ mol^{-1}$

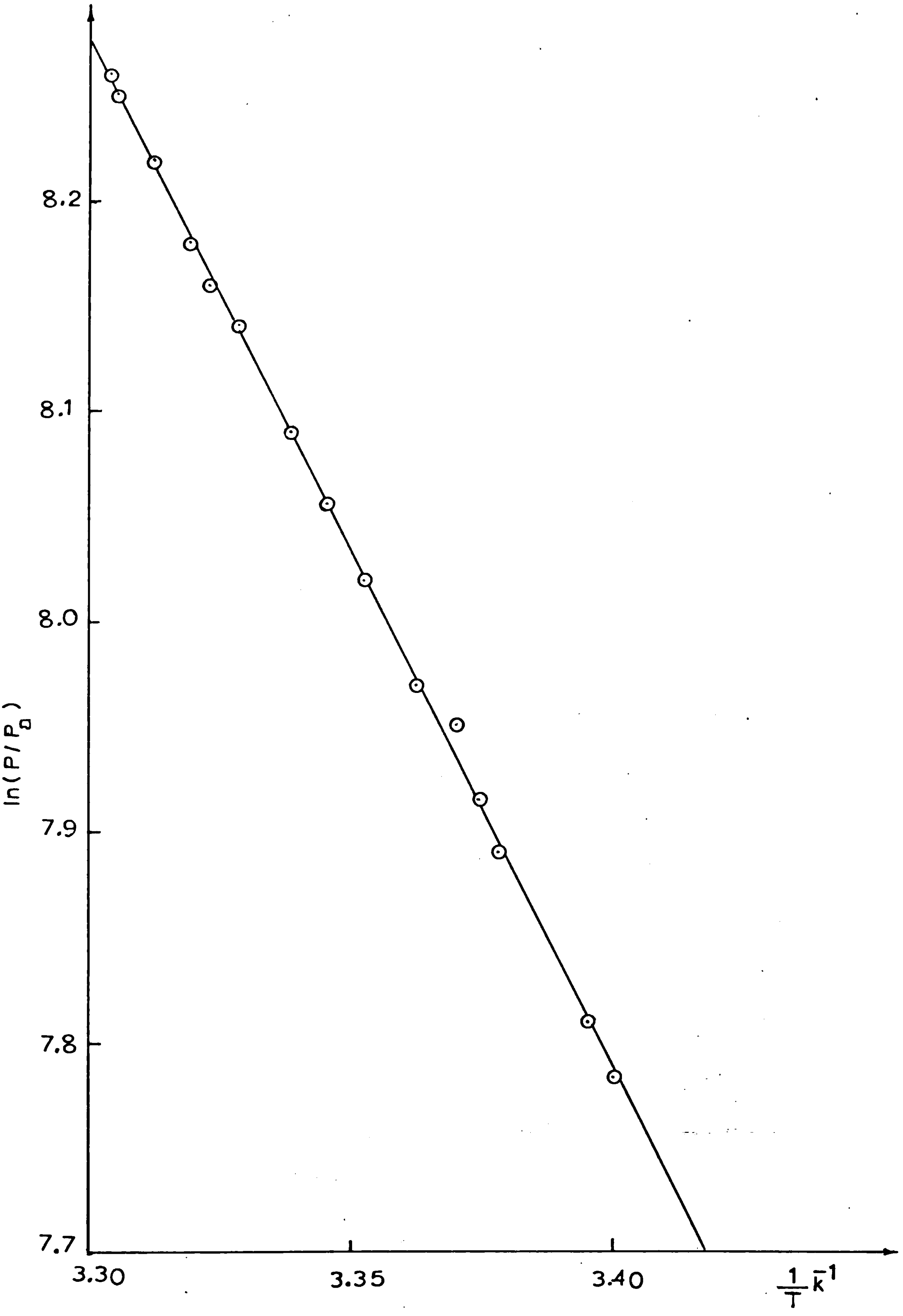

FIG. V.2. Plot of the vapour pressure (ln p/pa) for $n\text{-}C_3H_7OCOCl$ at various temperatures (1/TK)

V.4. Vaporization Calorimeter

Enthalpies of vaporization can be measured either by direct calorimetric methods, or by indirect vapour pressure methods. The latter is described in Section VI.3.1 and 2; related results are reported under Section V.3.1 and 2. The former is referred to in Section VI.4; related results, which follow, are based upon calorimetric measurements of enthalpies of vaporization at 298.15 K for n-propyl and benzyl chloroformates. In this method the amount of electrical energy need to vaporize a measured quantity of liquid was determined.

The key task in carrying out the calorimetric method is the pumping of liquid chloroformate at a constant rate into the vaporizing coil immersed in the calorimetric vessel. The calorimeter is described in Section (VI.3.2). The liquid was evaporated at the same rate that it was delivered from the infusion pump. The heat observed during the vaporization process was compensated electrically to keep the temperature of the calorimeter constant, a null measurement being made. The amount of electrical energy supplied per unit time can be calculated from equation 26

$$Q_i = I^2 R_{H+2L} \cdot t \qquad \text{J} \qquad (26)$$

where I is the current through the heater resistance (R_{H+2L}) in ohms and t is the time of heating in sec. I is measured indirectly, reading the potential V_{10} on a standard resistor R_{10}, connected in series with a heating resistor R_H (see: Section VI.3.2.4). Also the heat observed in the vaporization process has been measured using equation 27.

$$Q_{obs} = F/\text{mol sec}^{-1}) \times (\Delta H_v/\text{J mol}^{-1}) \ \text{J sec}^{-1} \qquad (27)$$

From equation 26 the heat introduced into the system during one sec. is

$$Q = I^2 . R_{H+2L} \qquad J\ sec^{-1} \qquad (28)$$

At the study state the rate of change of temperature, T, with time ($\partial T/\partial t$) is equal zero and this can be represented by ($\partial \theta / \partial t$) where ($\partial \theta/\partial t$) is the gradient and is proportional to ($\partial T/\partial t$)

$$\text{vapour power} = Q = \mathcal{E}(\frac{\partial \theta}{\partial t})$$ [Equation for the vaporization cal]

$$Q_{obs} = Q = \mathcal{E}(\frac{\partial \theta}{\partial t})$$

at ($\partial \theta/\partial t$) = zero

therefore $Q_{obs} = Q$

From equation's 27 and 28

$$F.\Delta H_v/J\ s^{-1} = I^2.R_{H+2L}/J\ s^{-1} \qquad (29)$$

$$\text{therefore } \Delta H_v = \frac{I^2\ R_{H+2L}}{F} \qquad J\ mol^{-1} \qquad (30)$$

The gradient ($\partial \theta/\partial t$) has been measured for each vaporization temperature/time trace and then corrected using the rate of change of the baseline (initial and final) slope, and the value of the heater power for each sample was measured where the heater

$$\text{power} = I^2.R_{H+2L} = (V_H^{\ 2}/R_H^2).R_{H+2L} \qquad (31)$$

The enthalpy of vaporization ΔH_v can be measured by plotting the heater power vs. the correcting gradient ($\partial \theta/\partial t)_{corr}$ and measuring the value of the heater power at ($\partial \theta/\partial t)_{corr} = 0$

ΔH_v = Intercept/(sample flow rate F mol s^{-1}) kJ mol^{-1}

or by plotting V_H^2 vs. $(\partial \theta / \partial t)_{corr.}$ and measuring the value of V_H^2 at $(\partial \theta / \partial t)_{corr.}$ = zero and then applying equations 30 and 31 for measuring ΔH_v; (see Figure V.3).

The performance of the calorimeter was frequently checked by measurements using benzene as a test substance. Usually one measurement on benzene was made between each series of measurements on the actual compounds.

The enthalpy of vaporization of benzene was found to be ΔH_v (298.15K) = $\underline{33.6371 \pm 0.1251}$ kJ mol^{-1} which is in a very good agreement with the previous value measured from vapour pressure data, viz,

ΔH_v(298.15K) = $\underline{33.9362 \pm 0.4213}$ kJ mol^{-1} literature value ΔH_v (298.15 K) = $\underline{33.856 \pm 0.417}$ kJ mol^{-1}.

V.4.1. Enthalpy of vaporization of n-propyl chloroformate

Enthalpy of vaporization of n-propyl chloroformate at 298.15 K has been measured. The value obtained from five sets of experiments each with seven measurements are in reasonable agreement with those calculated from the vapour pressure measurements.

The results obtained for these five sets of experiments are tabulated in Table V.25, 26, 27, 28 and 29. Using the molecular weight of n-propyl chloroformate = 122.55, density (ρ) = 1.090 g cm^{-3} R_H = 101.862 ohm and R_{H+2L}=101.907 ohm enthalpy of vaporization of n-propyl chloroformate has been measured. Results are given in Table V.30. The mean value of enthalpy of vaporization result from these five runs is:

Mean: $\Delta H_{v\ (298.15K)}$ = $\underline{40.7415 \pm 0.4030}$ kJ mol^{-1}

which is in good agreement with the previous value obtained from vapour pressure measurements, viz,

Mean: $\Delta H_{v\ (298.15K)}$ = $\underline{40.6762 \pm 0.4092}$ kJ mol^{-1}

TABLE V.25 THE ENTHALPY OF VAPORIZATION OF n-PROPYL CHLOROFORMATE

(Run number 1)

$(\partial\theta/\partial t)^{*}$ mV min^{-1}	Heater power** $Q \times 10^{2}$/J sec^{-1}
0.8081	2.7474
0.7354	2.8915
0.4715	3.6872
0.4012	3.9158
0.3008	4.1712
0.3318	4.1712
0.2368	4.3627

$\Delta H_v(298.15\ \mathrm{K}) = \underline{41.0567}$ kJ mol^{-1}

---

[*] $(\partial\theta/\partial t)$ proportional to (∂ temperature/ ∂ t).

[**] $Q = (V_H^{2}/R_H^{2})\ R_{H+2L}$

TABLE V.26 THE ENTHALPY OF VAPORIZATION OF n-PROPYL CHLOROFORMATE

(Run number 2)

$(\partial\theta/\partial t)$ mV min^{-1}	Heater power $Q \times 10^2$/ J sec^{-1}
0.7803	2.8287
0.7728	2.8518
0.6640	3.1417
0.6420	3.2213
0.5586	3.2910
0.4372	3.7903
0.3546	4.0273

$\Delta H_v(298.15\ K) = \underline{40.2202}\ kJ\ mol^{-1}$

TABLE V.27 THE ENTHALPY OF VAPORIZATION OF n-PROPYL CHLOROFORMATE

(Run number 3)

$(\partial\theta/\partial t)$ mV min^{-1}	Heater power $Q \times 10^2$ / J sec^{-1}
0.8240	2.7588
0.7193	3.0150
0.6262	3.2703
0.5809	3.3150
0.4219	3.8798
0.2462	4.3525

$\Delta H_v(298.15\ \mathrm{K}) = \underline{40.6756}$ kJ mol^{-1}

TABLE V.28 THE ENTHALPY OF VAPORIZATION OF n-PROPYL CHLOROFORMATE

(Run number 4)

$(\partial\theta/\partial t)$ mV min^{-1}	Heater power $Q \times 10^2$ / J sec^{-1}
0.7860	2.8837
0.6823	3.1272
0.6101	3.3316
0.5526	3.3480
0.2770	4.2983
0.1522	4.6522

$\Delta H_v(298.15K) = \underline{40.9406 \quad kJ\ mol^{-1}}$

TABLE V.29 THE ENTHALPY OF VAPORIZATION OF n-PROPYL CHLOROFORMATE

(Run number 5)

$(\partial\theta/\partial t)$ mV min^{-1}	Heater power $Q \times 10^2$/ J sec^{-1}
0.7198	2.9268
0.5846	3.3198
0.5102	3.5407
0.4298	3.7713
0.3600	3.9767
0.2646	4.2553
0.1849	4.5160

$\Delta H_v(298.15\ \text{K}) = \underline{40.8142\ \text{kJ mol}^{-1}}$

TABLE V.30 ENTHALPY OF VAPORIZATION OBTAINED FOR n-PROPYL CHLOROFORMATE

Run	$\Delta H_{v\ obs.}$
1	41.0567
2	40.2202
3	40.6756
4	40.9406
5	40.8142

$\Delta H_{v\ (298.15\ K)}$ = $\underline{40.7415 \pm 0.4030}$ kJ mol^{-1}

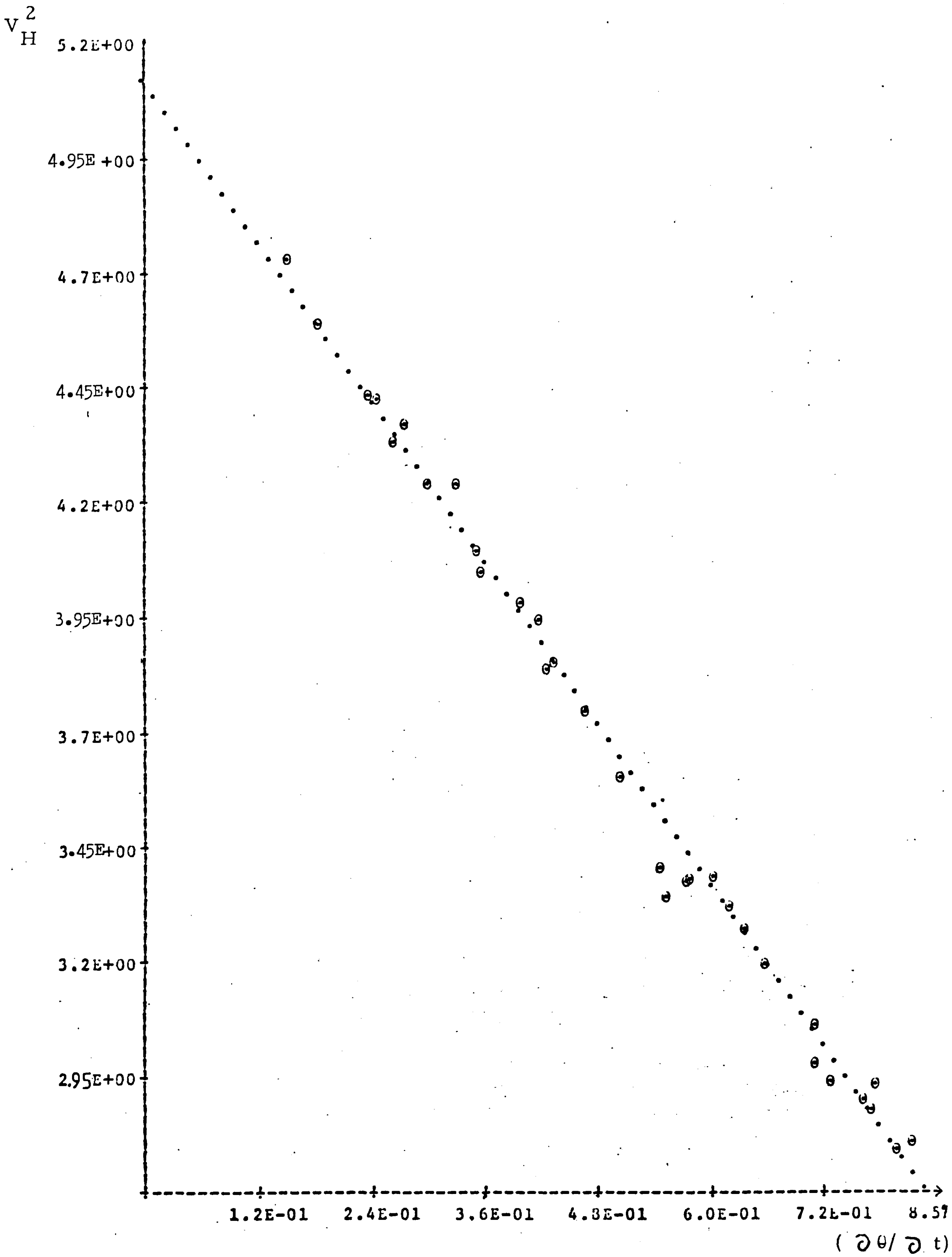

FIG. V. 3. Enthalpy of vaporization plot for n-propyl chloroformate

V. 4.2 Enthalpy of vaporization of benzyl chloroformate.

The use of a direct calorimetric method (vaporization calorimeter) to determine the enthalpy of vaporization of benzyl chloroformate at 298.15 K did not give the anticipated result,

$$\Delta H_v = \underline{1.9185 \pm 0.0113} \ \text{kJ mol}^{-1}$$

Result obtained from vapour pressure measurements, viz.,

$$\Delta H_v \ (298.57 \text{ K}) = \underline{38.527 \pm 0.110} \ \text{kJ mol}^{-1}$$

It was recognised that the amount of benzyl chloroformate that enters the vaporizing coil is not entirely vaporized, which means that the rate of infusion of liquid benzyl chloroformate may be high.

It was thought that decreasing the rate of infusion would decrease the amount of benzyl chloroformate per unit time. Experiments were performed to ensure this, but did not produce an apparent improvement.

The observation could be due to the low vapour pressure of benzyl chloroformate at that temperature 298.15 K.

Yet the direct calorimetric method might give good results for the enthalpy of vaporization of benzyl chloroformate at temperatures higher than 298.15 K, providing that the calorimetric liquid (decalin) is changed for a non-volatile material at 323.15 K or higher to prevent errors from evaporation of the calorimetric liquid.

V.5. Enthalpies of formations of n-propyl(g) and benzyl chloroformates(g).

Using the results obtained for $\Delta H^{\ominus}_{f, liq}$ (Table V. 13) in conjunction with the values of $\Delta H^{\ominus}_{vap}$ (assuming that $\Delta H_v = \Delta H^{\ominus}_v$) values of $\Delta H^{\ominus}_f$ for n-propyl and benzyl chloroformates in the gaseous state may be derived by applying the equation 32

$$\Delta H^{\ominus}_f \text{ (g)} = \Delta H^{\ominus}_f \text{ (l)} + \Delta H^{\ominus}_v \qquad (32)$$

The result obtained for the standard enthalpies of formation of n-propyl chloroformate in the gaseous state is thus:

$$\Delta H^{\ominus}_f \text{ [n-}C_3H_7OCOCl\text{, g, 298.15 K]} =$$

$$\underline{-483.720 \pm 0.864} \quad \text{kJ mol}^{-1}$$

and of benzyl chloroformate is:

$$\Delta H^{\ominus}_f \text{ [Ph-}CH_2OCOCl\text{, g, 298.15 K]} =$$

$$\underline{-336.717 \pm 1.094} \quad \text{kJ mol}^{-1}$$

V. 6. Discussion

The application and interpretation of the results of the enthalpies of formation obtained for n-propyl and benzyl chloroformates in terms of bond energy schemes, such as that of Allen (221), is difficult. This is due to the impossibility of separating interactions involving RO from those intrinsic to the -(CO)Cl group in RO-(CO)-Cl group ($R = n\text{-}C_3H_7$ and $C_6H_5CH_2$).

Using the value obtained from the calorimetric measurements for the standard enthalpy of formation of gaseous n-propyl chloroformate, $\underline{-483.7 \pm 0.9}$ kJ mol^{-1}, in conjunction with the tabulated values for bond and bond-interaction parameters, the contribution of -(CO)Cl to the enthalpy of formation in gaseous state can be calculated.

Applying Allen's scheme (154) leads to the following equation for the standard enthalpy of formation of n-propyl chloroformate.

$$\Delta H_f^{\ominus}(n\text{-}C_3H_7OCOCl,\ g, 298.15) = \sum \Delta H_f^{\ominus}(\text{gaseous elements}) -$$
$$[\,7B\,(C-H) + 2B\,(C-C) + 2B\,(C-O) + B\,(C=O) + B\,(C-Cl)$$
$$+\Gamma(CCC) + \Gamma(CCO) + \Gamma(COC_d) + \Gamma(OC_dO_d) + \Gamma(OC_dCl)$$
$$+\Delta\,(OO_dCl)\,]$$

where the values of 7, 2 and 2 are the numbers of C - H, C - C. and C - O bonds;

B (C - H), B (C - C) and B (C - O) etc. are the single bond energy terms;

is the bond-bond interaction parameter (e. g. ΓCCC is the interaction energy associated with $C \overset{\frown}{- C -} C$ and ΓOC_dO_d associated with $O \overset{\frown}{- C =} O$)*;

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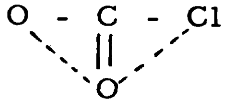
* the subscript d signifies a double-bonded atom.

Δ is the three-centre interaction parameter (e.g. $\Delta(OO_dCl)$ which is associated with the trio



and $\sum \Delta H_f^\ominus$ (gaseous element) is the sum of the heats of formation of gaseous carbon, hydrogen and chlorine in the proportions indicated by the molecular formuli.

Substituting the appropriate date (154)*

gives

$$[\,B\,(C=O\,) + B\,(C\ -\ Cl) + \Gamma(OC_dO_d) + \Gamma(OC_dCl)\ +\ \Delta\,(OO_dCl)] = \underline{-301.7}\ \text{kJ mol}^{-1}$$

This value represents the contribution of the -(CO)Cl group to the enthalpy of formation.

This value can be compared with the corresponding contribution of the -(CO)Cl group derived from the standard enthalpy of formation of gaseous acetyl chloride (197). Using $\Delta H_f^\ominus$ (CH_3COCl, g, 298.15K) = $\underline{242.8 \pm 0.6}$ kJ mol^{-1} the contribution of -(CO)Cl obtained is - $\underline{214.4}$ kJ mol^{-1}.

From these results we may conclude that the ethoxy-oxygen of chloroformates causes significant stabilization of the -(CO)Cl group compared with an alkyl carbon.

The difference between the contribution of the -(CO)Cl group in n-propyl chloroformate and that in acetyl chloride, i.e. $\underline{-87.3}$ kJ mol^{-1}, is in good agreement with that obtained by Davies et al. (183) in which the difference

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* Using the numerical values (in terms of contributions to $\Delta H_f^\ominus$ Table 51 Ref (154).

between the contribution of -(CO)Cl group of ethylchloroformate and acetyl chloride = $\underline{-84\cdot0}$ kJ mol^{-1}.

This difference of $\underline{-87.3}$ kJ mol^{-1} can be expressed in terms of the bond and bond-interaction parameter, Γ, and the three-centre interaction parameter, Δ, of Allen's scheme for the -(CO)Cl contribution of n-propyl-chloroformate and acetyl chloride.

$$\{\Gamma(OC_dO_d) + \Gamma(OC_dCl) - \Gamma(CC_dO_d) - \Gamma(CC_dCl)\} +$$

$$\{\Delta(OO_dCl) - \Delta(CO_dCl)\} = \overline{-87.3} \text{ kJ mol}^{-1}$$

Substituting the values of $\Gamma(OC_dO_d)$ (-144.4) and $\Gamma(CC_dO_d)$, (-47.9 kJ mol^{-1}), from Allen's scheme, we obtain the composite expression

$$\{\Gamma(OC_dCl) - \Gamma(CC_dCl)\} - \{\Delta(OO_dCl) - \Delta(CO_dCl)\}$$

$$= \underline{+9.2} \text{ kJ mol}^{-1}$$

(the corresponding literature value for ethyl chloroformate is $\underline{+11}$ kJ mol^{-1} (183).

As Allen's scheme does not include any data for aromatic compounds, it is not possible to calculate the contribution of -(CO)Cl group to benzyl chloroformate. However, Laidler parameters may be used in this context so they include contributions for aromatic molecules.

The application of the Laidler scheme (154) has been carried out for n-propyl and benzyl chloroformates as follows:

ΔH_f° (n-C_3H_7OCOCl, g, 298.15K) = $\sum \Delta H_f^\circ$ (gaseous elements)

- [3 E $(C - H)_p$ + 2E$(C - H)_s$ + 2E $(C - H)_s^o$ + 2E (C - C)

2E (C - O) + E (C = O) + E $(C_d$ - Cl)]

and

ΔH_f° ($C_6H_5CH_2OCOCl$, g, 298.15K) = $\sum \Delta H_f^\circ$ (gaseous elements)

- [6E $(C_b - C_b)$ + 5E $(C_b$ - H) + E$(C_b$ - C) + 2E $(C - H)_s^o$

+ 2E (C - O) + E (C = O) + E $(C_d$-Cl)]

where the symbols C_d and C_b are used for carbon atoms that are doubly bonded and benzenoid respectively;

E (C - C), E (C - O) and E (C - H) are the bond energy terms; the symbols p and s in E (C - H) signify the primary and secondary group; and $\sum \Delta H_f^\circ$ (gaseous elements) is the sum of the heats of formation of gaseous carbon, hydrogen, oxygen and chlorine in the proportions indicated by the molecular formuli.

The value of E (C = O) + E $(C_d$ - Cl) is taken as the contribution of -(CO)Cl group to the enthalpy of formation.

Using the numerical values of the Laidler parameter* we obtained contribution of the -(CO)Cl group, viz, -260.3 kJ mol^{-1}, for ΔH_f° (n-C_3H_7OCOCl, g, 298.15 K), in good agreement with that derived C_2H_5OCOCl, viz -256.5 kJ $mol.^{-1}$ The contribution from the -(CO)Cl group in acetyl chloride using Laidler parameters is -161.9 kJ mol^{-1}. This treatment also suggests that the presence of the ethoxy-oxygen in chloroformate causes significant stabilization of the -(CO)Cl group, compared with an alkyl carbon. In addition, the differences between the values obtained for the contributions of -(CO)Cl group by Laidler's scheme compared with those obtained from Allen's scheme can be qualitatively explained in terms of steric factors

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* Using the numerical values (in terms of contributions to ΔH_f° - Table 50 Ref (154).

which have been ignored in Laidler's scheme.

The application of the Laidler method to benzyl chloroformate using our value of $\Delta H_f^{\ominus}$ [$PhCH_2OCOCl$, g, 298.15 K] = - 336.6 kJ mol^{-1} has resulted in a value of -268.5 kJ mol^{-1} for the contribution of -(CO)Cl group. This is a more negative value than that obtained for n-propyl and ethyl chloroformates and this must be due to the presence of phenyl group in benzyl chloroformate. Yet, the deviation in the result of benzyl than that obtained in the results of both ethyl and propyl chloroformates could be considered within the range of the experimental error.

CHAPTER VI

EXPERIMENTAL TECHNIQUES

CHAPTER VI

EXPERIMENTAL TECHNIQUES

VI. 1. Preparation and analysis

VI. 1. 1 n-Propyl Chloroformate

A commercial sample (Pfaltz and Bauer, Inc.) was purified by repeated distillation under dry nitrogen using a fractionating column packed with glass helices; the first and last 5 cm^3 of distillate were discarded, b.p found 114.2°C; lit. value (1) 114.5 °C.

The analysis was by hydrolysis in aqueous solution (56) followed by determination of chloride ion via Volhard's method; a purity of 99.85% was indicated. This can be considered as mole per cent if any impurity is assumed not to contain hydrolysable halide.

VI. 1. 2 Benzyl chloroformate

A commercial sample (B D H) of benzyl chloroformate was purified by fractionation under reduced pressure, b.p. found 75°C at 1.2 mm Hg., lit. value (141) b.p. (76 - 78°C/1 - 2 mm Hg). The purity was then determined the method described in section III. 1. 3. 2. Analysis for free Cl^- indicated 99. 76% purity.

VI. 1. 3 Sodium hydroxide

Sodium hydroxide solution (B D H 1 mol dm^{-3} A V S) was used. The concentration was checked by titration against potassium hydrogen phthalate, using phenolphthalein as indicator.

VI. 1. 4 Sodium Chloride and Carbonate

A commercial sample (B D H Analar grade) was dried before use (151)

VI. 1. 5 1, 4 Dioxan

A commercial sample (Koch-Light 99% pure) was purified using the method described by Hess (198) and Green (199) i. e. refluxing dioxan (2000 cm^3) for 12 h. with hydrochloric acid (27 cm^3) and water (200 cm^3) in a stream of nitrogen, then treating with pellets of potassium hydroxide and finally separation of the aqueous layer. The liquid was stored over sodium wire for several days and fractionally distilled from sodium b. p. found 101.0°C lit. (199) value 101.1°C. It was stored under nitrogen in the presence of benzophenone ketyl.

VI. 1. 6 Benzyl alcohol

A commercial sample (Aldrich Chemical Company, Inc.) was dried over calcium sulphate and then fractionally distilled over magnesium, the middle fraction being retained, b. p. found 204.8°C lit (215) value 205.1°C. The enthalpy of solution for the purified benzyl alcohol was checked by measuring the enthalpy of solution in water at 298.15K, the value obtained 0.561 ± 0.002 kJ mol^{-1}, compares well with that of Karishnam and Friedman (200), viz., 0.544 kJ mol^{-1}.

VI. 1. 7 Propan-1-ol

A commercial sample (B D H Analar grade) b.p. 97°C was redistilled and then the enthalpy of solution was checked by measuring the enthalpy of solution in water at 298.15 K, the value obtained -10.14 ± 0.080 kJ mol^{-1}, compares well with that of Alexander (201) and Avegard (202), viz., -9.205 and -10.13 ± 0.079 kJ mol^{-1}.

VI. 1. 8 Benzene

A commercial sample (B D H Analar grade) was purified by shaking with concentrated H_2SO_4 until free from thiophen, then with water followed by dilute aqueous NaOH, finally drying with 4 Linde molecular sieves and subsequent distillation. As a further purification step, benzene was carefully fractionally redistilled from sodium then the AlH_4 under nitrogen b.p. found 80.05°C lit. (203) value 80.1°C.

VI. 2. Solution Calorimetry (apparatus and procedure)

The enthalpy of reaction of n-propyl and benzyl chloroformates (liquid) with aqueous sodium hydroxide solution (1 mol dm^{-1}) were determined using an L K B 8700 precision calorimetry system. Details of the construction and operating procedures are given in the instruction manual. The basic principle of the calorimeter is identical to that of an older calorimeter which is fully described elswhere (204), but certain experimental details differ. A block diagram of the L K B 8700-1 calorimeter is shown in Figure VI. 1. The L K B calorimeter used in this work operated at 298.15 K.

VI. 2. 1. Experimental procedure.

A standard glass ampoule, Figures VI. 2. A for solid and B for liquid, was charged with the sample. A small glass funnel, Figure VI.2 C, and a syringe were employed respectively to ensure that all the solid and liquid samples rested in the bulb of the ampoule. The ampoule was sealed as described in the instruction manual, and was then introduced into the calorimeter vessel. The calorimeter vessel is a thin-walled pyrex cylinder of 100 cm^3 capacity. A thermistor and calibration heater are contained in glass oil-filled wells supported from the lid of the vessel. The stirrer consists of a stainless steel spindle attached to a gold ampoule holder. Ampoule breaking is achieved by lowering the stirrer/ampoule assembly vertically on to a sapphire tipped glass rod located in the base of the vessel.

The power dissipated in the heater could be selected from the values of 20, 50, 200 and 500 mW. The value selected, 500 mW gives a heating period of ca. 110 s.

The equipment was modified to display the out-of-balance bridge potential from the Wheatstone bridge, Figure VI.3.A. A chart recorder (Bryans Ltd., model 2700) has been used to monitor the out-of-balance potential from the Wheatstone bridge. The sensitivities of the null potentiometer and the chart recorder were adjusted to give 0.1 = 1 cm of chart paper.

VI.2.2. Reaction, calibration traces and determination of the enthalpy of reaction.

The reaction trace is shown in Figure VI.4. The value of R_2 was found by extrapolating the aft-linear parts of the calorimetric curve to the time corresponding to 63% of the heat evolution (Dickinson's extrapolation method

(205 and 206) However, the exact position of $t_{0.63}$ must be estimated, probably giving an uncertainty of ca ± 0.005 in the value of R_2, which is within experimental limits.

The calibration has been carried out as described in the Instruction Manual (after cooling the calorimeter to 25°C using liquid nitrogen) and setting the resistance to the initial value, which has been used in the reaction experiment. A fore and aft-period of 15 min were recorded and the heating time noted, Figure VI. 5 illustrates a typical calibration resistance - time profile during heating. R_3 and R_4 were obtained from the extrapolated fore and aft-periods at the time corresponding to half the resistance change (50% of the heat evolution).

The resistance of the heater was found by the use of the circuit shown in Figure VI. 3. B, the current was adjusted so that the potential drop across the standard 50 resitor was 1.000 volt. The potential drop across the heater was then measured and its resistance calculated.

The total heat Q, evolved in an experiment was calculated from the expression

$$Q = (\Delta R/R_m)$$

where ΔR is the corrected thermistor resistance change $(R_{initial} - R_{final})$ and R_m is the mean resistance value $[R_{initial} - (\Delta R/2)]$ in the reaction experiment. The value for the calibration constant ($\mathcal{E}$) was calculated from the expression.*

$$\mathcal{E} = Q_c\ (R\ m, c\ /\Delta R_c)$$

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* Footnote on page 184

where Q_c is the electrical energy introduced in the calibration experiment, ΔR_c is the change in thermistor resistance and $R_{m,c}$ is the mean resistance.

In order to perform calorimetric measurements, the following terms are defined.

$$Q_c = R_h I^2 t$$

where R_h = the corrected resistance of the built-in heater
t = the calibration time
I = the calibration current

Then the equation used to determine the enthalpy change during the reaction is:

$$-\Delta H_R = \mathcal{E} Q \, (M/W)$$

where
M = molecular weight of compound
W = weight of compound

Tris(hydroxymethyl) aminoethane (THAM B D H Anristar grade, min. 99.9% purity) was employed as the standard reference material (207)and (208). to check the accuracy and precision of the calorimeter. The enthalpy of neutralization of THAM in

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* For the determination of $\mathcal{E}$, the following points must be observed:

a) The calibration energy must be such that it corresponds to the amount of energy that is released or absorbed in the reaction under study.

b) The calibration time must be the same as the time for the reaction.

c) The calibration curve must be idential, in relation to R , with the curve obtained from the reaction.

in excess aqueous hydrochloric acid (0.100 M, B D H A V S) is measured. The results obtained for five consecutive runs are given in Table VI. 1 leading to

$\Delta H_{R\ 298.15K} = \underline{-29.691 \pm 0.22\ \mathrm{kJ\ mol^{-1}}}$ for $1487 < n < 2031$

(the mass of THAM was corrected to vacuo (151), using M W THAM = 121.37 and density 1.35 gm cm^{-3})

Prosen and Kilday (209) obtained

$\Delta H_{R\ 298.15K} = \underline{-29.769 \pm 0.007}$, n = 1345, Finch et al (210) obtained

$\Delta H_{R\ 298.15K} = \underline{-29.748 \pm 0.020}$, n = 1547 where n is the mole ratio of H_2O to THAM.

This calorimeter was also employed to measure the enthalpies of solution for 1,4 $C_4H_8O_{2(l)}$, $Na_2CO_{3(c)}$, $NaCl_{(c)}$, n-$C_3H_7OH_{(l)}$ and C_6H_5-$CH_2OH_{(l)}$ in NaOH solution (1 mol dm^{-3}) at 298.15°K as these quantities were required as ancillary measurements.

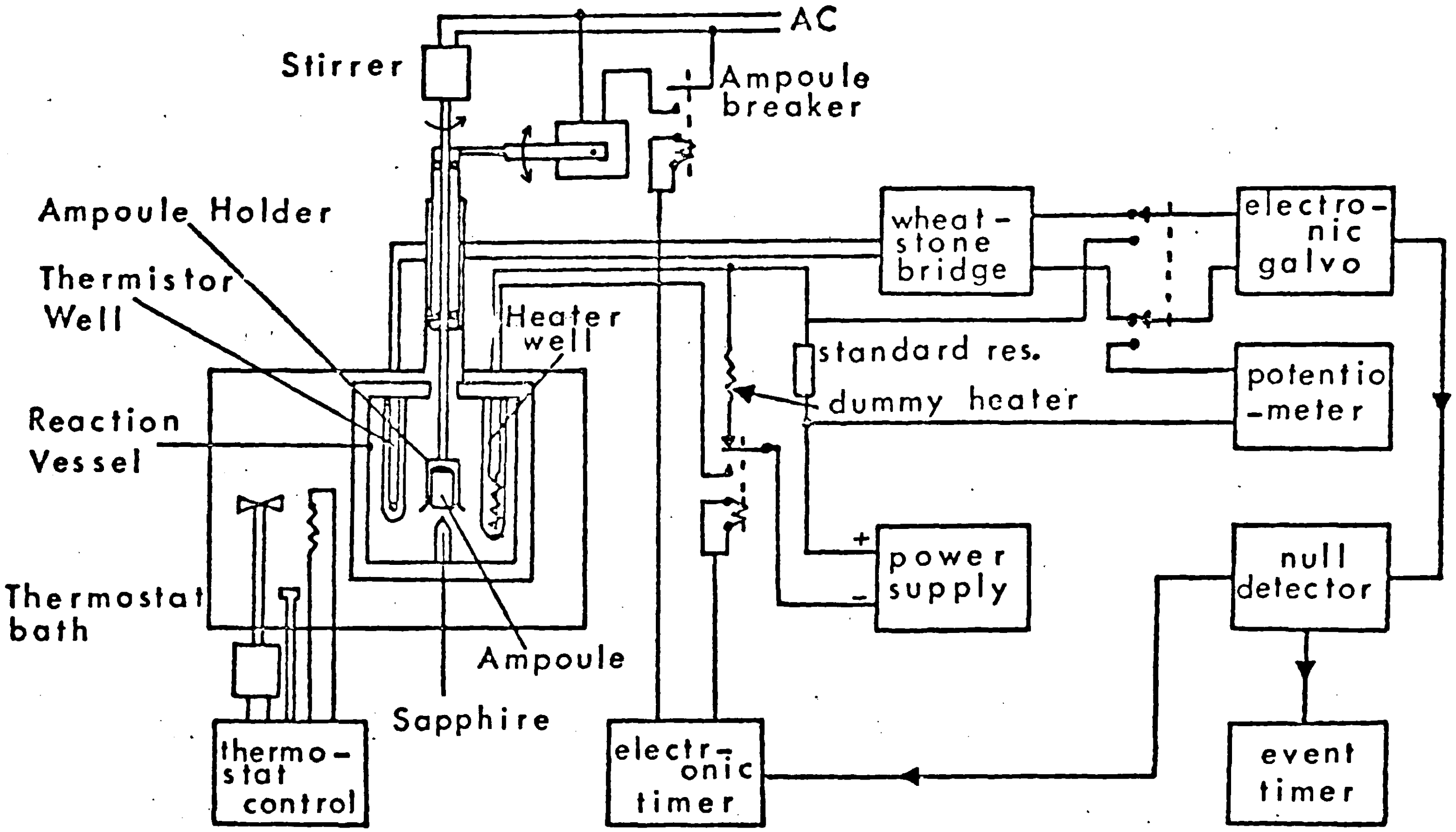

Fig. V. 1. Block Diagram of LKB Calorimeter.

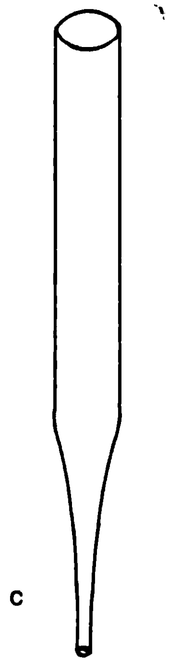

FIG. V. 2.c. glass funnel

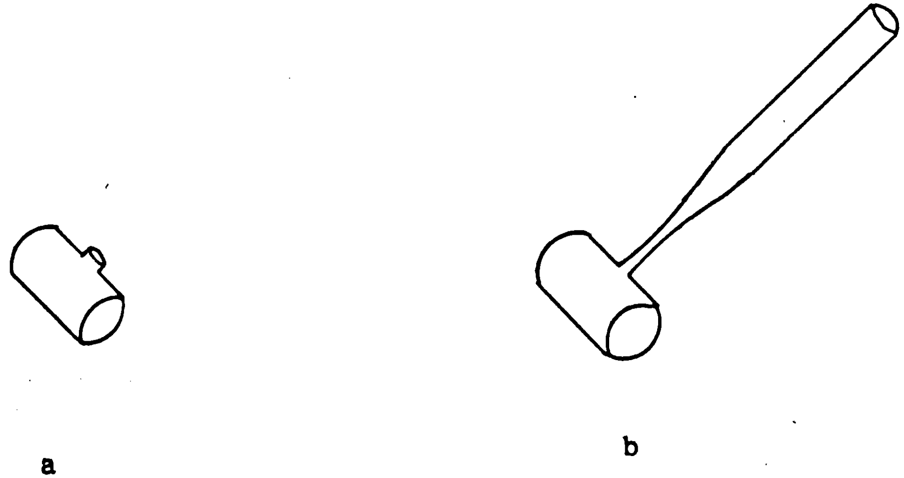

FIG. VI. 2 Types of ampoule

a) For solid
b) For liquid

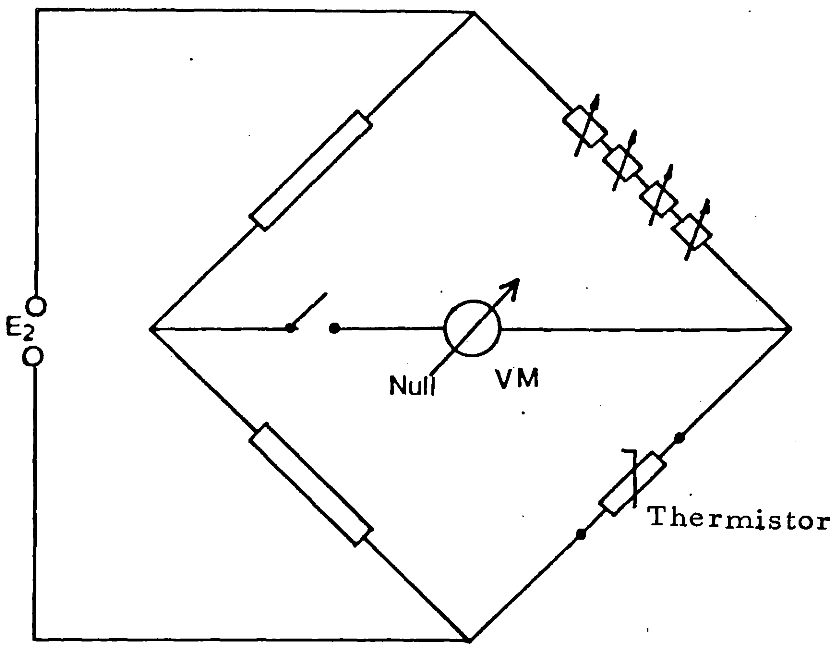

Fig VI.3. A LKB 8700 Precision Wheatstone Bridge.

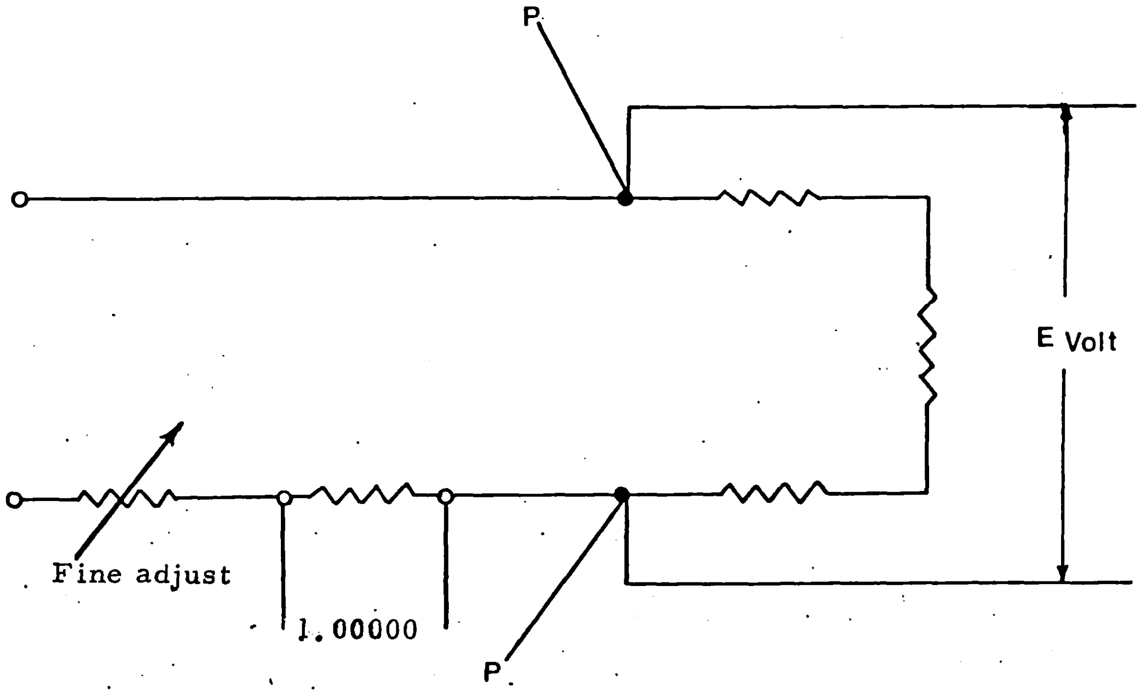

Fig Vi.3.B LKB 8700 Heater Circuit.

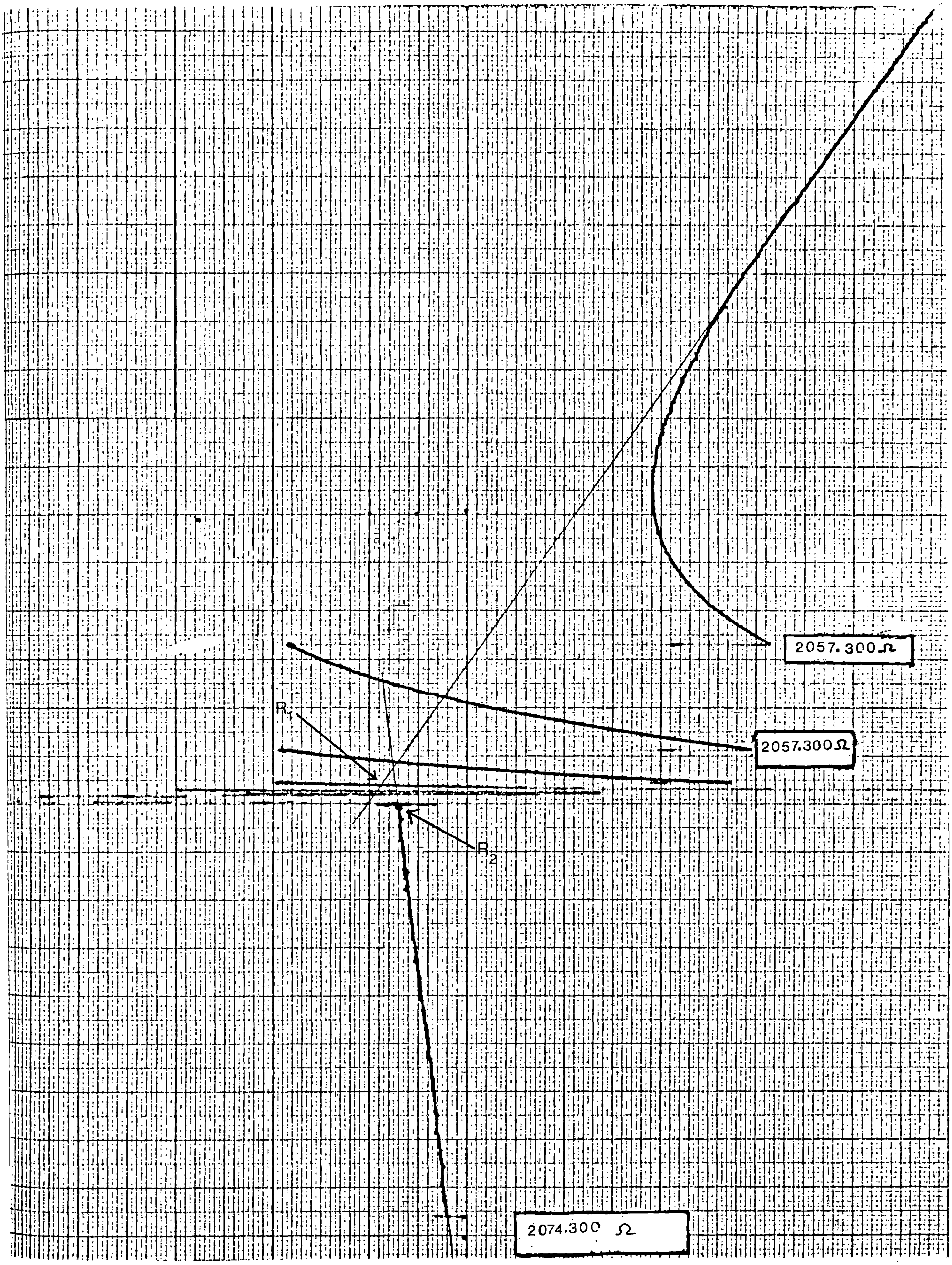

FIG. VI. 4 Typical $(C_6H_5CH_2OCOCl)_D$ / NaOH (1 mol dm^{-3}) reaction trace

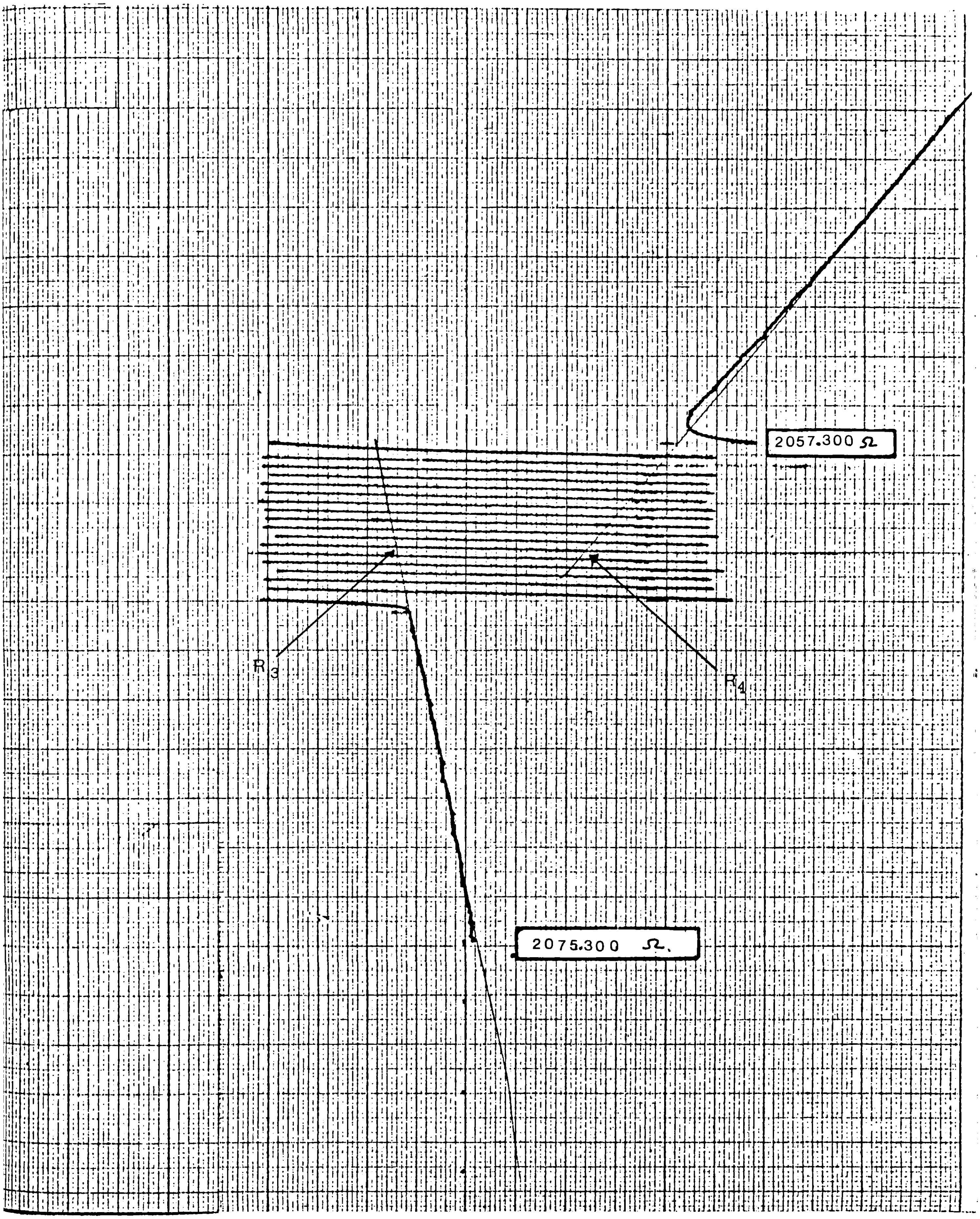

FIG. VI. 5 Typical $(C_6H_5CH_2OCOCl)_D$/ NaOH (1 mol dm^{-3}) calibration trace.

TABLE VI. 1 ENTHALPY OF REACTION OF THAM WITH EXCESS 0.1 mol dm^{-3} HCl

M(THAM)/g	dilution, n	$-\Delta H_R$/ kJ mol^{-1}
0.37364	1799	29.710
0.45210	1487	29.685
0.34748	1935	29.692
0.35070	1917	29.664
0.33101	2031	29.704

The enthalpy of reaction of (THAM) Table VI. 1 shows no significant dilution effect in the ΔH_R values, which is hence

$$\text{Mean: } \Delta H_{R\,(298.15K)} = \underset{1487 < n < 2031}{\underline{-29.691 \pm 0.022}} \text{ kJ mol}^{-1}$$

VI. 3 Enthalpy of vaporization

Two different methods were used in the course of this section of the work.

VI. 3. 1 Vapour pressure measurements.

The enthalpies of vaporization of benzyl and n-propyl chloroformates (Tables V. 19 and 24) were determined by measuring the vapour pressures of these materials in the temperature range 293. 13 to 306. 30 K.

A Texas Instruments pressure gauge (model 144- 01) with pressure capsules was used for pressure measurements. The high degree of accuracy of the gauge is attributable to the fused quartz Bourdon tube (type 11A capsules); the low internal viscosity of the fused quartz makes it the most perfectly elastic material known. The description and specification of both the precision pressure gauge and the pressure capsules are given in the instruction manual.

The gauge factor (f) was determined by measuring the vapour pressure of pure benzene over the temperature range 293. 77 K to 302. 34 K.

A sample was transferred and isolated in the vacuum line in order to out-gas satisfactorily. Three methods of degassing were attempted: evaporating a third of the sample whilst pumping with a diffusion pump and mechanical pump; distillation from liquid in one trap to solid in another with occasional pumping to remove released air; and pumping on the liquid in one trap whilst it was being frozen with acetone and solid CO_2. The sample then was condensed and sealed under vacuum into a break-seal ampoule, Figure VI. 6, which was blown on to the sample line of the gauge and immersed in a well-stirred water bath. The temperature of the water bath was measured using a calibrated mercury-in-glass thermometer, with the standard thermometers calibrated at the National Physical Laboratory to ± 0.02 K.

The system was then evacuated on both sides of the spiral in order to set the meter to zero. The sealed ampoule was immersed in a bath at the lowest temperature to be studied, and exposed to the gauge by fracturing the break-seal with a glass-covered magnetic follower. Thermal equilibrium was attained after 20-25 min and the gauge reading was recorded after 40 min. The gauge readings (G) were converted to the corresponding pressures using the equation described by Ambrose (see Section V.3). The results obtained from two separate runs of benzene are given in Tables VI.2 and 3, gauge factor obtained 114.531.

In typical experiments, as described above, the values of the gauge readings (G) were recorded for n-propyl and benzyl chloroformates at temperature range 293.13 to 306.30 K. These values have been converted to pressure by multiplying each reading by the gauge factor f (f = 114.531).

The results of the vapour pressure measurements of benzyl and n-propyl chloroformates are given in Tables V.14 - 18 and V.20 - 23. Also the values of the enthalpies of vaporizations of these compounds have been measured and the results are tabulated in Tables V.19 and 24.

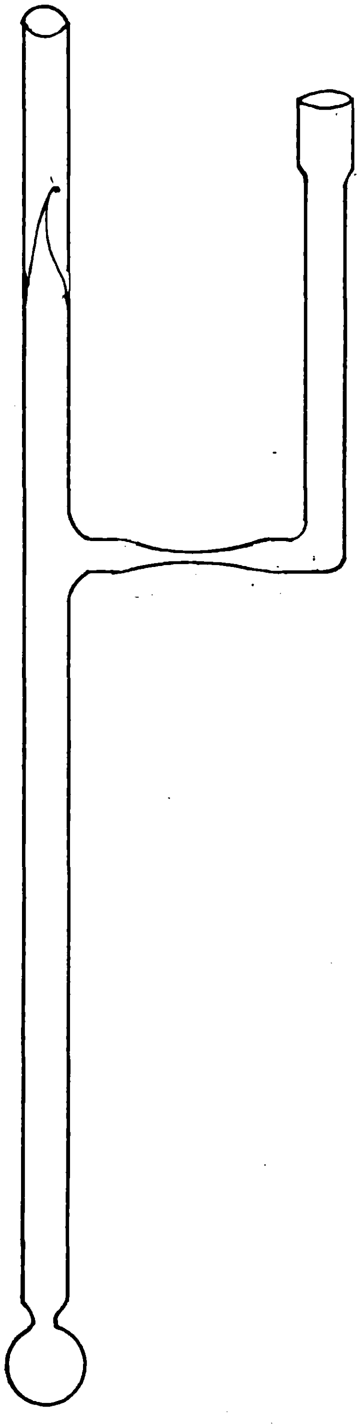

FIG. VI. 6. Ampoule used for vapour pressure measurements.

TABLE VI.2 VAPOUR PRESSURES P/KPa (Pascal) FOR BENZENE AT VARIOUS TEMPERATURES T/K

T/K	G	P/KPa	f
293.77	90.085	10.334	114.712
296.00	100.815	11.565	114.715
297.77	108.511	12.451	114.744
298.20	111.180	12.720	114.409
299.70	119.101	13.651	114.617
300.25	121.728	13.969	114.761
298.93	115.018	13.172	114.521
301.70	130.312	14.913	114.441
302.34	133.679	15.346	114.797

TABLE VI.3 VAPOUR PRESSURES P/KPa (Pascal) FOR BENZENE AT VARIOUS TEMPERATURES T/K

T/K	G	P/KPa	f
294.23	93.110	10.652	114.402
296.91	105.011	12.051	114.759
298.15	111.017	12.691	114.316
298.35	111.905	12.808	114.454
300.06	121.584	13.874	114.110
300.46	123.335	14.099	114.319
300.65	127.011	14.560	114.636
302.05	132.485	15.145	114.315

VI. 3. 2. Vaporization Calorimeter

The results obtained of enthalpies of vaporization for n-propyl chloroformate contained in Tables V. 25-30 were determined by a vaporization calorimeter. This calorimeter has been designed and constructed in this laboratory by Davies (211). The basic principles and the electrical system of this calorimeter are identical to the calorimeter described by Arnett (179) and (180).

It is convenient to describe briefly the vaporization calorimeter used in the course of this work.

VI. 3. 2. 1. Description of the Calorimeter.

Details of calorimeter arrangements and the calorimetric vessel are shown in Figures VI. 7 and 8, the calorimetric vessel which is 300 cm^3 Dewar jar, immersed in a thermostatic water bath. The rubber cap of the calorimeter is carefully shaped to fit snugly into the top of the Dewar jar. This rubber cap contains holes for resistance-heater, thermistor, stirrer and the terminal of vaporization/cooling coil. The liquid is supplied through a length of capillary teflon tubing by means of a constant speed syringe pump.

VI. 3. 2. 2. Constant delivery rate syringe.

A 2 cm^3 precision syringe ('Pressure-Lok' precision sampling Corp. Baton Rouge, Louisiana) was actuated by electrically operated syringe drive (Compact infusion pump, Harvard apparatus U S A Model 975). The syringe was connected via hypodermic needle to a length of polyethylene tubing (ca. 3 metres length and 1mm diameter), the other end of the tube being inserted into the vaporizing coil. The tubing was immersed in the thermostating bath. The liquid, therefore, delivers at the same temperature as the calorimetric fluid and then enters the vaporizing coil to which it is cemented with Araldite. The motor speed could be set by a dial (reading 00 to 30) and a setting of 18 was used throughout the vaporization experiments.

In a performance test of the syringe the weight of water delivered with time, and the reproducibility in delivery of a fixed mass of water was measured.

VI. 3. 2. 3. Procedure

The calorimeter vessel was charged by 200 cm^3 decalin (liq.), and the rubber cap fitted into the top of the Dewar jar. The temperature of the bath was adjusted to 298.15K using a Precision Temperature Controller Bridge (Model-1040) and the stirrer of the calorimeter was adjusted to 400 r p m. The syringe and vaporizing reservoir were fitted with liquid chloroformate, care being taken to exclude air bubbles. By adjustment of the syringe plunger a small air bubble, volume ca. 0.05 cm^3, was produced at the tip of the vaporizing delivery tube. Any 'back-lash' between the syringe plunger shaft and drive ram was taken up by switching on the motor until the bubble at the tip started to reduce in size and then completely disappear. The temperature of the bath was adjusted to 298.15K and the calorimeter left to equilibriate for 3 h.

Using the millivolt source 10 cm of chart paper was checked to correspond to 10 mV. The millivolt source was then switched off and remained inoperative while recording a vaporization trace which was contained within one chart width. A chart speed of 1 cm min^{-1} was used. with the thermistor bridge, (Carwyn Instruments Type - 401A), and nitrogen carrier gas flow rate (400 cm^3/min). The bridge was unbalanced by use of the coarse back-off control, to monitor the potential across the standard 10 ohm resistance in the heater circuit (see: Section VI. 3. 2. 4). The recorder pen was positioned on the left hand side of the chart paper by adjustment of the pen zero control. A baseline of 10 min duration was recorded. The syringe drive was switched on to deliver the liquid to be vaporized which was stopped ca. 15 cm on the chart paper, and not of V_H (the potential across the heater). The syringe pump was then disengaged and the heater was disconnected. The system was then left until stable ca. 15 cm after period was drawn. Typical initial baseline vaporization and the final baseline temperature/time traces are shown in Figure VI. 9.

VI. 3. 2. 4. Measurement of Heater resistance

The current in the heater circuit is measured by monitoring the potential across the standard 10 ohm resistance. The resistance of heater chip R_H can be measured using the equation

$$R_H = \frac{V_H \times 10.00}{V_{10}}$$

where V_H and V_{10} are potential across heater and standard 10 ohm resistance respectively. A small correction for the heat dissipated through the heater leads, which takes the form of a correction to R_{H+2L} dependent of length of leads immersed. This value of 2L was taken as 0. 045 ohm and was added to R_H. The value of R_H has been measured, results are given in Table VI. 4, it was found that R_H = 101. 862 ± 0. 028 ohm.

The enthalpy of vaporization ΔH was calculated using the following expression

$$\Delta H_v = I^2 . R_{H+2L} (J. sec^{-1}) / F (mol. sec^{-1}) \quad J\ mol^{-1}$$

where

$$I^2 . R_{H+2L} \text{ (the heater power (Q))}$$

$$= \frac{V_H^{2}}{\substack{2 \\ R_H}} \cdot R_{H+2L}$$

and

F (the flow rates of liquid chloroformates)

$$= A\ (cm^3\ sec^{-1}). \quad \frac{\rho}{M}\ (mol. cm^{-3}) \quad mol\ sec^{-1}$$

where A is the volume flow rate, is the densities and M is the molecular weights for the chloroformates.

The results for enthalpies of vaporization measure for n-propyl and benzyl chloroformates are given in Section V.4. These results obtained using the following data.

$$R_H = 101.862 \pm 0.028$$

$$R_{H+2L} = 101.907 \pm 0.028$$

$$A = 1.3911 \times 10^{-4} \pm 0.001 \times 10^{-4}\ cm^3\ sec^{-1}$$

= 1.090 and 1.195 for n-propyl and benzyl chloroformates.

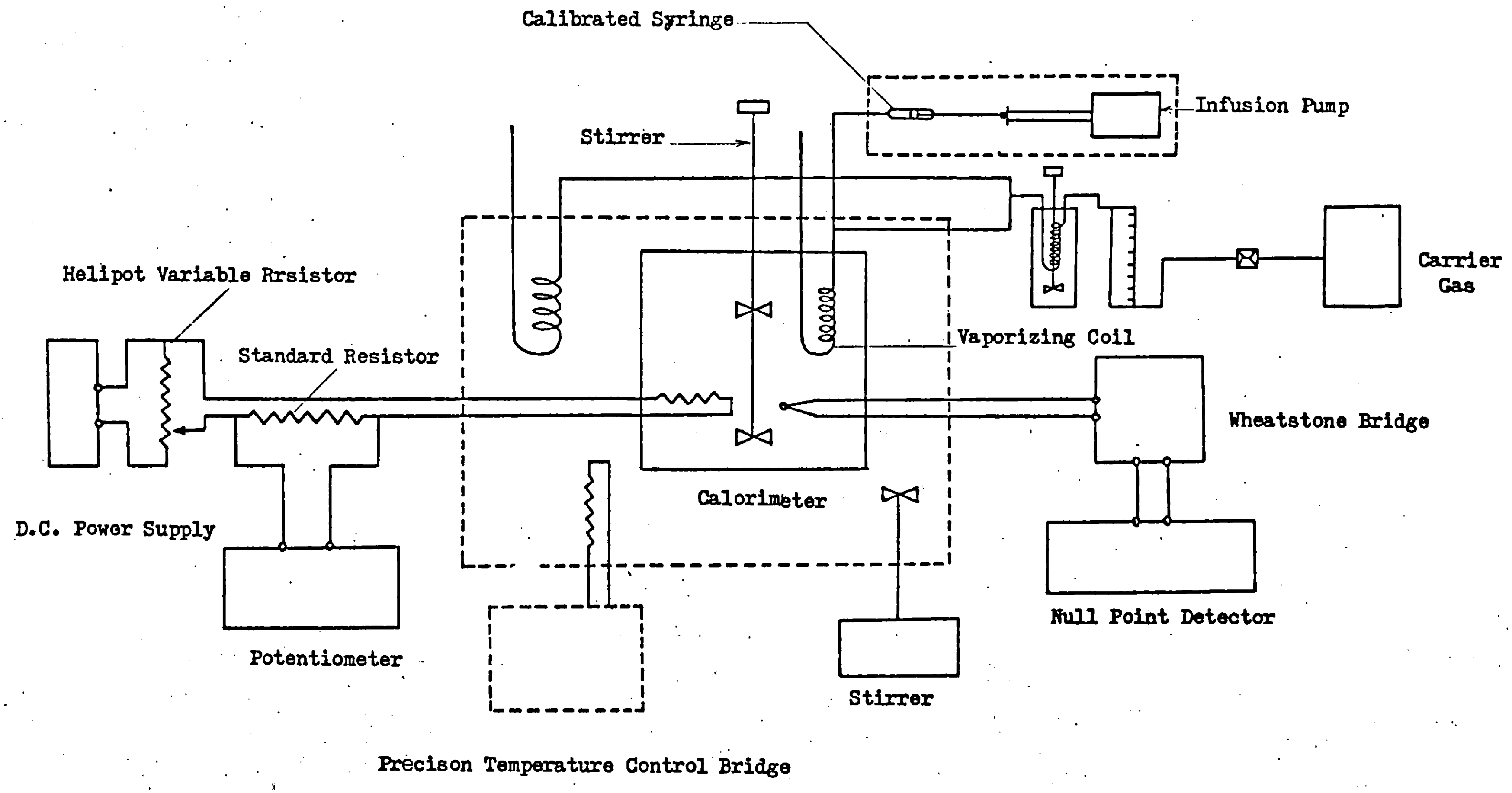

FIG. VI. 7 Block diagram of vaporization calorimeter.

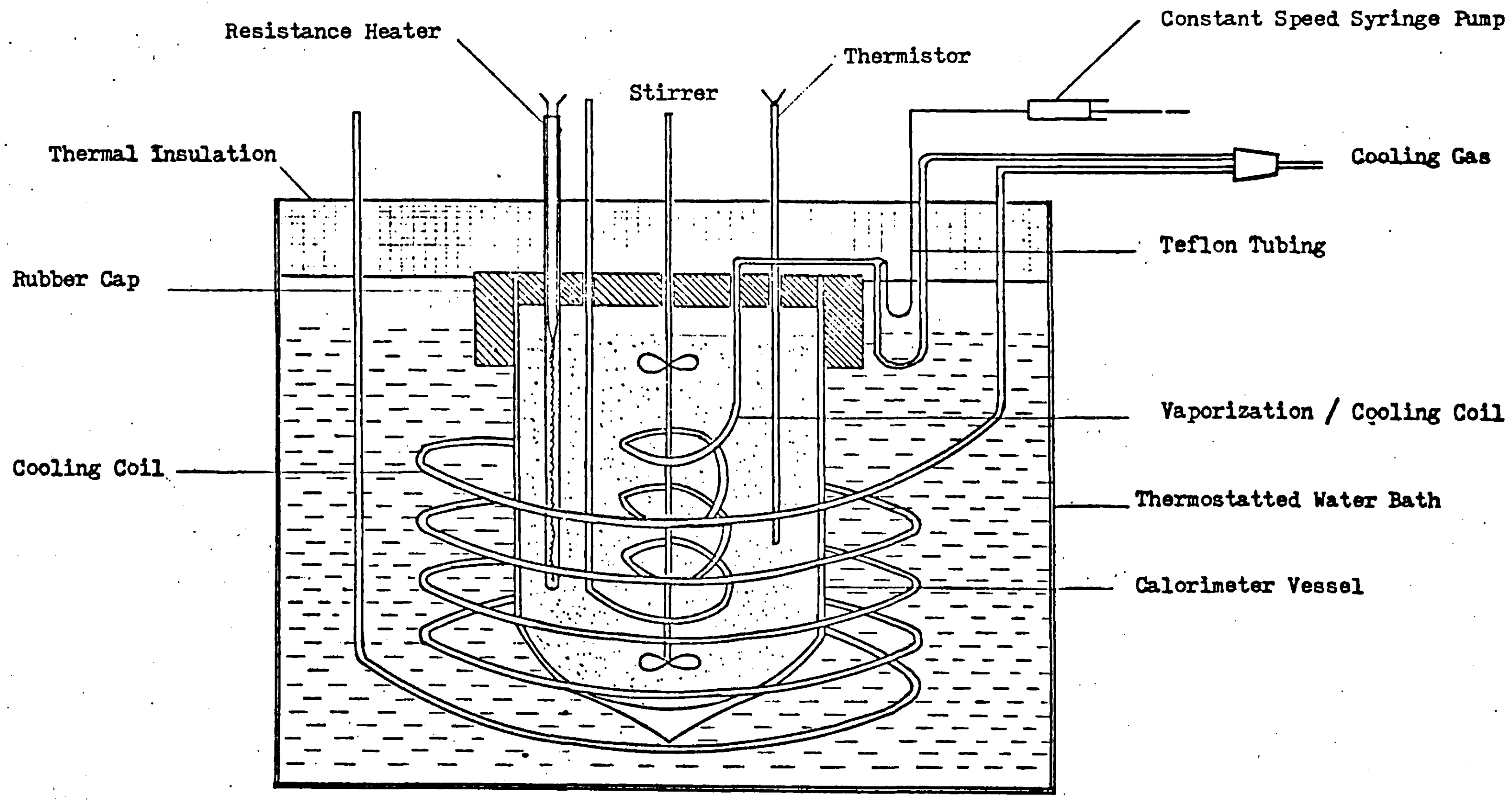

FIG. VI. 8. Detail of calorimeter vessel.

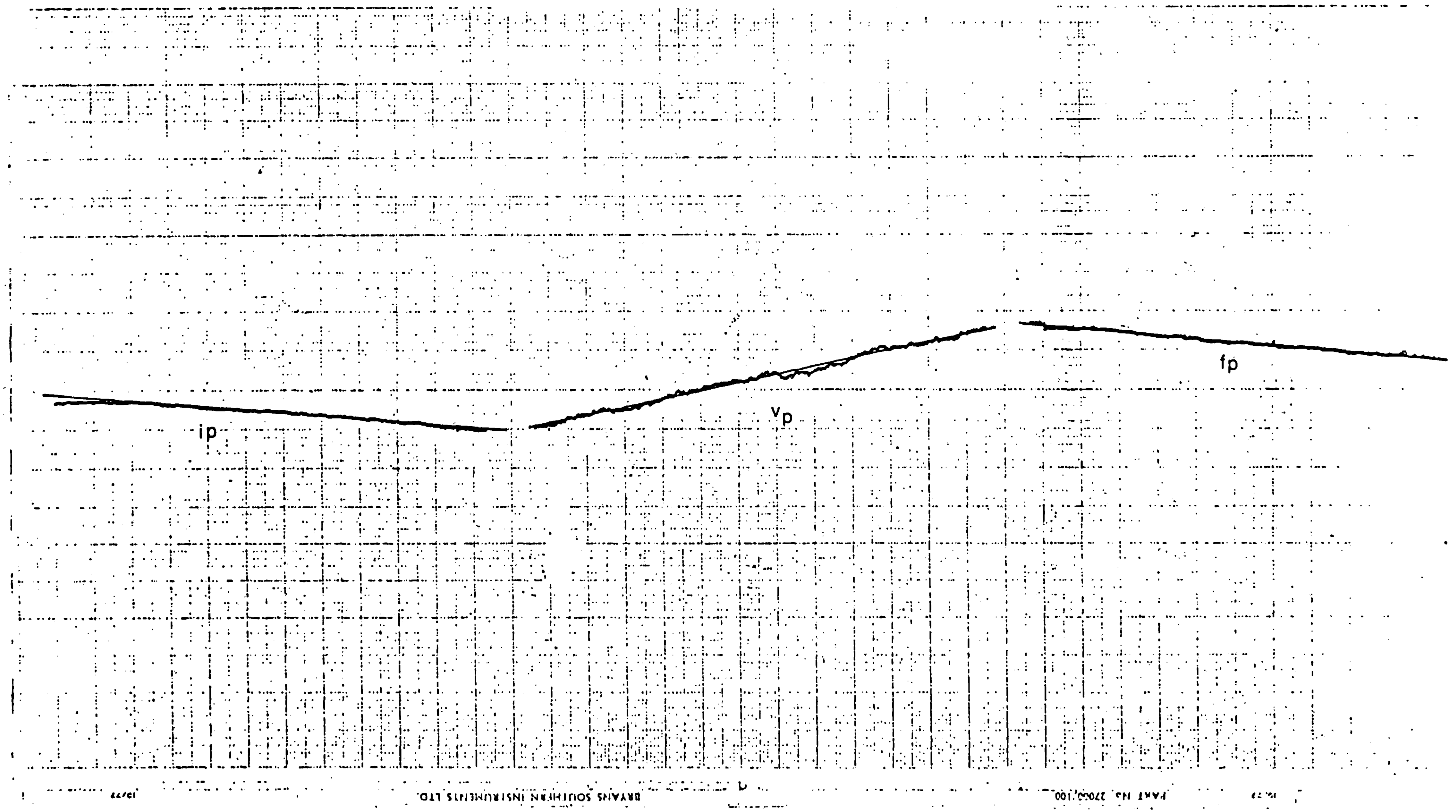

FIG. VI. 9. Typical initial, vaporization, and final lines temperature/time traces of the vaporization of n-C_3H_7OCOCl at 298.15 K.

TABLE VI. 4 THE RESISTANCE OF THE HEATER CHIP (R_H)

V_H* / volts	10 x V_{10}* / volts	R_H / ohms
2.4965	2.4485	101.919
2.4660	2.4210	101.859
2.4380	2.3945	101.838
2.3290	2.2850	101.226
2.2045	2.1650	101.848
2.0610	2.0230	101.878
1.9820	1.9660	101.814
1.8080	1.7750	101.859
1.6890	1.6570	101.932

$$R_H = \underline{101.862 \pm 0.028\ \Omega}$$

* V_H potential across heater

V_{10} potential across standard 10 ohm resistance.

APPENDICES

APPENDIX I

Correcting Weight to Vacuo

For experiments where very accurate weighings are necessary a correction should be made for the effect of the buoyancy of the air. This correction involves reducing the weighings to vacuo.

The weight of an object in vacuo = weight of the object in air + weight of air displaced by the object-weight of air displaced by the balance weight.

$$W_v = W_a + d_a \left(\frac{W_v}{d_b} - \frac{W_a}{d_w} \right)$$

where W_v = weight in vacuo, W_a = apparent weight in air, d_a = density of air, d_w = density of weights and d_b = density of body.

The density of air is normally about 0.0012 gm cm^{-3}. Since the difference in W_v and W_a does not normally exceed 1 - 2 parts per thousand

$$W_v = W_a + d_a \left(\frac{W_a}{d_b} - \frac{W_a}{d_w} \right)$$

The density of stainless steel balance weights is 8.0 g cm^{-3}

$$W_v = W_a + W_a \left[0.0012 \left(\frac{1}{d_b} - \frac{1}{8.0} \right) \right]$$

$$= W_a \quad \frac{K(W_a)}{1000}$$

where $K = 1.20 \left(\frac{1}{d_b} - \frac{1}{8.0} \right)$

The density of THAM is given as 1.35 g cm^{-3}.

APPENDIX II

Errors

The precision of experimentally determined enthalpies of reaction are usually quoted as twice the standard deviation of the mean, $\bar{S}$:

$$\bar{S} = \left[\frac{\sum (x - \bar{x})^2}{n\,(n - 1)} \right]^{\frac{1}{2}}$$

where $\bar{X}$ is the arithmetic mean of n results.
Results are expressed in the form $\bar{X} \pm 2\,\bar{S}$, assuming a normal distribution at the 95% confidence interval. However, for $n \leqslant 20$ the error is more correctly assessed by the 'students t' distribution. Results throughout this work are therefore reported as $\bar{X} \pm t\,\bar{S}$ where t is the'students t' value for (n-1) degrees of freedom at the 95% confidence interval (213).

For a series of values

$$\Delta H = \Delta H_1 + \Delta H_2 + \cdots\cdots \Delta H_n$$

where ΔH_1 has an uncertainty interval of $\pm X_i$ then the error for ΔH was taken as

$$\pm \left[\sum_{i=1}^{n} (X_i)^2 \right]^{\frac{1}{2}}$$

APPENDIX III

The statistical error in $E_a^{\ddagger}$ has been calculated from the expression:

$$\pm \frac{RT_2T_1}{T_2 - T_1}\left[(r_1/k_1)^2 + (r_2/k_2)^2 \right]^{\frac{1}{2}}$$

and the error in $\Delta S^{\pm}$ from the expression:

$$\pm \frac{R}{T_2 - T_1}\left[(T_2r_2/k_2)^2 + (T_1\, r_1/k_1)^2 \right]^{\frac{1}{2}}$$

where R is the gas constant; k_2 and k_1 are the rate coefficients determined at temperature T_2 and T_1; and r_2 and r_1 are the errors in these rate coefficients respectively (217).

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