A Systematic Approach to Cationic Polymerisation.

by

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A thesis
submitted to the University of Keele in
partial fulfilment of the requirements
for the Degree of Doctor of Philosophy.

March 1980

Aus der Kriegsschule des Lebens-
was mich nicht umbringt,
macht mich stärker.

F.Nietzsche 1889.

To my friends.

Acknowledgements.

I have often pondered over the page in a thesis entitled acknowledgements and questioned how others have made their research and produced their theses with so little help. I can unashamedly say that the number of people who deserve to be acknowledged here are too many to fit on one side of A4 paper. I must therefore say thank you to all those who have helped me by a general thank you. However, there are several people to whom I owe especial thanks.

I would like to thank the University of Keele for a studentship, 1976-9, and Professor I.T.Millar for provision of laboratory facilities and for a grant from Nov. 1979 - Jan. 1980.

I am indebted to all the staff, both academic and technical, of the Chemistry Dept., but especially Ralph Pattison, Peter Holbrook Chris Cork and Terry Bolam, for their unerring patience, guidance and help.

I wish to thank the Polish Academy of Science and Professor S. Penczek for enabling me to visit Poland during September and October 1979 and also the many others who made the whole journey both a scientific and a personal success.

To the Polymer Group (past and present) I owe gratitude for many stimulating discussions and considerable help.

I am beholden to David Sherwood and the 4082 for their perseverence while I typed this thesis.

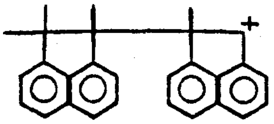
Finally, for the patience, care and affection of Ann, Professor Plesch and Mrs Plesch: Thank you.

ABSTRACT

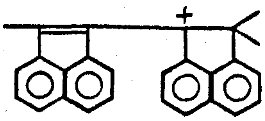
Chapter 1. A theoretical approach to choosing the best initiators for the cationic polymerisation of olefins starts with a clarification of what constitutes a good initiator. Thermodynamic data are used to show that several, so far untried, carbocation salts are worth investigation , e.g. $(p\text{-}ClC_6H_4)_3C^+TaF_6^-$ or WF_6^-, and to explain why SbF_6^- is more stable than PF_6^-. A scrutiny of the various methods for preparing carbocation salts shows the direct method (Eq.A.1.) to be the most useful. Preliminary tests of salt initiators with isobutylene in CH_2Cl_2 corroborate the prediction that $(C_6H_5)_2HC^+$ initiates polymerisation but that $(C_6H_5)_3C^+$ does not.

$$RX + MtX_n \longrightarrow R^+ + MtX_{n+1}^- \qquad A.1$$

Chapter 2 contains a kinetic study of the polymerisation of acenaphthylene in $C_6H_5NO_2$ with $C_2H_5CO^+$ and $(C_6H_5)_2HC^+$ salt initiators. During the first 70% of reaction the first-order rate-constant is independent of the type of initiator, and from it can be derived a $k_p^+ = 22.9 \pm 0.1$ l mol^{-1}s^{-1} at T = 298 K. The later stages of the reactions, which are internally of no simple order, involve development of intense colour which is explained by a rearrangement of the growing cation (I) into the more stable ion (II):



(I)



(II)

This explanation is confirmed by the experiments and molecular orbital calculations which are presented in Chapter 3. The calculated and observed absorption maxima for ions (I) and (II) are:

Ion	λ_{max}(obs)/nm	λ_{max}(calc)/nm
(I)	430-440	438
(II)	560-580	568

This work appears to settle a long-standing controversy about the spectra of these and related ions.

In Chapter 4 a critical appraisal of the Biddulph-Plesch adiabatic reaction calorimeter is followed by the design and construction of a miniature (30 ml) calorimeter.

Chapter 5 deals with attempts to synthesise and polymerise α- and β-halo vinyl ethers. No satisfactory method was found for producing these ethers adequately pure for successful polymerisation.

Chapter 6 contains an account of preliminary copolymerisation experiments with 1,3-dioxolan and tetrahydrofuran in CH_2Cl_2 with $C_6H_5CO^+SbF_6^-$ as the initiator, done by the author in Łodz, Poland. The coexistence of growing ends derived from tetrahydrofuran and 1,3-dioxolan was demonstrated by ion trapping with $(C_6H_5)_3P$ and subsequent ^{31}P NMR analysis of the solutions.

Chapter 7 contains details of several improvements in Rutherford's "mid-point method" for preparing vacuum filled phials. A statistical treatment of the errors indicates that the uncertainty in the weight of the contents is < 5% under usual conditions.

Contents

Chapter 1: Carbocation Salts.

1.1: Introduction.

For as long as chemists have been able to account for the polymerisation of monomers such as styrene and isobutylene by a cationic chain propagation there has been a quest for an understanding of the details of the mechanism. Although the cationic polymerisation of olefins has been recognised as such for over fifty years and the polymerisation of isobutylene with metal halide initiators has been an important industrial process for almost as long, it is still true, almost without exceptions, that no well defined rate-constants have been obtained for these reactions, despite the considerable effort expended to that end.

The major stepping stone towards a detailed knowledge of the polymerisation of isobutylene, and indeed this is true for most cationic polymerisations, has been to find and exploit a well defined initiator/solvent system. This point is exemplified by the considerable advances that have been made in the study of cationic polymerisations of oxacyclics since the advent of both triflic anhydride and oxocarbenium salt initiators.[1,2]

The preoccupation of cationic polymerisation kineticists with "clean" and "ultra dry" solvents is well known and does not need to be discussed here, as an extensive review is given by Plesch.[3] However, it is important to examine briefly what constitutes a good initiator and to summarise the reasoning behind the choice of initiators discussed in this work.

Before the desirable attributes of the ideal initiator can be discussed it is necessary to define two terms which are used frequently and which are often ambiguous; stability and reactivity. These terms are not antonyms, but are, rather, the general and specific terms relating to a given species in a specified environment. Thus, a solution under vacuum might be stable despite the very reactive nature of the salt with respect to hydrolysis or towards a base such as an olefin.

In order to define the kinetics of any system it is important to have a precise knowledge of what the reaction mixture contains. Without such a knowledge any rate constants that are derived from experiment are at best relative and may be spurious. Thus, a good initiator will give rise to ions via a simple and easily definable process. Ideally the equilibrium constants of ionisation and dissociation should be known so that at the start of the polymerisation reaction the species present in the reaction mixture and their respective concentrations are known.

It is essential, if a true value of k_p^+ is to be found, that the concentration of growing ends ($[P_n^+]$) is known throughout the reaction. The $[P_n^+]$ can be ascertained most easily if initiation is fast and quantitative so that $[P_n^+] = c_o$, the total initiator concentration, and further $[P_n^+]$ is constant throughout the reaction.

If the initiation step is to be eliminated from the kinetic equations developed for the treatment of polymerisation reactions, this step must be effectively instantaneous, ie: $k_i \gg k_p$. The kinetics of polymerisation are further simplified and the molecular weights of the polymers obtainable for any given monomer are maximised if chain breaking reactions are minimised.

In order to approach this ideal, the anion must be stable and unreactive towards both the growing end and the monomer. For this reason considerable attention must be paid to the anionogen in the design of the ideal initiator.

For anionic polymerisations the alkali metal cations have proved, from this point of view, to be ideal counterions and the so called "living" polymerisations of monomers such as styrene are now well characterised.[4] In cationic polymerisations the counterpart to the alkali metal ions might be the halide ions. Unfortunately, the halide ions, although simple, can form covalent bonds with the terminal cation of the growing chain, (Eq.1.1.1). Acid anions may form esters in the same way and many of the metal halide initiators can metalate or halogenate the growing ends, (Eq.1.1.2) and also form complexes with the monomer.(Eq.1.1.3)

$$R^{+} + X^{-} \longrightarrow RX \qquad \text{Eq.1.1.1}$$

$$R^{+} + MtX_{n+1}^{-} \longrightarrow RX + MtX_{n} \qquad \text{Eq.1.1.2}$$

$$R_2C{=}CR_2 + MtX_n \longrightarrow \left[\begin{array}{c} R_2C{=}CR_2 \\ \downarrow \\ MtX_n \end{array}\right] \qquad \text{Eq.1.1.3}$$

A final, and more practical, consideration is that a good initiator must have a solubility in the solvent of choice which is adequate for kinetic measurements. For ions in organic media this consideration can impose severe restrictions. The lower limit of solubility for an initiator to be useful depends on the kinetic method. Whatever the method, the concentration of the initiator in the reaction mixture must be significantly higher, say 100x, than that of any interfering impurities.

To summarise: A good initiator will yield a simple, stable anion and a cation with a high, specific reactivity towards monomers via simple, well defined, reactions. Thus, stable carbocation salts with well defined cations and anions are an obvious first choice as possible ideal initiators. But the question as to which salts to choose so that the cation will have maximum reactivity with respect to the monomer of choice, the initiator salt and the resultant pair of ions will have large equilibrium constants for both ionisation and dissociation and the initiator will have adequate solubility, demands a very close examination of the chemistry involved.

In the next section attempts are made to explain the influence of changes in the structure and composition of the salts on their solubility, their ionisation and dissociation equilibria and on the initiation reaction; these will provide a basis for selecting the most useful salt. The ideas are a development of the earlier work of Fairbrother[5] and Plesch[6] but more detailed use of the available data (See Sections 1.7.1-11) is made. The conclusions from this work are fundamental to a more systematic and detailed understanding of cationic olefin polymerisation.

1.2: A thermodynamic approach to carbocation salt initiators.

1.2.1: The solubility of carbocation salts.

The original intention of the work was to study the kinetics of isobutylene polymerisation in CH_2Cl_2 with carbocation salts as initiators. However, the first problem encountered in this work was the insolubility of many such salts in this solvent. From the earlier work of Nuyken[6] in this laboratory it was known that $CH_3CO^+SbF_6^-$ is not very soluble in CH_2Cl_2. Unfortunately, no other solubility data for carbocation salts are available in the literature; in order to predict how the salts could be so modified as to increase their solubility, several theoretical approaches were investigated.

Initially, a very facile procedure, using the ideal solubility equation, (Eq.1.2.1) was applied.

$$(\Delta H_f^{\ominus}/R)((1/T_f)-(1/T)) = \ln X_a \qquad \text{Eq.1.2.1}$$

Where: $\Delta H_f^{\ominus}$=Latent heat of fusion, R=Gas Constant, T_f=Temperature of fusion for the pure compound a, T=Temperature, X_a=Mole fraction of compound a.

It should be noted that this equation is derived assuming no solute/solvent interaction and does not, in any rigorous sense, apply to ionic solutes.

The literature contains no $\Delta H_f^{\ominus}$ data for carbocation salts so that the assumption was made that the solubility of a series of salts would be similar to that of the series of parent organic molecules, (for which the relevant data are available) provided that the anion remained constant.

For example, to predict the solubility of the alkoyl salts the $\Delta H_f^\ominus$ and T_f data of the acids were used in equation 1.2.1 to give the following order of solubility for the cations:

$$CF_3CO^+ > CH_3CH_2CO^+ > CH_3CO^+$$

This is also the order shown in Table 1.2.2 which gives experimental data. However, this approach failed to predict that aroyl and aryl carbenium salts are much more soluble than the corresponding alkoyl and alkyl salts.

A second, and more detailed, procedure was then explored. This involves the recent developments of the Born[7] equation, (Eq.1.2.2) by Abraham et al.[8] whose methods have been shown to produce calculated values of the free energy of solution, $\Delta G_{sol}^\ominus$, for a considerable range of solute and solvents, which agree with experimental results to within ±10 kJ mol^{-1}.

$$\Delta G_{sol}^\ominus = ((z^2e^2)/8\ e_oa)((1/e_s)-1) \qquad \text{Eq.1.2.2}$$

Where: z=charge on the ion, e=electronic charge, a=ionic crystal radius, e_o=permitivity in a vacuum and e_s=permitivity of the solvent.

Substitution for the universal constants and z=1 gives the equation 1.2.3:

$$\Delta G_{sol}^\ominus/\text{kJ mol}^{-1} = -34.7((1/a)-(1/b))+69.4((1/e_s)-1)(1/b) + \Delta G_n^\ominus \qquad \text{Eq.1.2.3}$$

Where: $\Delta G_n^\ominus$/kJ mol^{-1} is the non-electrostatic contribution to the total free energy of solution and b=a+r where: r=the radius of a solvent molecule. (All radii are in nm.)

The new equation retains the inverse relationship between the ionic radius and $\Delta G^{\ominus}_{sol}$, given by equation 1.2.2, but it also includes two new terms. Firstly, the new equation contains a non-electrostatic term, $\Delta G^{\ominus}_{n}$, associated with the transfer of an "uncharged" ion from the gas phase to solution and secondly, the new equation takes account of the discontinuity in the dielectric properties of the solvent near the ion. This is accomplished by including in the equation terms which relate to a shell of solvent molecules around the ion where the effective permitivity is 2 and which has a thickness, r, equal to the radius of the solvent molecule. Abraham et al.[9] have shown that the results from this "one layer" model are not significantly improved by taking more than one layer into consideration, particularly for non-polar, aprotic solvents.

In order to calculate the solubility of a salt it is also necessary to know the lattice energy, U_c, of the salt. This can be seen from the Born-Haber cycle for the process shown in Scheme 1.2.1 Equation 1.2.4 shows how the solubility product, $K^{\ominus}_{s}$, for any salt can be calculated from a knowledge of the free energy of solution of the crystalline salt, $\Delta G^{\ominus}_{s}$.

Scheme 1.2.1

$$\begin{tikzcd}
& A^{+}(g) + X^{-}(g) \arrow[dr, "G^{\ominus}_{sol}(A^{+}) + G^{\ominus}_{sol}(X^{-})"] & \\
A^{+}X^{-}(c) \arrow[ur, "-U_c"] \arrow[rr, "G^{\ominus}_{s}"] & & A^{+}(sol) + X^{-}(sol)
\end{tikzcd}$$

$$\Delta G^{\ominus}_{s} = -RT\ln K^{\ominus}_{s} \qquad \text{Eq. 1.2.4}$$

The lattice energy for any salt can be calculated[10] but this requires a knowledge of the ionic radii and the Madelung constant for the salt. Although approximations of the ionic radii are possible without a knowledge of the crystal geometry the Madelung constant cannot be calculated.

Thus, in order to test the validity of the above treatment for calculating solubility the available data for the solubility of the alkali metal halides in absolute ethanol[11] is tabulated in Table 1.2.1 with the other relevant data.

It is clear that the calculated solubilities are considerably lower than the actual solubilities; however, the predicted order and the relative magnitudes of the solubilities are correct. The significant difference between the experimental and the calculated solubilities is not surprising in view of their exponential relation to $\Delta G_s^\ominus$ and the uncertainty in that quantity, but the fact that the calculated solubility is always low is probably, in part, due to the lack of consideration of the ion pairs in this treatment. This problem could be alleviated by use of the ideal solubility equation and the equilibrium constant for dissociation, K_D, values for the salts in the solvent under consideration, but this will not be considered here since for the carbocation salts no $\Delta H_f^\ominus$ data are available.

Since for carbocation salts no data are available on the crystal geometry, the U_c for these salts cannot be calculated so that the value of $K_s^\ominus$ for such salts cannot be calculated either. Therefore it is interesting, and important, to examine the results in Table 1.2.1 to extract some general correlations between ionic size and solubility.

Table 1.2.1

Data Concerning the Solubility of Alkali Metal Halides in Absolute Ethanol.

MtX	$K_s^{\ominus}$[32]	K_s(calc)	$-\Delta G_{sol}^{\ominus}$[8]	$-U_c$[10]	$\Delta G_s^{\ominus}$	a_+/a_-	$\Sigma a_+, a_-$
	mol l^{-1}		kJ mol^{-1}				pm
NaI	8.2	3.2×10^{-14}	615.5	692	77.0	0.37	313
NaCl	1.2×10^{-4}	2.4×10^{-23}	651.9	780	129.0	0.54	278
KI	1.1×10^{-2}	6.6×10^{-18}	541.4	639	98.0	0.64	354
KCl	2.0×10^{-5}	7.3×10^{-24}	577.8	710	132.0	0.76	319
RbI			522.2	621	98.8	0.68	363
RbCl			558.6	686	127.4	0.81	328
CsI			485.8	599	113.2	0.77	383
CsCl			522.2	651	128.8	0.92	348

For definition of symbols, see text. In all calculations involving temperature this was taken as 298 K.

Table 1.2.2.

Solubilities of Carbocation Salts in Dichloromethane at 298 K.

Salt	a_+	a_-	$a_+ + a_-$	a_+/a_-	Obs.Sol.*	$-\Delta G^{\ominus}_{sol}$	Predicted
		pm			$mol\ l^{-1}$	$kJ\ mol^{-1}$	Solubility
CH_3COSbF_6	187	261	448	0.72	3.0×10^{-4}	415	
$CH_3CH_2COSbF_6$	210	261	471	0.80	4.5×10^{-3}	395	$>CH_3COSbF_6$
$CH_3CH_2COPF_6$	210	237	447	0.89	2.3×10^{-3}	407	$<C_2H_5COSbF_6$ $>CH_3COSbF_6$
CF_3COSbF_6	218	261	479	0.84	6.0×10^{-3}	389	$>CH_3CH_2COSbF_6$
$(C_6H_5)COSbF_6$	331	261	592	1.27	$<10^{-1}$	338	$>>RCOSbF_6$
$(C_6H_5)_3CSbF_6$	490	261	751	1.88	$>10^{-1}$	263	$>>C_6H_5COSbF_6$

Ionic radii were calculated on the basis of bond lengths and covalent radii given in refs. 12, 13 & 14. It should be noted that for a salt, such as $CH_3-C^+=O$, the C=O and C-C bonds are shorter than those for the isoelectronic species.

* Observed solubilities are derived from preparative experiments. (For details see Section 1.3.2.)

$\Delta G^{\ominus}_{sol}$ was calculated by using Abraham's equations, given in Section 1.7.11.

The data in Table 1.2.1 demonstrate that the inverse relationship between ionic size and $-\Delta G^{\ominus}_{sol}$ for the individual ions also holds for the sum of the ionic radii, $a_{+}+a_{-}$ in a similar way. However, since the solubility is determined by the difference $\Delta G^{\ominus}_{sol}-U_{c}$, the sum, $a_{+}+a_{-}$, is not related to the solubility in any simple manner. Nevertheless, from Table 1.2.1, it can be seen that where $a_{+}/a_{-}\leqslant 0.8$, as the radius of the cation increases, so does the solubility. However, when the two ions are of similar size, e.g. where $a_{+}/a_{-}\geqslant 0.8$, the solubility is proportional to $a_{+}+a_{-}$ and therefore inversely proportional to $\Delta G^{\ominus}_{sol}$. From a general consideration of the origin of these effects of relative ionic size on the solubility of the salt it can be predicted that where both ions are large, e.g. where $a>200$ pm, the solubility will also be proportional to $a_{+}+a_{-}$.

With these ideas in mind we can now assess rapidly the effects of modifications to the salt with respect to solubility.

Table 1.2.2 shows the data for a variety of salts considered in this work, their relative, predicted solubilities and the solubilities measured during the course of this work. It should be noted that the experimental solubilities are derived from preparative experiments where temperature control was no better than ±10 K.

It can be seen that the general statements made above with regard to solubility and ionic size do give the correct predictions of relative solubility within the scope of the available evidence.

1.2.2: The equilibria associated with carbocation salts: Introduction.

Now that the method has been established by which we can determine whether any initiator found suitable according to other criteria will also have a useful solubility, it is important to examine two equilibria (Eq.1.2.5 and .6) in order to select the carbocation salt which looks the most promising initiator for olefin polymerisation.

$$Ag^+ + MtX_n^- + RCl \xrightleftharpoons{K_5^\ominus} R^+ + MtX_{n+1}^- + AgCl \qquad \text{Eq. 1.2.5}$$

$$RX + MtX_n \xrightleftharpoons{K_6^\ominus} R^+ + MtX_{n+1}^- \qquad \text{Eq. 1.2.6}$$

The equilibrium constants, $K_5^\ominus$ and $K_6^\ominus$, which are needed to make predictions about the usefulness of the salts, are not generally available in the literature but they could be calculated from equation 1.2.7.

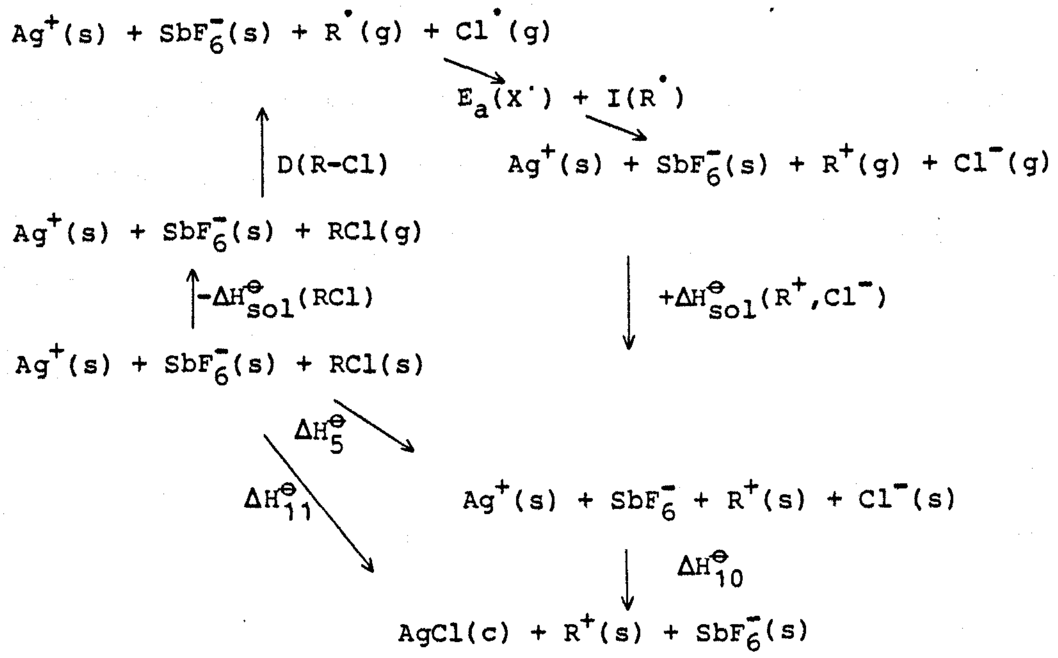
$$\Delta G^\ominus = -RT\ln K^\ominus \qquad \text{Eq. 1.2.7}$$

Unfortunately, most of the available data are for $\Delta H^\ominus$ but, since the $T\Delta S^\ominus$ for these systems is usually small relative to $\Delta H^\ominus$, the approximation:

$$\Delta H^\ominus = \Delta G^\ominus \qquad \text{Eq. 1.2.8}$$

is often made. Although the few studies on such systems[15, 16, 17], (See also section 1.7.1) suggest that the entropy term is certainly more important than this assumption implies, the lack of information on entropy, forces one to use equation 1.2.8 to obtain a first approximation for these systems. Further, it must be emphasised that the major contributuion to the overall $\Delta S^{\ominus}$ for reactions such as those in equations 1.2.5 and 1.2.6 arises from the solvation of the ions and by using the $\Delta G^{\ominus}_{sol}$, as calculated in equation 1.2.3, this contribution can be included in the overall energy change for the reaction as represented by the $\Delta H^{\ominus}$ in the following discussion.

Scheme 1.2.2.



$$\Delta H^\ominus_5 = -\Delta H^\ominus_{sol}(RCl) + D(R-Cl) + I(R^\bullet) + E_a(Cl^\cdot) + \Delta H^\ominus_{sol}(R^+,Cl^-) \qquad \text{Eq.1.2.9}$$

For R = CH_3COCl

$$\Delta H^\ominus_5 = +455 \text{ kJ mol}^{-1} \qquad \text{Eq.1.2.10}$$

$$\Delta H^\ominus_{11} = \Delta H^\ominus_{10} + \Delta H^\ominus_5 = +200 \text{ kJ mol}^{-1} \qquad \text{Eq.1.2.11}$$

n.b. The $\Delta H^\ominus_{sol}$ of the ions in $\Delta H^\ominus_5$ and $\Delta H^\ominus_{10}$ are calculated from Eq.1.2.3 for CH_2Cl_2 as the solvent.

1.2.3: The double decomposition reaction.

The double decomposition reaction by which most of the salts were prepared during the course of the work described in this thesis is given by equation 1.2.5. It was found that for $CF_3CO^+PF_6^-$, $CCl_3CO^+SbF_6^-$ and $C_6F_5CO^+SbF_6^-$ the preparation of salt solutions free of silver was not possible even when a considerable excess of the acid chloride was used. (It is important that all silver is removed from these salt solutions since silver makes them unstable.) This difficulty has been discussed by Lindner and Kranz[18] and will be discussed further in Section 1.3.2. One way of explaining this practical problem comes from an examination of the Born-Haber cycle for the process. (Scheme 1.2.2) It can be seen that even when the energy gain from the precipitation is included to produce an overall enthalpy change, $\Delta H^\ominus_{11}$, the reaction still has a positive $\Delta H^\ominus$.

For many systems this reaction goes to completion because as the AgCl is precipitated, and is thus removed from the system, the equilibrium moves to the right hand side (as shown in Eq.1.2.3). The solubility of AgCl in many systems is so small that the amount of it remaining in solution is negligibly small for most purposes and the reaction can be considered complete.

If, however, in solutions of acid chloride in CH_2Cl_2 the partial molar free energy of Ag^+ and Cl^- is decreased, for example by specific solvation, then the precipitation of AgCl stops when the partial molar free energies of AgCl in solution and the solid state become equal. Thermodynamic equilibrium is then attained and silver cannot be removed from the system without shifting the equilibrium and thus reducing the yield of the desired salt.

Two factors are put forward for our inability to produce the three salts mentioned, free of silver. Firstly, the sum of D(R-Cl) and $I(R^{\bullet})$ increases in the sequence:

$$CH_3COCl < CCl_3COCl < CF_3COCl < C_6F_5COCl$$

and therefore $\Delta H_5^{\ominus}$ (Scheme 1.2.2) becomes more positive.

The second factor is specific solvation of Ag^+ by RCOCl or RCO^+,[19]. This is most easily understood for the $C_6F_5CO^+$ salt where complexation of Ag^+ can be explained in terms of the π-electron system in the benzene ring.

Scheme 1.2.3.

$$\begin{tikzcd}
R^+(g) + X^-(g) + MtX_n(g) \arrow[dr, "A_{X^-}(MtX_n)"] & & \\
 & R^+(g) + MtX^-_{n+1}(g) \arrow[dddd, "+\Delta H^\ominus_{sol}(R^+,MtX^-_{n+1})"] & \\
R^\bullet(g) + X^\bullet(g) + MtX_n(g) \arrow[uu, shift left=6, "E_a(X^\bullet)"'] \arrow[uu, shift right=6, "I(R^\bullet)"] \arrow[ur, "E_a(MtX_{n+1})", "-D(MtX_n-X) + I(R^\bullet)"'] & & \\
RX(g) + MtX_n(g) \arrow[u, "D(R-X)"'] & & \\
RX(l) + MtX_n(c) \arrow[u, shift right=6, "\Delta H^\ominus_v(RX)"'] \arrow[u, shift left=6, "\Delta H^\ominus_{sub}(MtX_n)"'] & & \\
RX(s) + MtX_n(s) \arrow[u, "-\Delta H^\ominus_s\ (RX,MtX_n)"'] \arrow[r, "\Delta H^\ominus_6"] & R^+(s) + MtX^-_{n+1}(s) & \text{Eq.1.2.6}
\end{tikzcd}$$

$$\Delta H^\ominus_{12} = -\Delta H^\ominus_s(RX) + \Delta H^\ominus_v(RX) + D(R-X) + I(R^\bullet) + E_a(X^\bullet) + \Delta H^\ominus_{sol}(R^+)$$ Eq.1.2.12

$$\Delta H^\ominus_{13} = -\Delta H^\ominus_s(MtX_n) + \Delta H^\ominus_{sub}(MtX_n) + A_{X^-}(MtX_n) + \Delta H^\ominus_{sol}(MtX^-_{n+1})$$ Eq.1.2.13

$$\Delta H^\ominus_6 = \Delta H^\ominus_{12} + \Delta H^\ominus_{13}$$ Eq.1.2.14

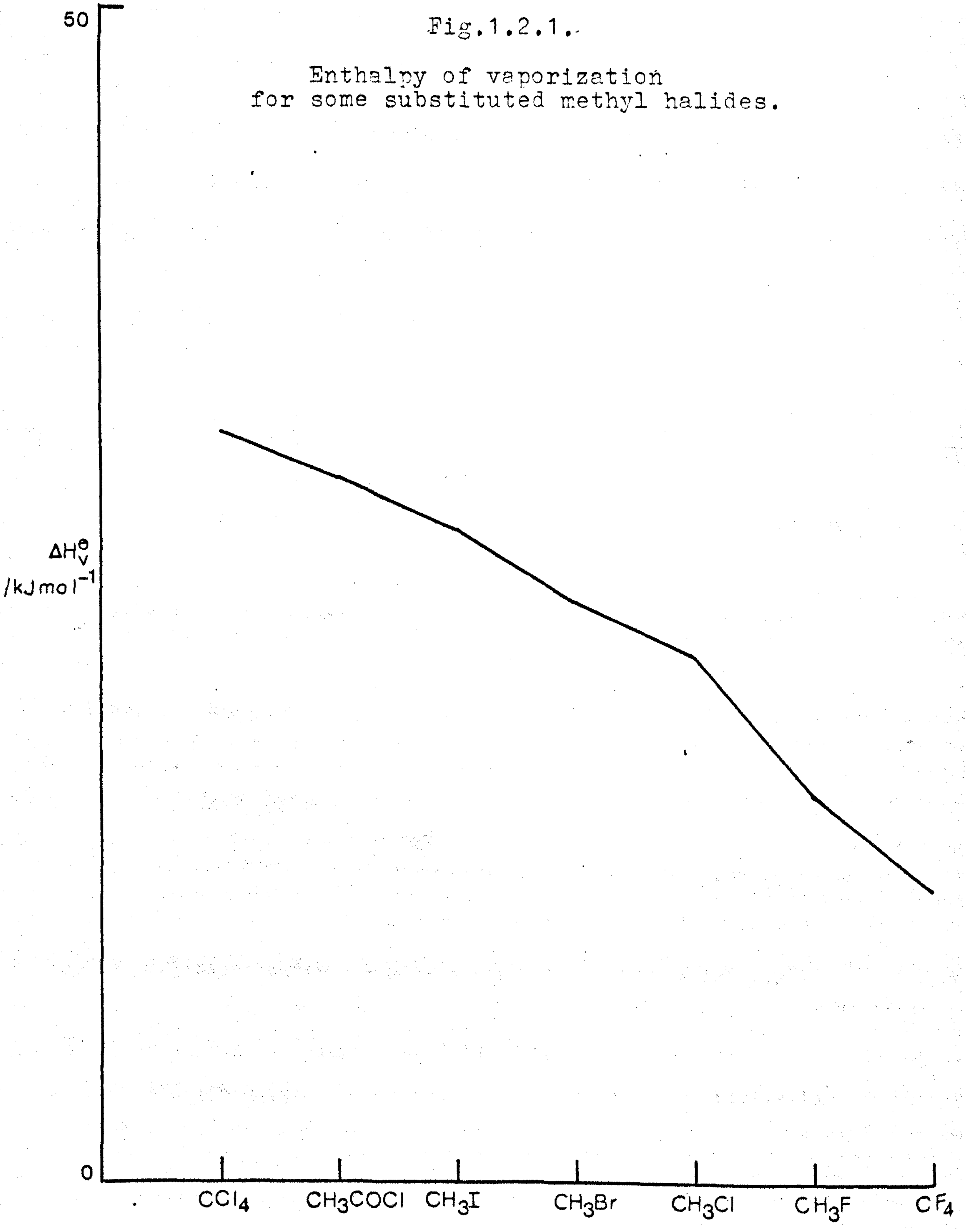


Fig.1.2.1.

Enthalpy of vaporization for some substituted methyl halides.

1.2.4: The alkyl halide + metal halide equilibrium.

The Born-Haber cycle for the binary ionisation equilibrium (B.I.E.) describing the carbocation salt initiator and also the growing polymer ions is given in Scheme 1.2.3 and is summarised in equation 1.2.12 and .13. It is important to emphasise that once initiation has taken place the growing polymer is also involved in the same type of equilibrium with $R^+ = P_n^+$. It is clear that the only important moiety of the initiator salt, at this stage, is the anion.

In order to derive some general conclusions as to how changes in the salt will affect the overall position of the B.I.E. described in Scheme 1.2.3 it is necessary to examine the effects of changes in the salt on each of the individual terms in $\Delta H^\ominus_{12}$ and $\Delta H^\ominus_{13}$.

First, consider, by means of equation 1.2.12, how variations in the RX moiety will affect $\Delta H^\ominus_{12}$. $\Delta H^\ominus_s(RX)$ is small, of the order of 5-10 kJ mol^{-1},[20] and the variation in this term can be excluded from discussion. $\Delta H^\ominus_v(RX)$ is also small relative to the other terms and the maximum variation in this term is only ca.18 kJ mol^{-1}. (Fig.1.2.1) However, it should be noted that, for molecules such as Ph_3CCl, the term required here is $\Delta H^\ominus_{sub}(RX)$ which is considerably larger than $\Delta H^\ominus_v$ and is of the order of 80 kJ mol^{-1}.

It is important to emphasise that $\Delta H^\ominus_s$ is defined as the enthalpy of reaction 1.2.15:

$$RX(\ominus) \longrightarrow RX(sol) \qquad \Delta H^\ominus_s(RX) \qquad \text{Eq. 1.2.15}$$

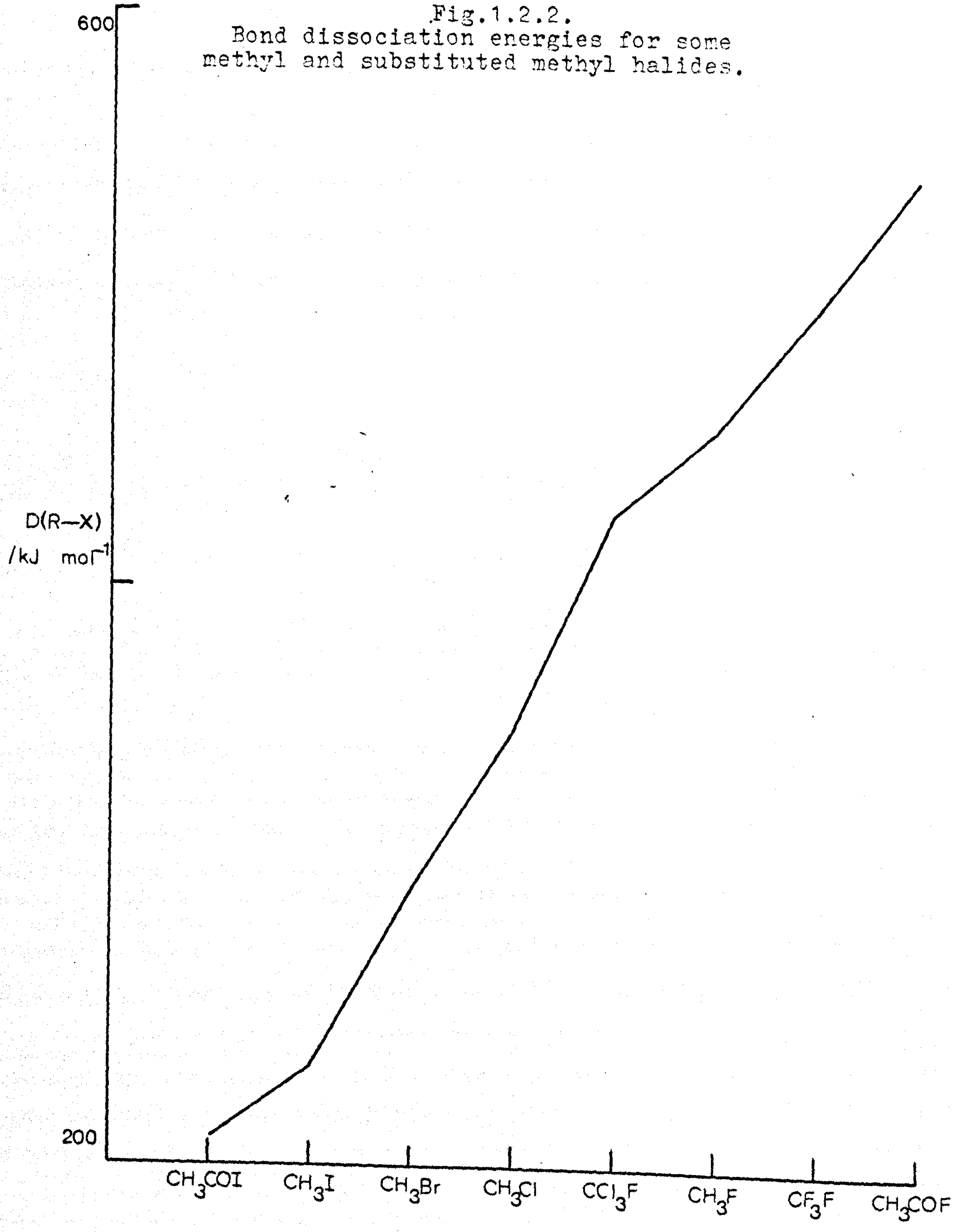


Fig.1.2.2.
Bond dissociation energies for some methyl and substituted methyl halides.

Where (θ) signifies the standard state of the material RX. This is not the same as $\Delta H^{\ominus}_{sol}(RX)$, defined by equation 1.2.16 which can be approximated, very roughly, by $\Delta H^{\ominus}_{v}$(solvent).

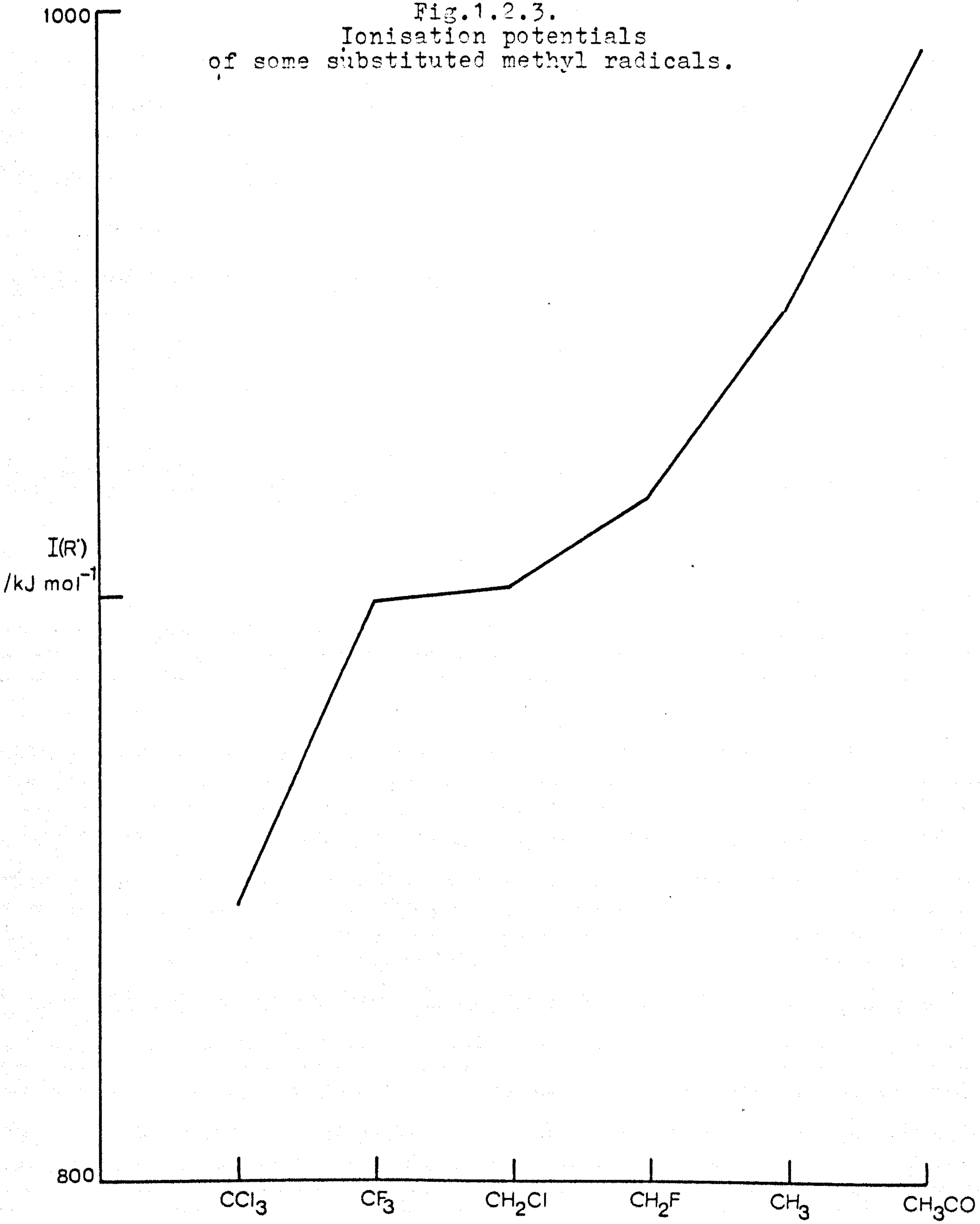
$$RX(g) \longrightarrow RX(sol) \quad \Delta H^{\ominus}_{sol}(RX) \qquad \text{Eq.1.2.16}$$

Since $\Delta H^{\ominus}_{v}(RX)$ and $\Delta H^{\ominus}_{sub}(RX)$ are known for many alkyl halides (and metal halides) the use of $\Delta H^{\ominus}_{s} + \Delta H^{\ominus}_{v}$ or $\Delta H^{\ominus}_{sub}$ rather than $\Delta H^{\ominus}_{sol}$ allows a more accurate approximation to be made of the enthalpy change associated with the transfer of a substance from the gas phase to solution, since $\Delta H^{\ominus}_{s}$ can be said to be small, and insensitive to changes in RX and the $\Delta H^{\ominus}_{v}(RX)$ (or $\Delta H^{\ominus}_{sub}$) term is known.
Although the difference in the two approximations is not significant for similar organic halides, where a difference in the standard state is involved the two approximations do yield very different answers.

The first of the more significant terms in $\Delta H^{\ominus}_{12}$ is the bond dissociation enthalpy, (B.D.E.), D(R-X), for which the variation for a number of methyl derivatives is shown in Fig.1.2.2. It can be seen that by changing X from fluoride to iodide, where $R = CH_3$ $\Delta H^{\ominus}_{12}$ will become less positive by ca.240 kJ mol^{-1}. For $R = CH_3CO$ the same change makes $\Delta H^{\ominus}_{12}$ less positive by ca. 290 kJ mol^{-1}. Some of the B.D.E. values searched for the during the course of this work, for example those for the halogen substituted acetyl halides, are not available but those values that are available are generally well established and errors in this term are usually of the order of 1%.[21]

Another important term in $\Delta H^{\ominus}_{12}$ is the ionisation

Fig.1.2.3.
Ionisation potentials
of some substituted methyl radicals.



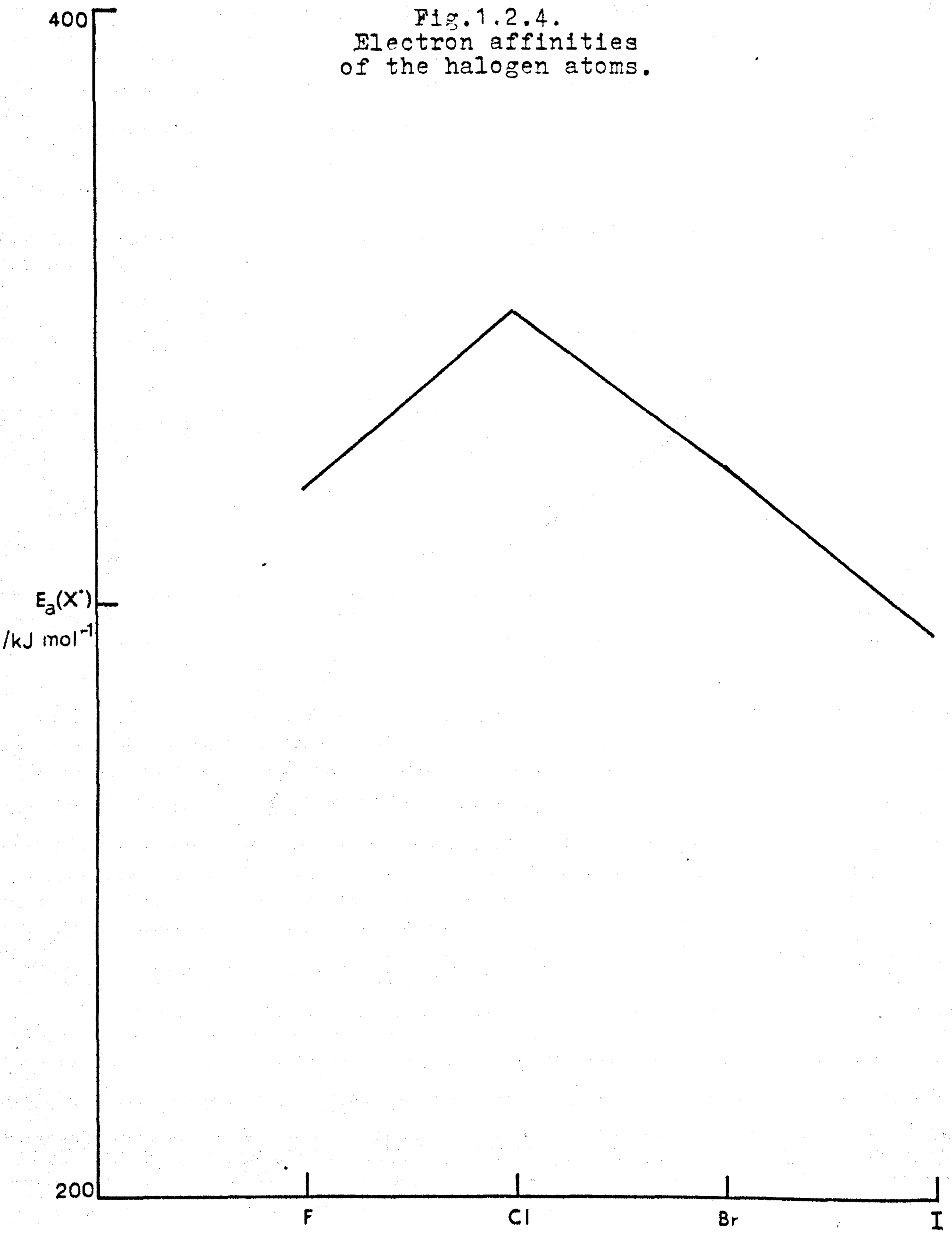


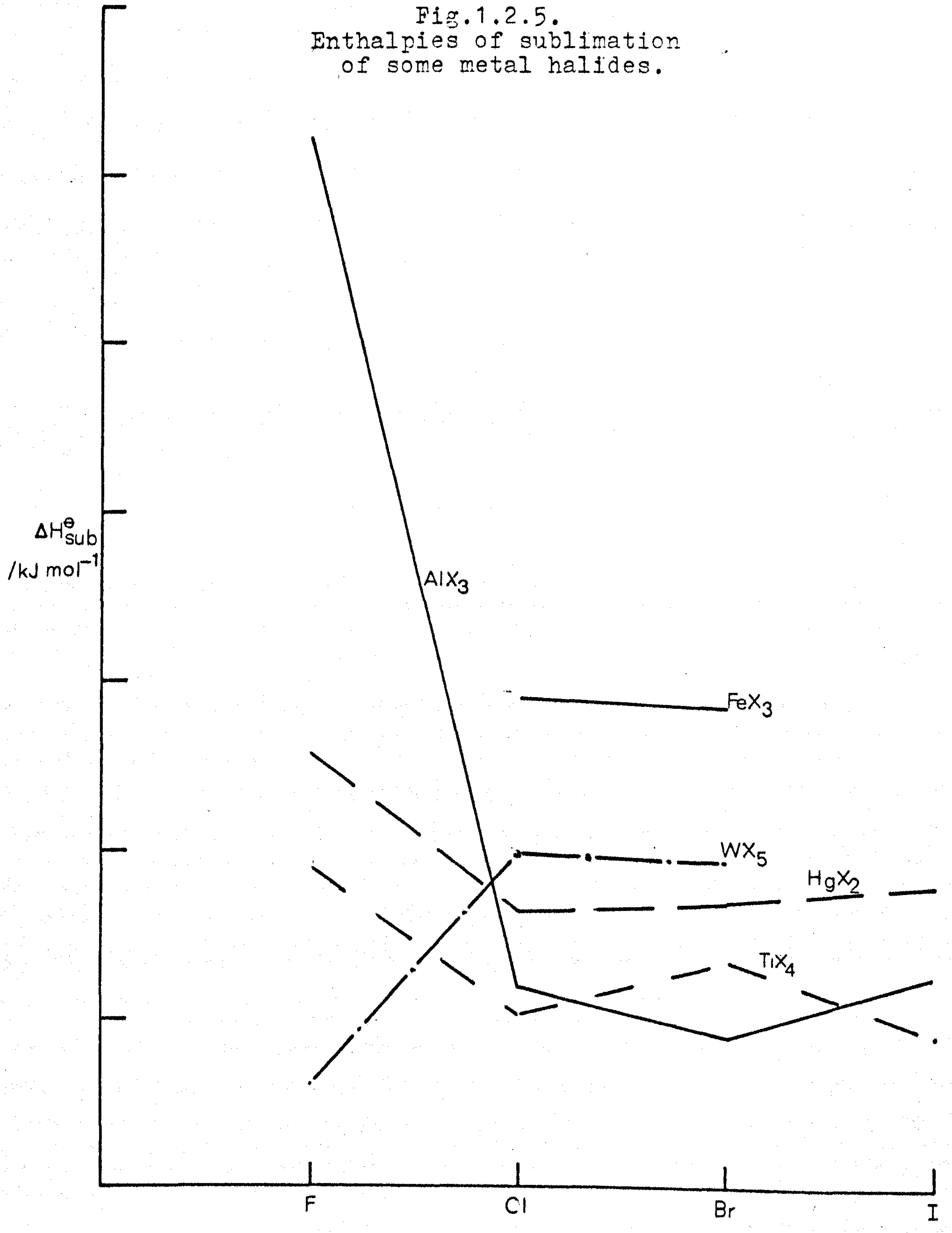
Fig.1.2.4.
Electron affinities
of the halogen atoms.

potential for the organic radical, $I(R^{\bullet})$. Although there are many values for this term available in the literature, care must be taken when comparing data from different sources. Some of the earlier data can be in error by as much as 15 kJ mol^{-1},[22] and indeed, different methods can sometimes yield different results[23] despite the very low errors quoted by the authors for the individual methods; these are usually ±1%. A selection of values of $I(R^{\bullet})$ for substituted methyl radicals is shown in Fig.1.2.3. The maximum difference in $I(R^{\bullet})$, shown on the graph is ca. 145 kJ mol^{-1}. There are no $I(R^{\bullet})$ values for the halogen substituted acetyl radicals but by comparing the ionisation potentials of the acetyl and propionyl radicals and those of methyl cyclohexane and trifluoromethylcyclohexane it can be suggested that the ionisation potentials of the halogen substituted acetyl radicals are greater than that of the acetyl radical and, further, that although the modulus of $D(CF_3CO{-}F)-D(CH_3CO{-}F)$ is unlikely to be greater than 30 kJ mol^{-1}, the difference in the ionisation potentials of the corresponding radicals could well be as much as 200 kJ mol^{-1}. That is, by changing R from CF_3CO to CH_3CO, $\Delta H^{\ominus}_{12}$ will probably be made more positive by ca. 170 kJ mol^{-1}.

Two other terms included in $\Delta H^{\ominus}_{12}$ that require comment are the electron affinity of the halogen atoms (Fig.1.2.4) which, although large, shows only small variation, (ca. 30 kJ mol^{-1}), and the $\Delta H^{\ominus}_{sol}(R^{+})$. The latter term will be discussed together with the similar term for the metal halide anion at the end of the discussion of $\Delta H^{\ominus}_{13}$.

It is clear, from what has been said so far, that for the alkoyl salts, those changes in R which tend to increase the solubility of the salt, tend also to disfavour the formation of ions from the B.I.E. in equation 1.2.6. The ionisation of the organic

Fig.1.2.5.
Enthalpies of sublimation of some metal halides.



halide is promoted by using the iodide rather than the fluoride and by having electron donating groups adjacent to the ionogenic carbon.

Equation 1.2.13 shows the terms which relate to the ion formation from the metal halide involved in the B.I.E. of equation 1.2.6. The $\Delta H_s^{\ominus}(MtXn)$ term is probably small and relatively insensitive to changes in the metal halide . Only one representative example of a $\Delta H_s^{\ominus}(MtXn)$ in an organic solvent could be found in the literature:[24] $\Delta H_s^{\ominus}(MoF_6) = 4.06$ kJ mol^{-1} in C_4Cl_6.

Fig.1.2.5 shows a selection of $\Delta H_{sub}^{\ominus}$ data for four metal halides often encountered in cationic polymerisation. Although the variation in $\Delta H_{sub}^{\ominus}$ for the mercury and titanium halides is small (30-40 kJ mol^{-1}) this is not the case for the aluminium halides. It can be seen that even if aluminium fluoride were sufficiently soluble to be worth considering as an ionogen, its extremely high $\Delta H_{sub}^{\ominus}$ makes $\Delta H_{13}^{\ominus}$ so positve that it seems to hold little promise. For the tungsten halides the trend in $\Delta H_{sub}^{\ominus}$ on changing from chloride to fluoride is the opposite to that shown by the aluminium halides. Thus, this is not a term with respect to which overall generalisation is possible and great care must be taken where the value of $\Delta H_{sub}^{\ominus}$ is not available.

The next term in equation 1.2.13 is the halide affinity of the metal halide, $A_{X^-}(MtX_n)$. This is a very important term for the final value of $\Delta H_6^{\ominus}$ and a term which, were it generally available , would allow some worthwhile conclusions as to which metal halide would be the best anionogen. However, as far as is known only two single halide affinities for the metals of interest are known: the fluoride affinities of BF_3 and WF_5. There are numerous values of double halide affinities, (see Section 1.7.4a), but the errors involved in these terms are considerable, (±80-100

Scheme 1.2.4.

$$\begin{tikzcd}
\mathrm{MtX}_{n+1}(g) \arrow[rrdd, "E_a(\mathrm{MtX}_{n+1})"] & & \\
& \mathrm{MtX}_n(g) + X^-(g) \arrow[dr, "A_{X^-}(\mathrm{MtX}_n)"] & \\
\mathrm{MtX}_n(g) + X(g) \arrow[uu, "-D(X_n\mathrm{Mt}-X)"] \arrow[ur, "E_a(X\ )"'] \arrow[rr] & & \mathrm{MtX}^-_{n+1}(g)
\end{tikzcd}$$

Eq. 1.2.17.

kJ mol^{-1}) and therefore it is not pertinent to draw even tentative conclusions from these data.

In Scheme 1.2.4 the role of the halide affinity in the Born-Haber cycle for the B.I.E. (Eq.1.2.6) is emphasised and an alternative route for obtaining the same energy contribution to $\Delta H^{\ominus}_6$ is given. The individual B.D.E., $D(X_n\mathrm{Mt}-X)$, is, like the halide affinity, known for only a few examples of interest and it is more useful, in order that some general conclusions can be made, to look at the more widely and reliably known average B.D.E. $\bar{D}(\mathrm{Mt}-X)$. It should be mentioned that even by the "alternative route", (Scheme 1.2.4), the electron affinity of the metal halide is required. This term is known for very few metals of interest and the only statement that can be made with any certainty is that the magnitude of this term decreases in the order:

$$\mathrm{F} > \mathrm{Cl} > \mathrm{Br}$$

Before discussing the average B.D.E.term it is appropriate to emphasise the difference between $D(X_n\mathrm{Mt}-X)$ and $\bar{D}(\mathrm{Mt}-X)$, (Eq.1.2.18) and .19) so that the following discussion can be seen in its proper context.

$$\mathrm{MtX}_n \xrightarrow{H^{\ominus}_{18}} \mathrm{Mt}^{\bullet} + n\mathrm{X}^{\bullet} \qquad \text{Eq. 1.2.18}$$

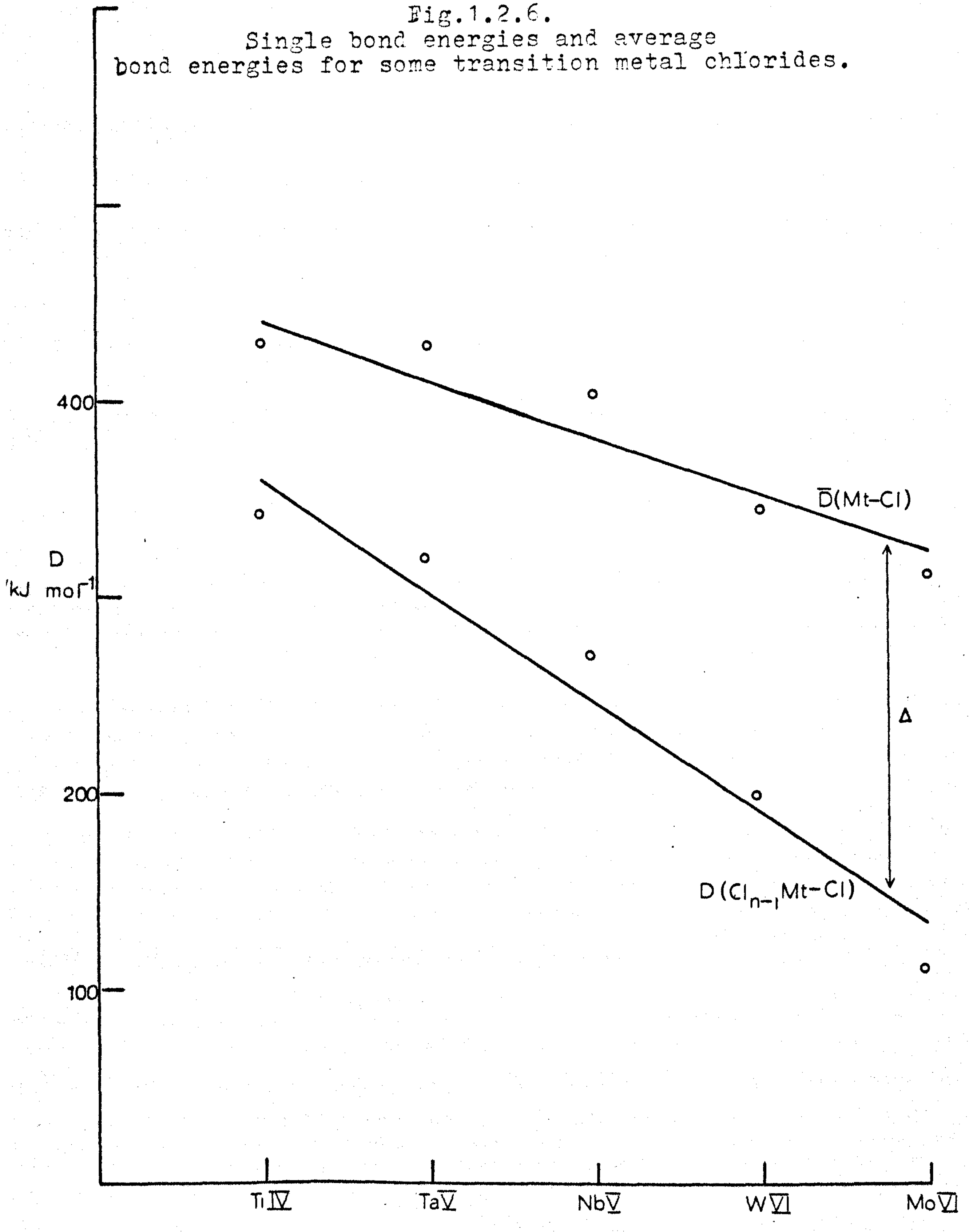
$$H^{\ominus}_{18} = \bar{D}(\mathrm{Mt}-X)$$

$$\mathrm{MtX}_n \xrightarrow{H^{\ominus}_{19}} \mathrm{MtX}^{\bullet}_{n-1} + \mathrm{X}^{\bullet} \qquad \text{Eq. 1.2.19}$$

$$H^{\ominus}_{19} = D(X_{n-1}\mathrm{Mt}-X)$$

The difference between the average and the individual B.D.E.'s is best demonstrated by the data in Section 1.7.7b which are presented in graphical form in Fig. 1.2.6. It can be seen that for the transition metals shown the difference $(\bar{D}(\mathrm{Mt}-X) - D(X_n\mathrm{Mt}-X))$,

Fig.1.2.6.
Single bond energies and average bond energies for some transition metal chlorides.



increases from group IV to group VI and decreases with increasing atomic number down any group. This difference is due, in part, to the allowance made in $D(X_nMt-X)$ for the reorganisation energy, E_r, involved with the stepwise change in the coordination number of the metal whereas the $\bar{D}(Mt-X)$ are derived from heats of atomization (Eq.1.2.18) and therefore do not take account of the relative stabilities of the various oxidation states of the metals. Although very few values of E_r are known, and these are from empirical studies; it can be seen in Fig.1.2.7 that the magnitude of E_r decreases in the order:[25]

$$F > Cl > Br > I$$

so that this term decreases the advantage gained in terms of $\Delta H_6^{\ominus}$, due to $Ea(MtX_{n+1})$ and $\bar{D}(Mt-X)$) by using the fluoride rather than the iodide of any metal.

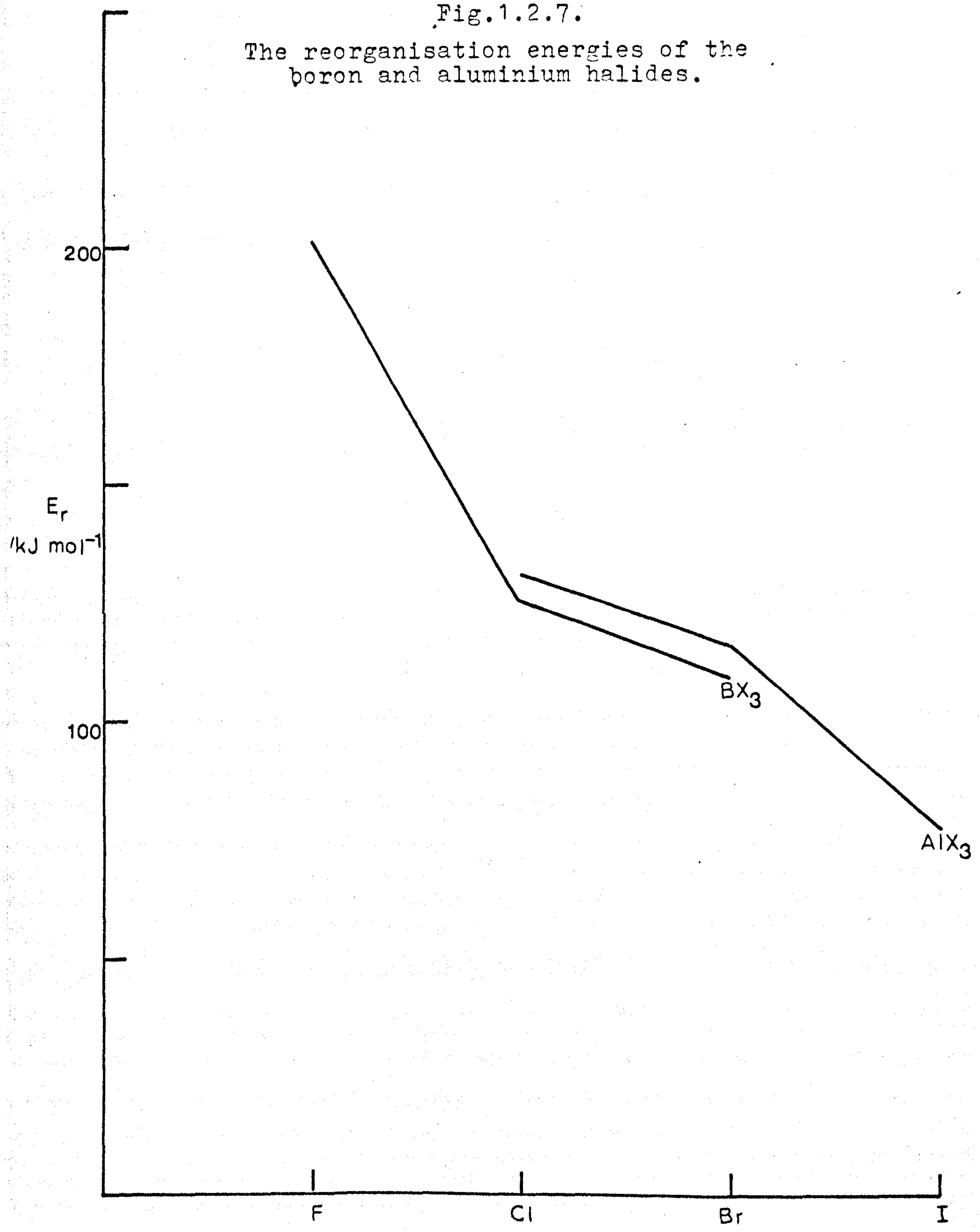
To demonstrate how significantly $\Delta H_6^{\ominus}$ is decreased by using the fluoride instead of the iodide due to the differences in $\bar{D}(Mt-X)$ those average B.D.E.'s which are known for the metals of interest are given in Section 1.7.7a and are shown graphically in Fig.1.2.8. It is clear that $\Delta H_6^{\ominus}$ (Eq.1.2.6) becomes less positive by ca.200 kJ mol^{-1} when the fluoride rather than the chloride is involved and further that $\Delta H_6^{\ominus}$ becomes less positive as the metals are changed in the sequence:

$$As(III) < P(V) < W(V) < B(III) < Al(III)$$

Since considerable use is now being made in cationic polymerisation of the SbF_6^- and AsF_6^- it is regretable that no data are available for the Sb(V) and As(V) fluorides.

Fig.1.2.7.

The reorganisation energies of the boron and aluminium halides.



However by considering the known $\bar{D}$(Mt-X), several trends can be seen which allow estimation of these $\bar{D}$(Mt-X) which are not available. Thus, the anions such as SbF_6^- can be included in the conclusions.

Firstly, a striking feature of Fig.1.2.8 is the similarity in the pattern of changes in $\bar{D}$(Mt-X) for any one metal, such that given any one value of $\bar{D}$ for a halogen X' a reasonable prediction of $\bar{D}$ for other halogens X'' etc. is possible. Secondly, the data for W(V) and W(VI), and P(III) and P(V) indicate that for any one metal the change of $\bar{D}$(Mt-X) with halogen is similar for two adjacent oxidation states. This is illustrated in Fig.1.2.9. where the change in $\bar{D}$(Mt-Cl) with changing oxidation state of the metal is shown graphically. (Data in Section 1.7.7b.) It can be seen that the average B.D.E. increases as the formal oxidation state of the metal decreases; one reason for this may be the increased electron density in the lower oxidation states.[26,27]

In conclusion, although the choice of fluoride instead of iodide as the halide will increase the $\Delta H^\ominus_{sub}$, and therefore make$\Delta H^\ominus_6$ (Eq.1.2.6) more positive, the sum of the differences in these terms will generally be less than the advantage gained from the other terms in $\Delta H^\ominus_{13}$ (Eq.1.2.13) by using the fluoride, so that this is the halide of choice.

As far as the metal is concerned, and the term metal here is used to include some elements which are normally termed non-metals, considerable care must be taken before drawing any conclusions. For example, the E_r may apparently increase the advantage gained by using B(III) instead of Al(III), (Fig.1.2.8) and it would also lead one to believe that W(V) is a better choice than both of these because the estimated reorganisation energy for W(V)$\rightarrow$ W(VI) is only ca. 60 kJ mol^{-1}; this conclusion would, however, be contrary

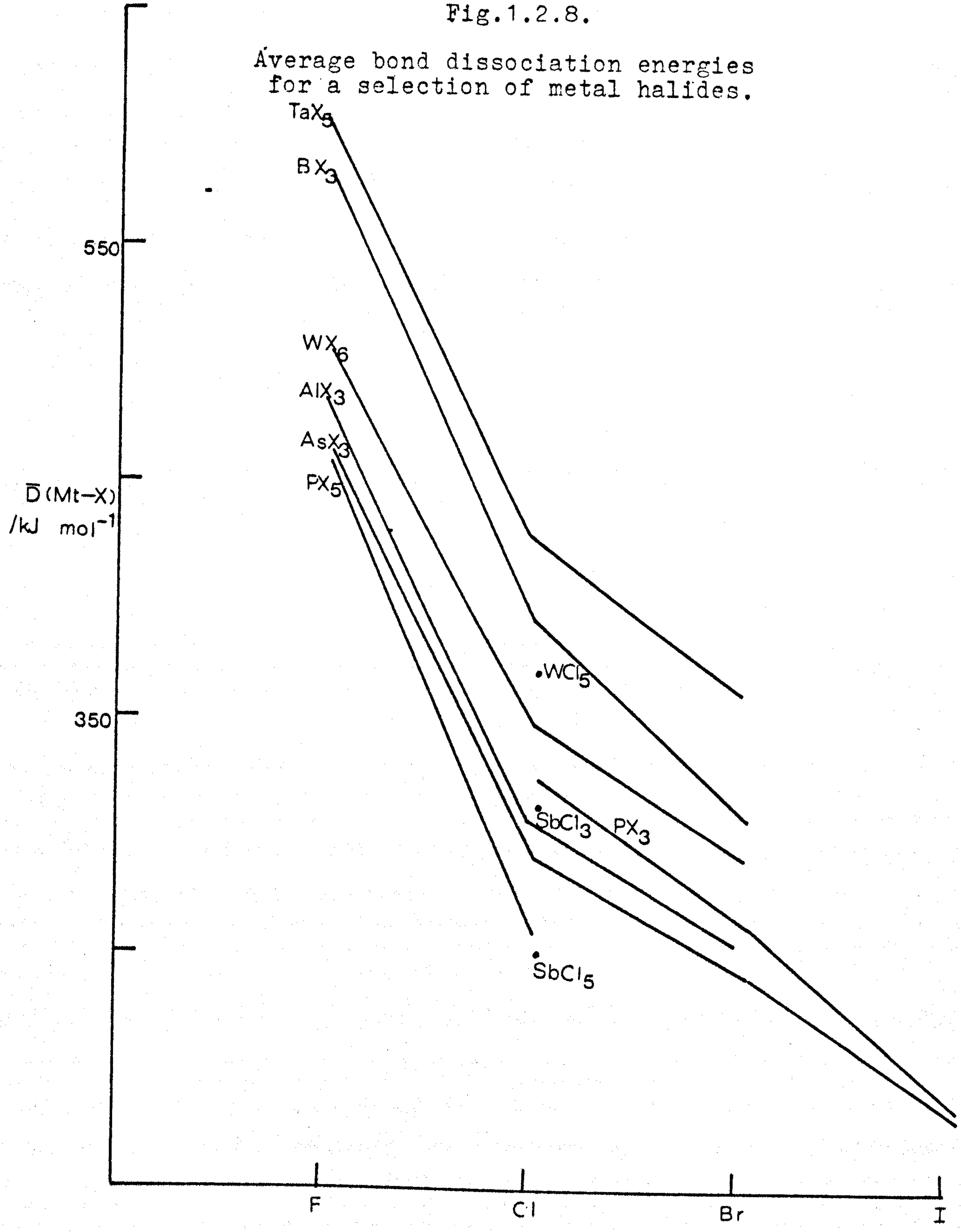


Fig.1.2.8.

Average bond dissociation energies for a selection of metal halides.

to the evidence in Fig.1.2.8. In addition although the stability of the anions:[28]

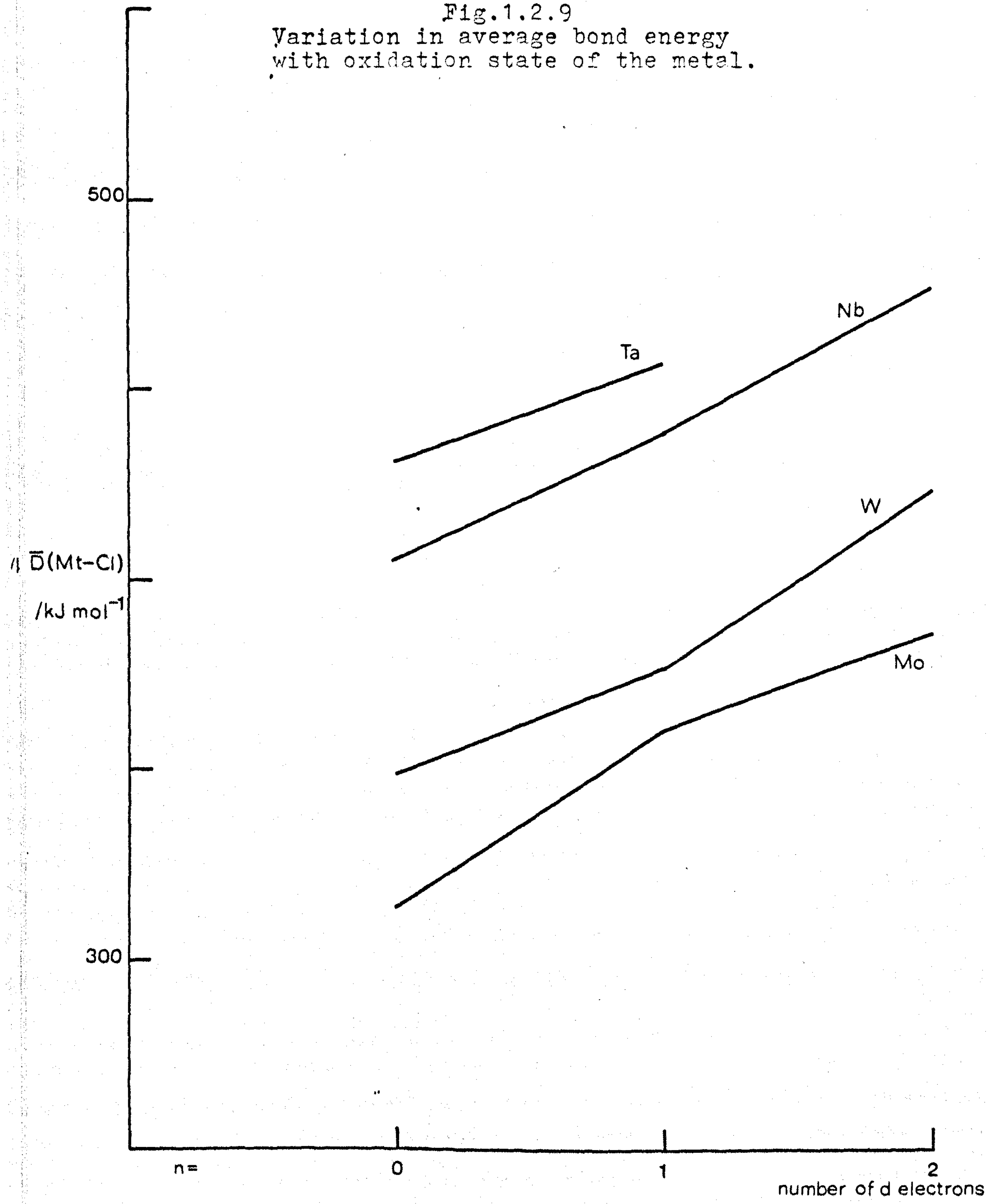
$$SbF_6^- > PF_6^- > SbCl_6^-$$

can be predicted simply on the basis of the $\bar{D}(Mt\text{-}X)$, the comparative instability of BF_4^- vis-a-vis SbF_6^- seems to present an anomaly which can only be explained in terms of the reorganisation energies and the electron affinities of the species concerned.

Lastly, the evidence in Fig.1.2.8 suggests that the lower oxidation states of any metal might provide "better" anionogens than the higher ones, but the estimated increase in E_a for the higher oxidation state(s) probably makes the choice of these more favourable; for example WF_5 rather than WF_4 and SbF_5 rather than SbF_3. Thus, although the available data do not provide a precise basis for selecting a metal, there are adequate grounds for trying for example: TaF_6^-, WF_6^-, AlF_4^- and MoF_6^-.
In addition, the evidence presented here helps to explain some experimental findings.

There remain two terms in $\Delta H_6^\ominus$ (Eq.1.2.6) which have not been discussed: $\Delta H_{sol}^\ominus(R^+)$ and $\Delta H_{sol}^\ominus(MtX_{n+1}^-.)$
As far as is known, no data for these terms in any solvent are available for those ions of interest. Nevertheless, the work of Abraham et al.[8] has provided equations from which these terms can be calculated. However, since the aim of this work is to predict the position of the equilibrium in equation 1.2.6 for which $\Delta G_6^\ominus$ is required and since the entropy of solvation is relatively large[8] it is more useful to calculate $\Delta G_{sol}^\ominus(R^+,MtX_{n+1}^-)$ and to use these results to calculate

Fig.1.2.9
Variation in average bond energy with oxidation state of the metal.



$\Delta H_6^{\ominus}$ which then becomes a closer approximation to $\Delta G_6^{\ominus}$.
(The full equations for CH_2Cl_2 are given in Section 1.7.11)
As will be seen, in the next section, the solution energies of the ions ($\Delta G^{\ominus}_{sol}(R^+, MtX^-_{n+1})$) are the over-riding factor in pushing equilibria, such as that in Eq.1.2.6, towards the ion side.

Table 1.2.3.

Worked Examples of Calculation of $\Delta H_6^\ominus$ (Eq. 1.2.6)

System	$\Delta H_6^\ominus$/kJ mol^{-1}
$CCl_4 + AlCl_3$	$+505 + \Delta H_{sol}^\ominus(R^+, MtX_{n+1}^-)$
$CH_3COCl + AlCl_3$	+608 + " "
$CH_3COF + WF_5$	+712 + " "
t-BuF + MoF_6	+5.3

1.2.5: The alkyl halide + metal halide B.I.E.: Conclusion.

The calculated solution energies of the ions are included only for tBuF + MoF_6, Table 1.2.3, to emphasise the importance of these terms. In general the advantage gained for $\Delta H_6^\ominus$ by changing the metal halide in terms of the solution energy of the ion is less than the errors involved in the rest of the terms in equations 1.2.12 and .13. As has been demonstrated earlier in this section, the smaller the ion, the greater the solution energy. The importance of $\Delta G_{sol}^\ominus(R^+,MtX_{n+1}^-)$ is further emphasised by comparing the data presented so far with the overall equilibrium constants that have been measured. (See Section 1.7.1)

In Table 1.2.3 four worked examples are given for $\Delta H_6^\ominus$ (Eq.1.2.6). The error in $\Delta H_6^\ominus$ is the sum of the errors in the individual terms discussed above and is therefore in excess of 100 kJ mol^{-1} even where all the terms required are known. The consequent uncertainty in, $K_6^\ominus$, (Eq.1.2.6) is correspondingly large and the value of $K_6^\ominus$ therefore meaningless.

In addition the situation which has been considered here is, of course, a simplification. It is well documented that metal halides can take part in a self-ionisation reaction[29], that is, a B.I.E. involving only the metal halide. The Born-Haber cycle for such an equilibrium is given in Scheme 1.2.5. There is also a 1:2 equilibrium associated with the organic halide[30,31] and a molecular aggregate ⇌ single molecule equilibrium associated with the metal halide. Thus, a solution of a carbocation salt is more closely described by the series of linked equilibria summarised in Scheme 1.2.6. However, for those systems where measurements have

Scheme 1.2.5.

$$\begin{tikzcd}
MtX^{\bullet}_{n-1}(g) + X^{\bullet}(g) + MtX_n(g) \arrow[dr, "E_a(X^{\cdot})"] & \\
& MtX^{\bullet}_{n-1}(g) + X^{-}(g) + MtX_n(g) \arrow[d, "A_{X^-}(MtX_n)"] \\
MtX_n(g) + MtX_n(g) \arrow[uu, "D(X_{n-1}Mt-X)"] & MtX^{\bullet}_{n-1}(g) + MtX^{-}_{n+1}(g) \arrow[d, "I(MtX^{\bullet}_{n-1})"] \\
MtX_n(c) + MtX_n(c) \arrow[u, "2\Delta H^{\ominus}_{sub}(MtX_n)"] & MtX^{+}_{n-1}(g) + MtX^{-}_{n+1}(g) \arrow[dd, "\Delta H^{\ominus}_{sol}(MtX^{+}_{n-1})\ \Delta H^{\ominus}_{sol}(MtX^{-}_{n+1})"] \\
MtX_n(s) + MtX_n(s) \arrow[u, "-2\Delta H^{\ominus}_{s}(MtX_n)"] \arrow[dr] & \\
& MtX^{+}_{n-1}(s) + MtX^{-}_{n+1}(s)
\end{tikzcd}$$

Eq.1.2.20

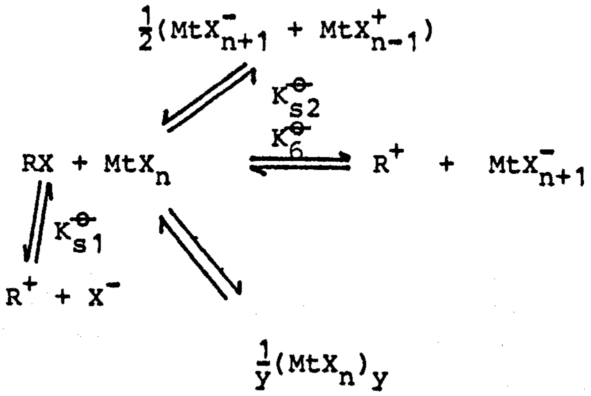
$$\Delta H^{\ominus}_{20} = \Delta H^{\ominus}_{a^+} + \Delta H^{\ominus}_{a^-}$$ Eq.1.2.21

$$\Delta H^{\ominus}_{a^+} = -\Delta H^{\ominus}_{s}(MtX_n) + \Delta H^{\ominus}_{sub}(MtX_n) + D(X_{n-1}Mt-X) + I(MtX^{\bullet}_{n-1}) + \Delta H^{\ominus}_{sol}(MtX^{+}_{n-1})$$ Eq.1.2.22

$$\Delta H^{\ominus}_{a^-} = -\Delta H^{\ominus}_{s}(MtX_n) + \Delta H^{\ominus}_{sub}(MtX_n) + E_a(X^{\cdot}) + A_{X^-}(MtX_n) + \Delta H^{\ominus}_{sol}(MtX^{-}_{n+1})$$ Eq.1.2.23

been made[25] and from a consideration of the data presented in this chapter it can be seen that $K_6^{\ominus}$, (Eq.1.2.6) is so much larger than any of the other equilibrium constants involved, that consideration of the system can validly be restricted to the simple system described so far. However, it should be recognised that to some extent the relative magnitudes of the equilibrium constants in Scheme 1.2.6 do depend on the nature of the solvent.

Sceme 1.2.6.



Eq.1.2.6

Despite the errors invoved and the simplifications that have been made, it is interesting to note, indeed this is a powerful corroboration of the method, that the result for $\Delta H_6^{\ominus}$(t-BuF+MoF$_5$), Table 1.2.3. is of the same magnitude as the experimental values available in the literature. (See Section 1.7.1)

Scheme 1.2.7.

$$\begin{tikzcd}
R'_2\dot{C}\text{-}\dot{C}H_2(g) + R^{\bullet}(g) \arrow[r, "-D(C\text{-}C)"] & R'_2C^{\bullet}\text{-}CH_2\text{-}R(g) \arrow[d, "I(R'_2C^{\bullet}C\text{-}R)"'] \\
 & R'_2C^{+}\text{-}CH_2\text{-}R(g) \arrow[ddd, "\Delta H^{\ominus}_{sol}(R'_2C^{+}\text{-}CH_2\text{-}R)"] \\
R_2C{=}CH_2(g) + R^{+}(g) \arrow[uu, "+\frac{1}{2}D(C{=}C)", "-I(R^{\bullet})"'] & \\
R'_2C{=}CH_2(l) + R^{+}(g) \arrow[u, "\Delta H^{\ominus}_{v}(R'_2C{=}CH_2)"'] & \\
R'_2C{=}CH_2(s) + R^{+}(s) \arrow[u, "-\Delta H^{\ominus}_{sol}(R_2C{=}CH_2)", "-\Delta H^{\ominus}_{sol}(R^{+})"'] \arrow[r, "\Delta H^{\ominus}_{24}"] & R'_2C^{+}\text{-}CH_2\text{-}R(s)
\end{tikzcd}$$

$$\Delta H^{\ominus}_{24} = -\Delta H^{\ominus}_{s}(R_2C{=}CH_2) - \Delta H^{\ominus}_{sol}(R^{+}) + \Delta H^{\ominus}_{v}(R_2C{=}CH_2) + \frac{1}{2}D(C{=}C) - I(R^{\bullet}) - D(C\text{-}C) + I(R'_2C^{\bullet}C\text{-}R) + \Delta H^{\ominus}_{sol}(R'_2C^{+}\text{-}CH_2\text{-}R) \tag{Eq.1.2.25}$$

1.2.6: The initiation reaction.

It has been shown that by consideration of the Born-Haber cycle for the B.I.E. (Eq.1.2.6) valuable guidelines may be drawn as to which salts might prove promising initiators but in order that an initiator will initiate the polymerisation of the chosen monomer ΔG_{24}, under the reaction conditions, must be negative. As a guide to ΔG_{24} we use, as usual, the $\Delta G^{\ominus}_{24}$.

$$P_1 + R^+ + MtX^-_{n+1} \xrightarrow{\Delta G_{24}} R\text{-}P^+_1 + Mt^-_{n+1} \qquad \text{Eq.1.2.24}$$

where: P_1 is the monomer molecule.

Before discussing the thermodynamics of equation 1.2.24 it is worth emphasising that the arguments presented here are about equilibrium constants and are not concerned with the kinetics of the systems. The latter would require information about the bond strengths in the activated complexes of the reactions and are thus beyond the scope of this work. However, for reactions between molecules and cations in solution it is generally found that if ΔG is negative, the reaction proceeds at a reasonable rate.

In equation 1.2.24 MtX^-_{n+1} appears on both sides, so that the Born-Haber cycle for the process, Scheme 1.2.7, can be considered, in the first instance, without reference to this moiety. A more detailed enquiry might take into account energetic differences arising from differences in the extent of ion-pairing for the initiator and the polymer, especially in solvents of low polarity.

It is interesting to examine the cycle for the trityl and dityl cations as initiating salts for isobutylene and to offer a theoretical explanation of the experimental fact (See Section 1.4) that trityl salts do not initiate isobutylene polymerisation but

Table 1.2.5

Calculation of $\Delta H^{\ominus}_{24}$ from Scheme 1.2.7.

Where $R'_2C=CH_2$ = isobutylene.

R^+	$I(R^{\bullet})$	$D(R^{\bullet}-tBu)$	$I(R'-tBu^{\bullet})$	$\Delta H^{\ominus}_{24}/kJ\ mol^{-1}$
ϕ_3C^+	658	191	669	$+37\ +\Delta\Delta H^{\ominus}_{sol}(R^+)$
ϕ_2C^+H	706	223	669	$-45\ +\Delta\Delta H^{\ominus}_{sol}(R^+)$

$\frac{1}{2}D(C=C)$ for isobutylene = 217.6 kJ mol^{-1}

It has been assumed that $I(R^{\bullet})$ of the initiator-isobutylene adduct is the same as that for $t\text{-}C_4H_8^{\bullet}$.

dityl salts do. Table 1.2.5 shows the relevant data. The solution energy terms have been omitted since on the basis of a "tumbling" radius these two ions are of the same size, but since the trityl ion has a propellor rather than a planar structure and also has a more diffuse charge than the dityl ion, it is probable that the $\Delta G^{\ominus}_{sol}$(trityl) is smaller than $\Delta G^{\ominus}_{sol}$(dityl).

Further, it is difficult to know what value to use for the ionic size of the isobutylene adducts of the two ions, but it is probable, on the grounds that the charge is more concentrated and the effective ionic size smaller, that the $\Delta G^{\ominus}_{sol}$(adducts) will be greater than the $\Delta G^{\ominus}_{sol}$(trityl) or $\Delta G^{\ominus}_{sol}$(dityl).
Thus, although no absolute value of the difference in the solution enthalpies ($\Delta\Delta H^{\ominus}_{sol}$)is included in Table 1.2.5, it is possible to infer that the difference in $\Delta H^{\ominus}_{24}$ for trityl and dityl additions to isbutylene is smaller, and that both values are probably less positive, than those shown.

Despite these limitations the results in Table 1.2.5 predict correctly that dityl salts will initiate the polymerisation of isobutylene but that trityl salts will not, provided that under the reaction conditions ΔH_{24} has the same sign as $\Delta H^{\ominus}_{24}$ and that the $\Delta H_{sol}(R^{+})$ and the $T\Delta S$ terms are such that the ΔG_{24} have the same sign as the corresponding $\Delta H^{\ominus}_{24}$, all of which seems to be probable.

For any given monomer the terms in Scheme 1.2.7 which show the greatest variation are $I(R^{\bullet})$ for the initiator and the B.D.E. for the initiator monomer bond. The minimum required value of $I(R^{\bullet})$, such that the corresponding R^{+} will add exergonically to any given olefin, can be estimated in many instances because $I(R^{\bullet})$ and $D(R'_2\dot{C}.C\text{-}R)$ usually vary symbatically. From the available data we can estimate this limiting $I(R^{\bullet})$ for isobutylene as ca.690 kJ mol^{-1}. For styrene the limiting I($R^{\bullet}$) is probably closer to 660 kJ mol^{-1}.

On the basis of this argument it is probable that the tris-p-halogen substituted trityl salts may prove promising initiators for the polymerisation of isobutylene since their ionisation potentials probably exceed 690 kJ mol^{-1},[32] and the p-substitution would inhibit the back-biting reactions which lead to instability for both trityl and dityl salts.[33]

1.2.7: Conclusion.

The discussion presented here demonstrates that the selection of a carbocation salt initiator is not straightforward. It involves reconciling the constraints imposed by the desire for maximum solubility and maximum extent of ionization and by the method of preparation. Many of these constraints are not compatible. Above all, the practical stability of the salt has to be considered, and its reactivity with respect to the monomer under study imposes further restrictions.

Thus, only by considering the thermodynamics of the various aspects of the salt initiator and the initiation reaction, albeit naively, a systematic approach to the choice of novel carbocation salt initiators can be made.

1.2.8: Postscript.

All the data used in the foregoing discussion can be found in Sections 1.7.1-11. In addition to the numerical data presented in the more manageable, graphical form, other data available have been included, (with the reference source) partly because such data were also used in drawing the overall conclusions and partly because the collection of such data, which it is hoped will be useful to other students of this topic, is extremely time consuming. No attempt is made to comment on the validity of the individual numbers and for an assessment of this the sources should be consulted. Neither should the data given here be considered to exhaust the literature, although every effort was made to find as many data for all the energy terms in the Born-Haber cycle as time allowed.

1.3: Materials and experimental method.

1.3.1: Materials.

Silver hexafluorophosphate and silver hexafluoroantimonate. (Fluorochem Ltd.) These compounds were used as supplied. They were dried by continuous pumping in vacuo for 24 h. before use. Only white, or very pale yellow, free flowing powders were used for the preparation of carbocation salts.

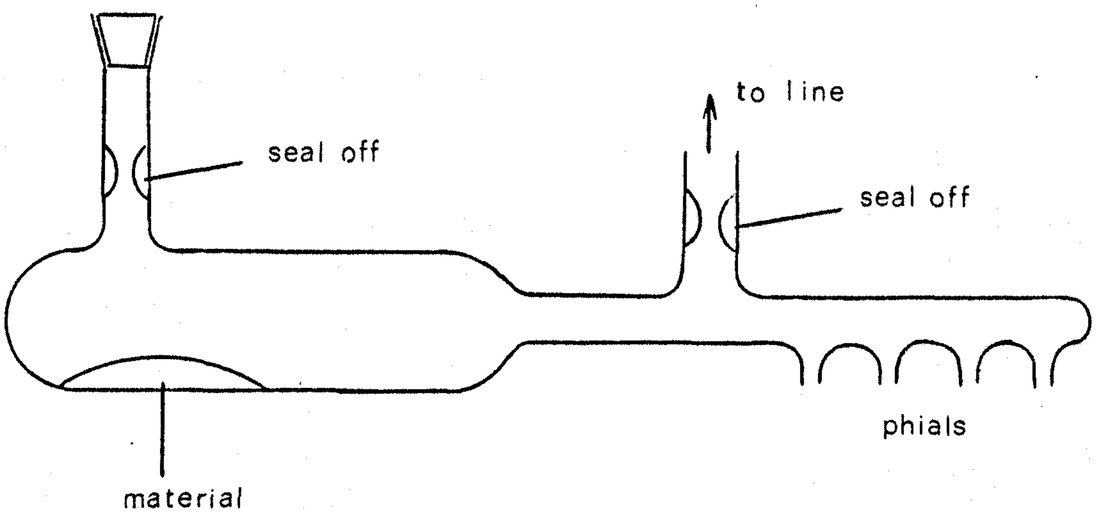
Ferric chloride. (Hopkins and Williams.) The anhydrous compound was put into the apparatus shown in Fig.1.3.1 and vacuum sublimed into phials (See Chapter 7.). After sublimation the fine, black platelets had a bright metallic lustre.

Niobium pentachloride. (Fluka. A.G. puriss.) The white, free flowing powder was rapidly transferred to the apparatus shown in Fig.1.3.1. and after drying in vacuo, by continuous pumping for 16 h, was vacuum sublimed into phials ready for use.

Aluminium chloride. (B.D.H. Ltd.) The grey powder was sublimed three times in vacuo in the apparatus shown in Fig.1.3.2. The procedure was as follows: The chloride was put into flask 1 via the ground glass joint A which was then stoppered . The apparatus was slowly evacuated and the joint sealed off at B. The apparatus was then thoroughly evacuated and flamed. The two flasks were isolated from the vacuum pumps by sealing the restriction, C, and the $AlCl_3$ could then be sublimed from flask 1 to flask 2 without it travelling into the main vacuum line. When most of the chloride had been transferred to flask 2, flask 1 was sealed off at D. The break-seal was broken and after a short period of pumping the apparatus was sealed off at E and the $AlCl_3$ was sublimed into the

Fig.1.3.1: Apparatus for vacuum sublimation of $FeCl_3$ and $NbCl_5$.

Fig.1.3.2: Apparatus for vacuum sublimation of $AlCl_3$.


to line
seal off
seal off
phials
material

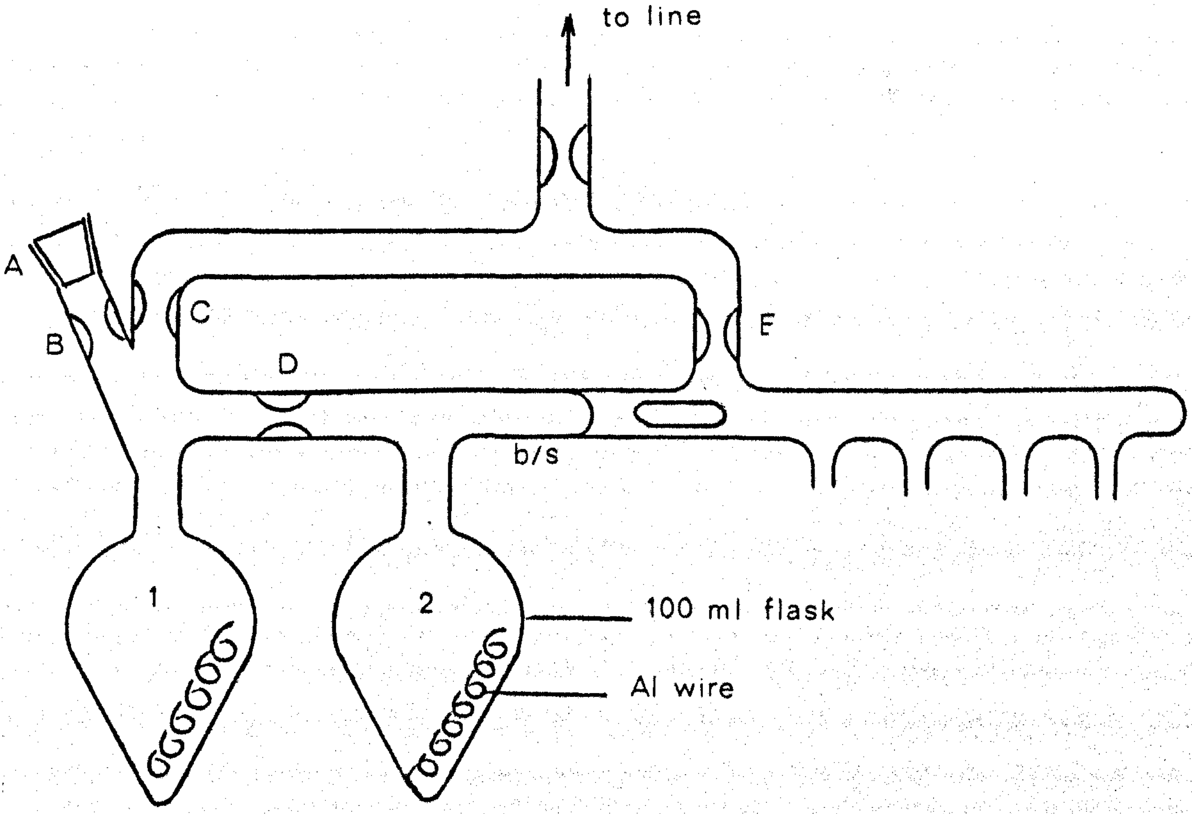

to line
A
B
C
D
E
b/s
1
2
100 ml flask
Al wire

Table 1.3.1.

The Conductivity Changes During the Purification of Dichloromethane.

T = 298 K

Conductivity/ S cm^{-1}	Purification Stage.
1.28×10^{-7}	After vac. $dist^{n}$. from CaH_2.
1.97×10^{-8}	After subsequent $dist^{n}$. from Na.
1.01×10^{-8}	After $dist^{n}$. from 2nd Na mirror.
1.80×10^{-9}	After $dist^{n}$. from $AlCl_3$ and subsequent $dist^{n}$. from fresh Na.

phials. NOTE that unless precautions are taken the $AlCl_3$ will travel into the main vacuum line which is then very difficult to clean.

Dichloromethane. (Fisons Ltd.) This solvent was initially purified as described by Grattan[34] but after vacuum distillation onto the first sodium mirror it was distilled onto freshly sublimed $AlCl_3$ before being stored over a fresh sodium mirror. This procedure was adopted for two reasons. Firstly, it was shown that this procedure ensured that for the preparation of $CH_3CH_2CO^+SbF_6^-$, provided that the method described in Section 1.3.2 was carried out precisely, no discolouration of the product occurred, and secondly because it was shown that this extra purification stage caused a significant reduction in the conductivity. (Table 1.3.1)

Hexane.(B.D.H.Ltd.) This solvent was purified as described,[35] after which it was distilled from CaH_2 and then transferred to the vacuum line where it was stored over CaH_2. It was freshly distilled in vacuo before use.

Isobutylene.(Esso,Fawley Refinery.Special Purity.) This was purified as described.[34] It became opportune to test the effectiveness of the materials available for shielding the isobutylene reservoir. The test was done thus: About 10 ml of isobutylene was put into a 100 ml pear-shaped flask under vacuum and the flask sealed off from the line. The flask was then protected, allowed to warm to room temperature and then struck with a brick. This was done inside a brick enclosure built for the purpose. A lighted candle inside the enclosure gave an indication of the force of the shock wave, and the efficiency of the shielding in containing the broken glass was visually determined. Table 1.3.2 shows the materials tested and the results.

Table 1.3.2.

Results of Tests on Screening Materials for the Isobutylene Reservoir.

Screening	Efficiency of Containment of:		Comment.
Material	glass	shock wave*	
Al gauze (16 mesh)	poor	No	The gauze shield collapsed.
Stainless steel "Knitmesh"			
9031/ss/Nat	poor	Yes	Double thickness of "stocking" used and sealed with wire staples.
9031/ss/0.25/Nat	poor	No	
Nylon "Polynet"	good	Yes	Single thickness only.
Insulating tape	good	Yes	12 vertical strips on a 250 ml flask.

* Yes = candle remained alight, No = candle extinguished.

Although the tests were only qualitative they do show that "Polynet" and black insulating tape are the best materials to use for enclosing the isobutylene reservoir. An additional Perspex screen was placed around such flasks by the author to protect the flasks from being accidentally hit.

Propionyl chloride. (Koch Light Lab.Ltd.) This compound was partially evacuated in the apparatus shown in Fig.1.3.3 and the joint sealed off at A. The C_2H_5COCl was then degassed and distilled into the phials. Trichloroacetyl chloride, (Fisons Ltd.) p-chlorobenzoyl chloride (Aldrich Cem.Co.Ltd.) and pentafluorobenzoyl chloride (Lancaster Synthesis) were all treated in a similar way.

Diphenyl methyl chloride (dityl chloride), (Kodak/Eastman) was dried with Na_2SO_4 and then distilled under reduced pressure; it gave a colourless liquid b.p. 441 K/20 mm Hg. (Lit.[35] 440 K/17 mm Hg.) It was then distilled from $CaCl_2$ into vacuum phials in an apparatus similar to that in Fig.1.3.3.

Triphenyl methyl chloride (trityl chloride), (B.D.H.Ltd.) was recrystallised from hexane. m.p.384 K (Lit[36]. 384-6 K)

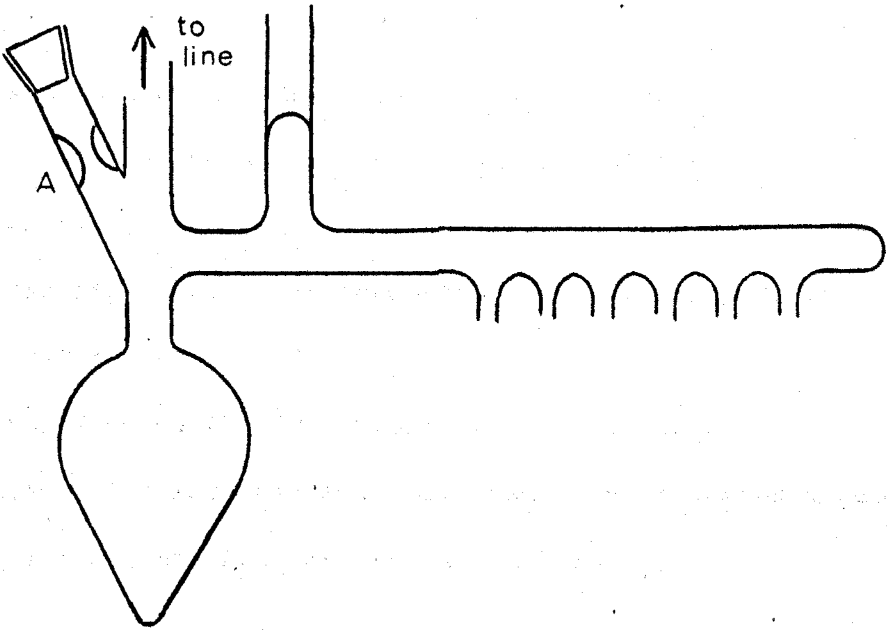
Triphenyl methanol (trityl carbinol), (B.D.H.Ltd.) was recrystallised from CCl_4. m.p. 434 K (Lit.[37] 434-5 K).

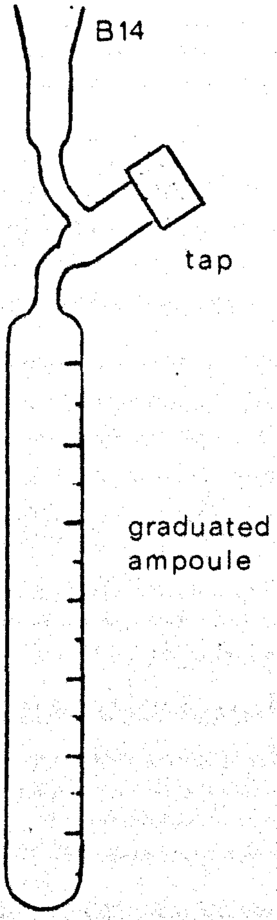
t-Butyl bromide, (Koch Light.puriss) was dried with CaO and then distilled in vacuo onto $CaBr_2$ in an apparatus similar to that in Fig.1.3.3. It was freshly distilled into a vacuum phial before use.

Trifluoroacetyl chloride was prepared immediately before use by the reaction of CF_3COOH (Eastman Org.Chem.) and C_6H_5COCl[38] (Koch Light.puriss) in the apparatus shown in Fig.1.3.6.. The reagents were refluxed for 24 h under nitrogen before ca. 50% of the expected amount (referred to CF_3COOH) of CF_3COCl was collected in the trap cooled with a dry ice/acetone mixture.

Fig.1.3.3: Apparatus for preparing vacuum phials of organic chlorides.

Fig.1.3.4: Ampoule for use with C_6H_5COF, SbF_5 and SO_2.


to
line
A


B14
tap
graduated
ampoule

Benzoyl fluoride. (Aldrich Chem.) 10 ml of this compound was transferred rapidly from the bottle to an ampoule (Fig.1.3.4) containing 0.2 g P_2O_5. The liquid was degassed by a freeze-pump-thaw technique and then vacuum distilled into a graduated ampoule.

Antimony pentafluoride. (Aldrich Chem.) A graduated ampoule (Fig.1.3.4) was evacuated and the SbF_5 was transferred rapidly from the bottle to the ampoule by sucking the liquid into the ampoule. The liquid was then degassed by the freeze-pump-thaw technique before use.

Sulphur dioxide (Polish supplier) was bubbled through concentrated sulphuric acid and collected in a graduated ampoule (Fig.1.3.4) containig P_2O_5 and cooled in liq. N_2.

1.3.2:Preparation of carbocation salts.

1.3.2.1: Introduction.

There are two reactions by which carbocation salts can be prepared. A double decomposition reaction, (Eq.1.3.1) and a direct combination reaction, (Eq.1.3.2).

$$Ag^+MtX^-_{n+1} + RX \longrightarrow Ag^+X^- + R^+MtX^-_{n+1} \qquad \text{Eq.1.3.1}$$

$$RX + MtX_n \longrightarrow R^+MtX^-_{n+1} \qquad \text{Eq.1.3.2}$$

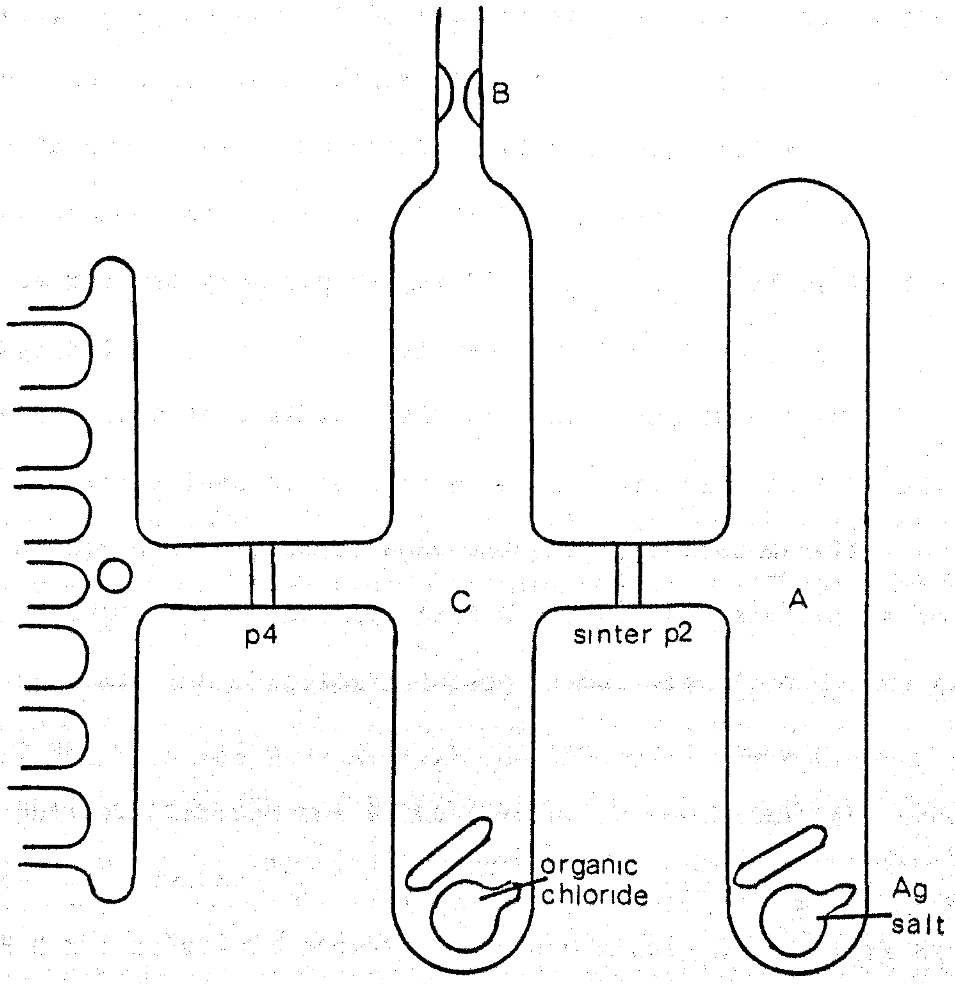
The double decomposition reaction was used initially by Sharp and Sheppard[39] in 1957 and it has been used many times by Olah et al. in the last decade.(e.g. ref. 40a and b.) The major difference between the techniques of these two groups and our work is that most of the preparations described in this thesis were carried out entirely in vacuo, since the exclusion of impurities, and particularly oxygen, is of paramount importance. The techniques of Olah et al.[40a] were tried on two occasions to prepare $C_2H_5CO^+SbF_6^-$ but the resulting salt was pale yellow and was therefore discarded. Three vacuum techniques have been used by the author in attempts to prepare a number of salts by the double decomposition reaction, these will be called: 1A, 1B and 1C.

The direct combination reaction, method 2, has also been used with considerable success by Olah et al.[40b] to prepare solid salts and salt solutions in strong acid media. Two attempts were made by the author to prepare solutions of salts by direct combination, with CH_2Cl_2 as the solvent, without success. However, in Poland the author was introduced to the much more successful method developed in Łodz for the preparation of $C_6H_5CO^+SbF_6^-$. This will be described here since it has not been described in detail elsewhere (See Section 1.3.2.6.).

1.3.2.2: Method 1A.

This method, which is fully described by Westermann[41], was used successfully for the preparation of $(C_6H_5)_3C^+SbF_6^-$ (I) from $(C_6H_5)_3CCl$ and $AgSbF_6$. This method should be useful for preparing any salt which has a solubility greater than ca. 0.1 mol l^{-1} in CH_2Cl_2 and also when excess of organic chloride during the preparation of the salt does not lead to any undesirable side-reactions. This method was also tried for the preparation of $(C_6H_5)_2HC^+$ (II), $C_6F_5CO^+$ (III) and CCl_3CO^+(IV) SbF_6^- without success. The solutions of II prepared in this way were not stable, as indicated by the rapid development of a deep brown colour and later a black precipitate. When this method was used for the preparation of III no AgCl precipitated and the resulting solution in CH_2Cl_2 was pale red. On freezing, the solution became a white solid but the colour returned when the solid melted. When the preparation of IV was attempted by this method , no precipitation of AgCl occurred despite a three-fold excess of the acid chloride . The solution of acid chloride and silver salt in CH_2Cl_2 was colourless, and remained so for several weeks.

Fig.1.3.5: Apparatus for method 1B.

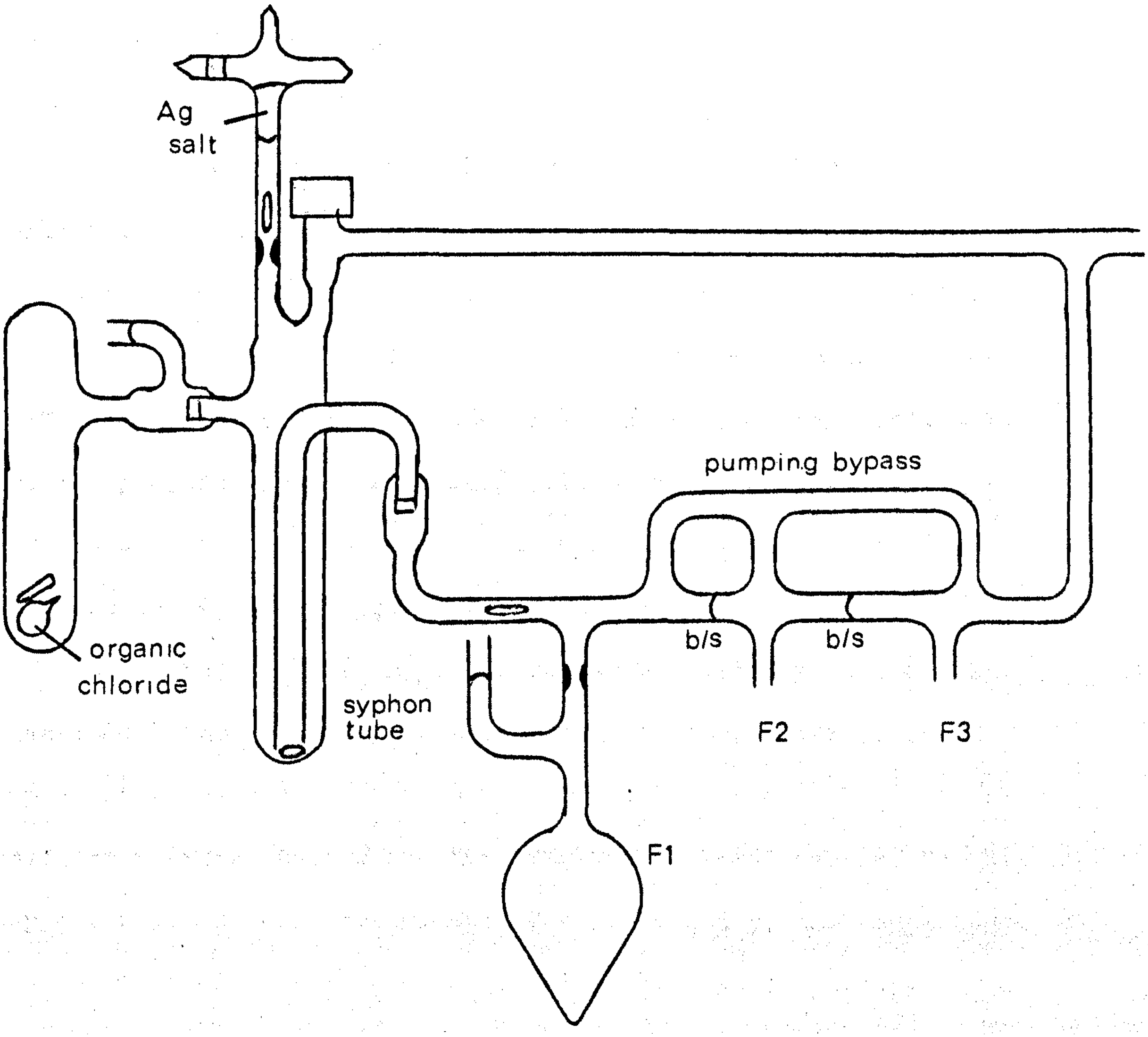

B
C
A
p4
sinter p2
organic chloride
Ag salt

1.3.2.3: Method 1B.

For the preparation of II a modification of method 1A was attempted to test whether the instability of the salt solution resulted from the initial presence of excess $(C_6H_5)_2HCCl$. The apparatus, shown in Fig.1.3.5, was sealed onto the vacuum line and evacuated for 8 h, during which time it was frequently flamed with a large "brush" flame. The phial of silver salt (5.0×10^{-3} mole) was then broken, ca. 20 ml of CH_2Cl_2 distilled into A and the apparatus removed from the vacuum line by sealing off at B. The phial of $(C_6H_5)_2HCCl$ (4.0×10^{-3} mole) was then broken and, by cooling the saturated silver salt solution ,the $(C_6H_5)_2HCCl$ slowly distilled into A. At this stage the solution in A became bright orange and much white AgCl was precipitated. Finally, a small amount of CH_2Cl_2 was distilled into C and washed back into A to ensure that all the chloride had been transferred from C into A. The solution was then filtered through the two glass sinters into vacuum phials. Although the initial solution was bright and gave the expected U.V. spectrum[42] after two days in the refrigerator at ca. 276 K the solutions became cloudy and slowly became dark brown.

This method was also tried for the preparation of $p\text{-}ClC_6H_4CO^+SbF_6^-$,(V) but the pale buff coloured solution produced obviously contained AgCl since very little precipitation occurred. The solution became, progressively: brown, green and finally black, at which stage a black precipitate also formed.

Fig.1.3.6: Apparatus for method 1C, the Nuyken apparatus.


Ag salt
pumping bypass
b/s
b/s
organic chloride
syphon tube
F2
F3
F1

1.3.2.4: Method 1C.

This method, originally devised by Nuyken[43] and later described by Kipnich,[16] is especially useful for the preparation of relatively insoluble salts and when an excess of organic chloride causes the salt solutions to be unstable . The apparatus, which was used successfully to prepare CH_2Cl_2 solutions of $C_2H_5CO^+PF_6^-$ (VI) and SbF_6^- (VII), is shown in Fig.1.3.6. The inclusion of the "pumping bypass" over the break-seals (b/s) between the collection flasks allows all three collection flasks to be sealed onto the apparatus from the start and eliminates the more complicated and difficult to operate arrangement described by Kipnich.[16] A more radical modification to the apparatus was made for the preparation of $CF_3CO^+SbF_6^-$ (VIII). The modification ensured that the very volatile acid chloride dissolved rapidly in the reaction mixture.(Fig.1.3.7 and .8)

The method for both apparatuses was essentially that already described[16] but several points are worth noting: Firstly, it is important to make sure that as the acid chloride distills into the reaction mixture it does not form regions of local excess. If this happens rapid colour development occurs. Secondly, the temperature of the reaction mixture must be kept below 273 K at all times. If the temperature rises above this, the solution becomes coloured. Lastly, if the solution becomes coloured it is best to abandon the experiment since the colour inevitably becomes deeper with time.

The saturated salt solutions, prepared by this method were distributed into four ampoules in the apparatus shown in Fig.1.3.9. The ampoules were painted black and stored in a cupboard at ambient temperature. For use in the polymerisation tests

Table 1.3.3.

Summary of Carbocation Salt Preparations

by the Double Decomposition Reaction.

Salt	Formula	Method	Stable*	Silver^x
I	$Ph_3C^+SbF_6^-$	1A	+	-
II	$Ph_2HC^+SbF_6^-$	1A&1B	-	-
III	$C_6F_5CO^+SbF_6^-$	1A	-	+
IV	$CCl_3CO^+SbF_6^-$	1A&1C	-	+
V	$p\text{-}ClC_6H_4CO^+SbF_6^-$	1B	-	+
VI	$CH_3CH_2CO^+PF_6^-$	1C	+	-
VII	$CH_3CH_2CO^+SbF_6^-$	1C	+	-
VIII	$CF_3CO^+SbF_6^-$	1C	-	+
IX	$(CH_3)_3C^+SbF_6^-$	1C	-	?

* Stable; + = solution did not develop inexplicable colours and gave a salt concentration which did not vary with time when analysed by U.V. with trityl carbinol.

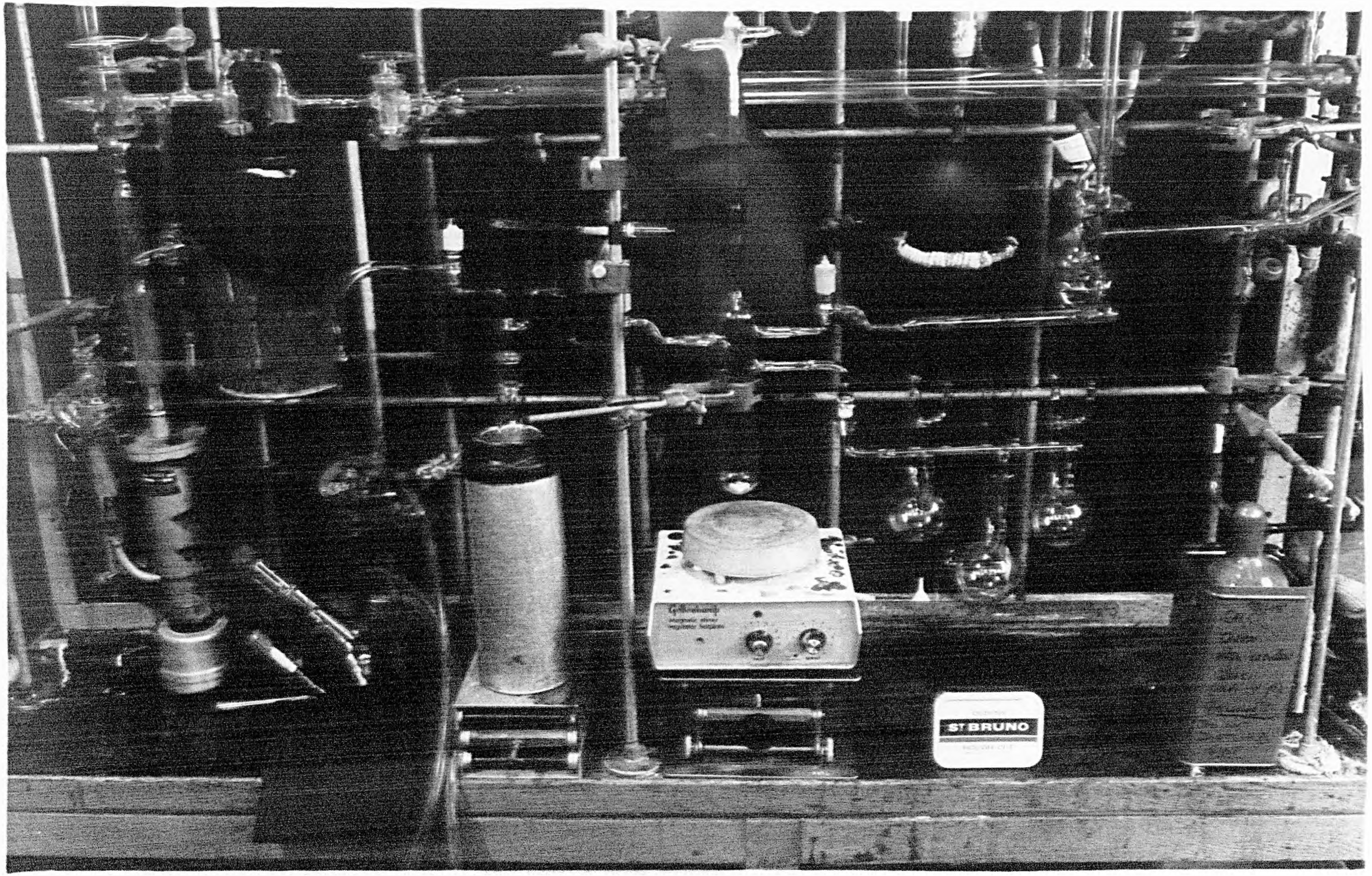
^{x} Silver; + = solution contained measurable amounts of Ag^+.

(Section 1.3.5) and other experiments needing only 1-2 ml of solution, the contents of the ampoules were distributed into smaller vacuum phials by using a tipping device.[44]

Despite the abundant precipitation of AgCl during the preparation, solutions of VIII were shown polarographically (See Section 1.3.7) to contain significant amounts of silver. In addition, after several days the solutions of (VIII) became dark purple. The preparation of $(CH_3)_3C^+SbF_6^-$ (IX) by this method was also attempted. The reaction mixture became dark brown even before all the t-BuBr had been distilled in. Only one attempt was made at this preparation.

A summary of the salts which we tried to make by double decomposition is given in Table 1.3.3.

Fig.1.3.7: Apparatus for preparing$CF_3CO^+SbF_6^-$.



St BRUNO

Fig.1.3.8: Sketch to show details of Fig.1.3.7. The CF_3COCl is bubbled into the salt solution via tube A from the cold trap B where it is collected after preparation.

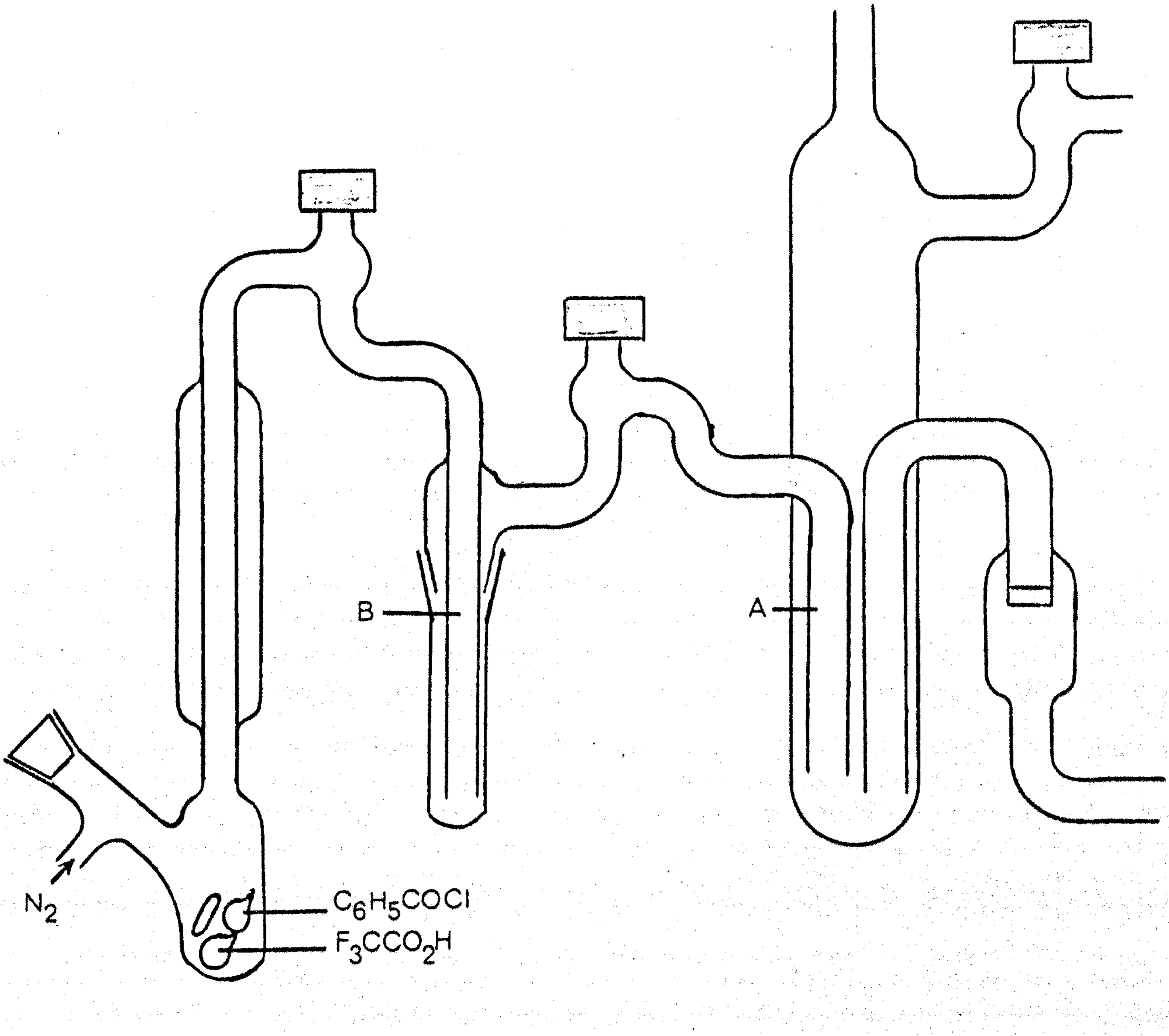
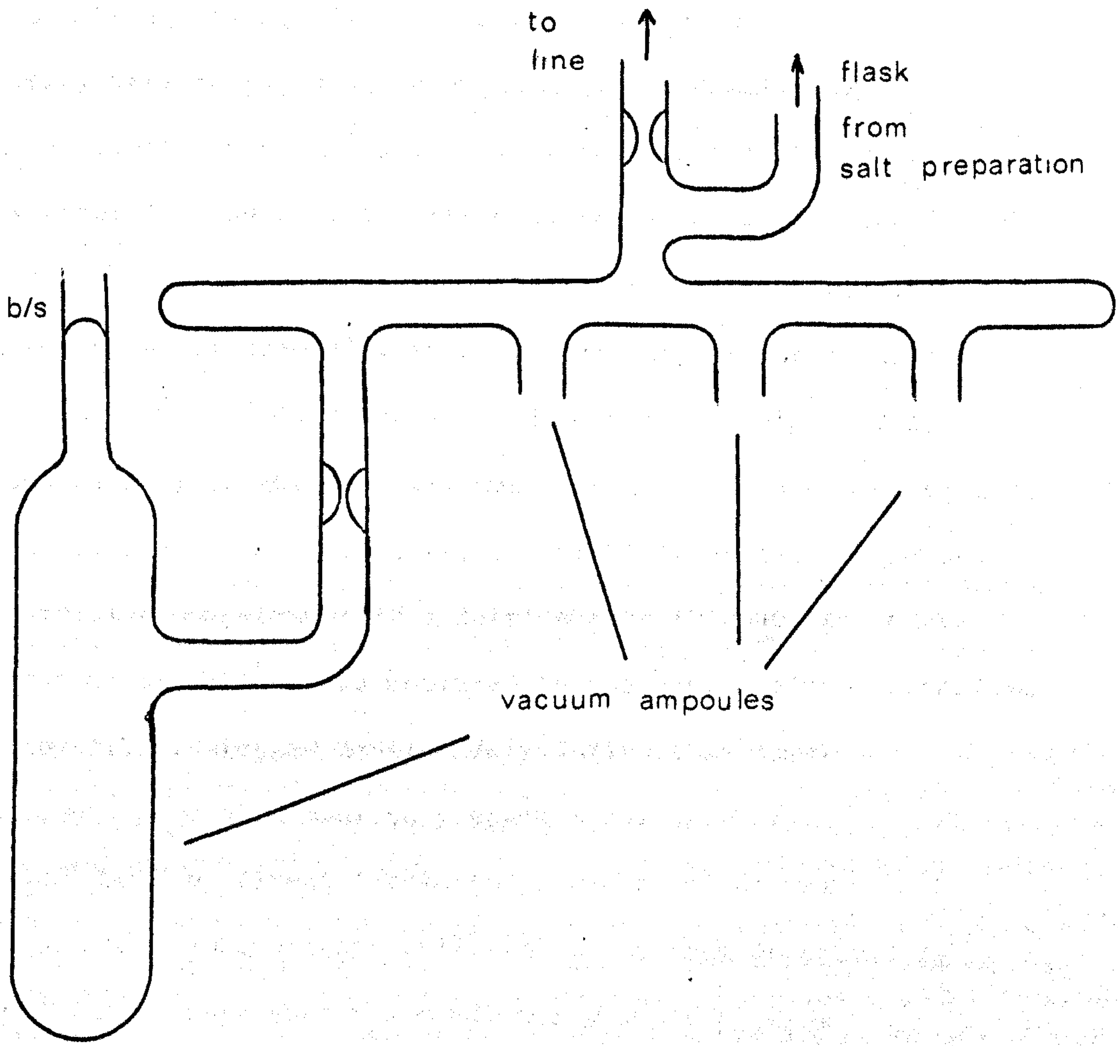

B
A
N_2
C_6H_5COCl
F_3CCO_2H

Fig.1.3.9: "Division device"; for dividing large volumes of salt solutions ready for use with a tipping device.


to line
flask
from salt preparation
b/s
vacuum ampoules

During the course of the work aimed at preparing stable salt solutions in CH_2Cl_2 three attempts were made to prepare salts by direct combination.(Eq.1.3.2)

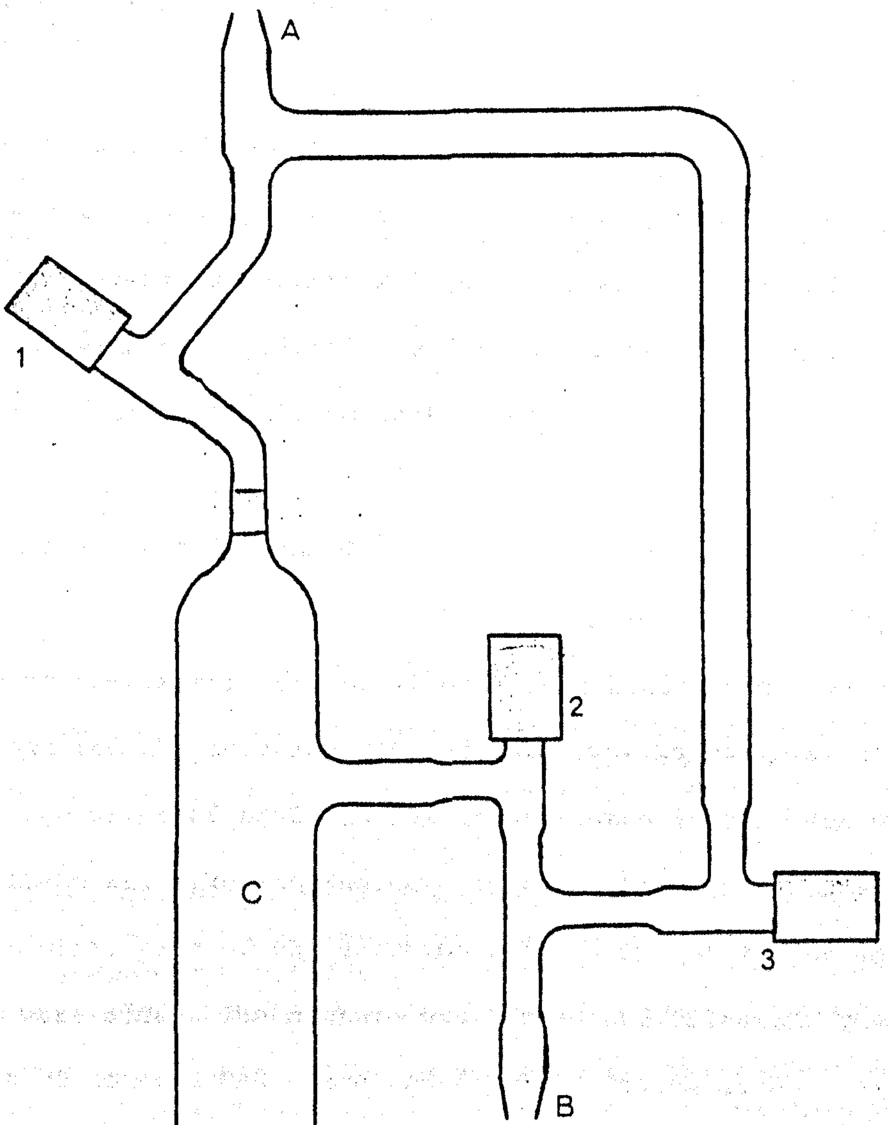
The first attempt was the preparation of $p\text{-}ClC_6H_4CO^+FeCl_4^-$. $FeCl_3$ (0.01 mole) and $p\text{-}ClC_6H_4COCl$ (2% excess) were combined in vacuo in CH_2Cl_2 (20 ml). The resulting solution was initially pale green but became progressively darker. After 1 h the solution was evaporated until only ca. 5.0 ml remained and a green/brown solid was precipitated. The remaining liquid was then filtered off, which removed any excess of chloride, and a fresh volume of CH_2Cl_2 was added to yield a deep emerald green solution. This solution was not stable: it became progressively darker until after two days it was almost black despite being stored in the freezing compartment of a refrigerator ($T = 269$ K) and the concentration of cations, as measured by the U.V. analysis described in Section 1.3.3, dropped considerably during this time.

Attempts were also made to prepare a solution of $p\text{-}ClC_6H_4CO^+NbCl_6^-$ by direct combination. The reaction was carried out in a conductivity cell similar to that described by Grattan[34] in the hope that the conductvity would provide information about the extent of reaction. However, $NbCl_5$ is almost insoluble in CH_2Cl_2 and dissolves very slowly. Thus, after breaking a phial of $NbCl_5$ into CH_2Cl_2 the conductivity increased almost linearly for about 24 h and then became constant before all the added chloride had dissolved. At this stage the acid chloride was added, with the only result that the conductivity decreased slightly and then remained constant for several days. The addition of the acid chloride did not apparently increase the solubility of $NbCl_5$. It was then decided to abandon this experiment.

1.3.2.6: Preparation of $C_6H_5CO^+SbF_6^-$.(Work done in the P.A.N. laboratory in Łodz,Poland.)

The apparatus for the direct combination of C_6H_5COF and SbF_5 is shown in Fig.1.3.10. The procedure was as follows: The apparatus was attached to the vacuum line via joint A and evacuated with taps 2 and 3 closed. An ampoule contaimg SO_2 (See Fig.1.3.4.) was attached to the joint B, tap 1 was closed and tap 3 opened to evacuate the space between tap 3 and the tap on the ampoule. Tap 3 was closed, tap 2 and that on the ampoule were opened and ca. 10 ml of SO_2 was distilled into C by cooling the tube C in liq. N_2. Tap 2 and that on the ampoule were closed and the procedure was repeated twice more. Once to distil 1.2 ml of C_6H_5COF into C and once to distil 0.7 ml of SbF_5 in. The solution was then kept at 240 K for 30 min to allow equilibrium to be attained. About 8.0 ml of the SO_2 was then distilled out of the apparatus via tap 1 into a residue flask and ca. 50 ml of Freon 113 was distilled into C. The salt precipitated immediately as fine white crystals. Tap 1 was closed and the apparatus removed from the vacuum line, turned upside down and reattached at joint B. A 100 ml flask was attached to the apparatus at joint A, evacuated via tap 3, and the Freon 113 pulled into this flask via tap 1 by gentle cooling, so leaving the salt in C. The salt was then washed with two fresh volumes of Freon 113, the procedure being the same as for the first volume. After this the salt was dried in vacuo by continuous pumping for 4 h before being distributed into vacuum phials. (See Chapter 6.) The yield of salt was ca. 80%, referred to C_6H_5COF. No analysis was done on the salt since this had already been done in the Łodz laboratory, but the white crystals in the vacuum phials showed no signs of deteriorating after 6 weeks in the refrigerator.(T = ca. 278 K) It was stated by other workers in Łodz that CH_2Cl_2 can also be used to precipitate and wash the salt.

Fig.1.3.10: Apparatus used in Łodz to prepare $C_6H_5CO^+SbF_6^-$


A
1
2
3
C
B

1.3.3: Analysis of salt solutions.

1.3.3.1: U.V. analysis of salt concentration.

For each batch of phials made by means of the tipping device, one phial was analysed by the method described by Kingston.[44] In addition, for several experiments $(C_6H_5)_3CCl$ was used as well as $(C_6H_5)_3COH$ with no significant difference between the two results for the desired salt concentration.

1.3.3.2: Analysis for Ag^+ and Cl^-.

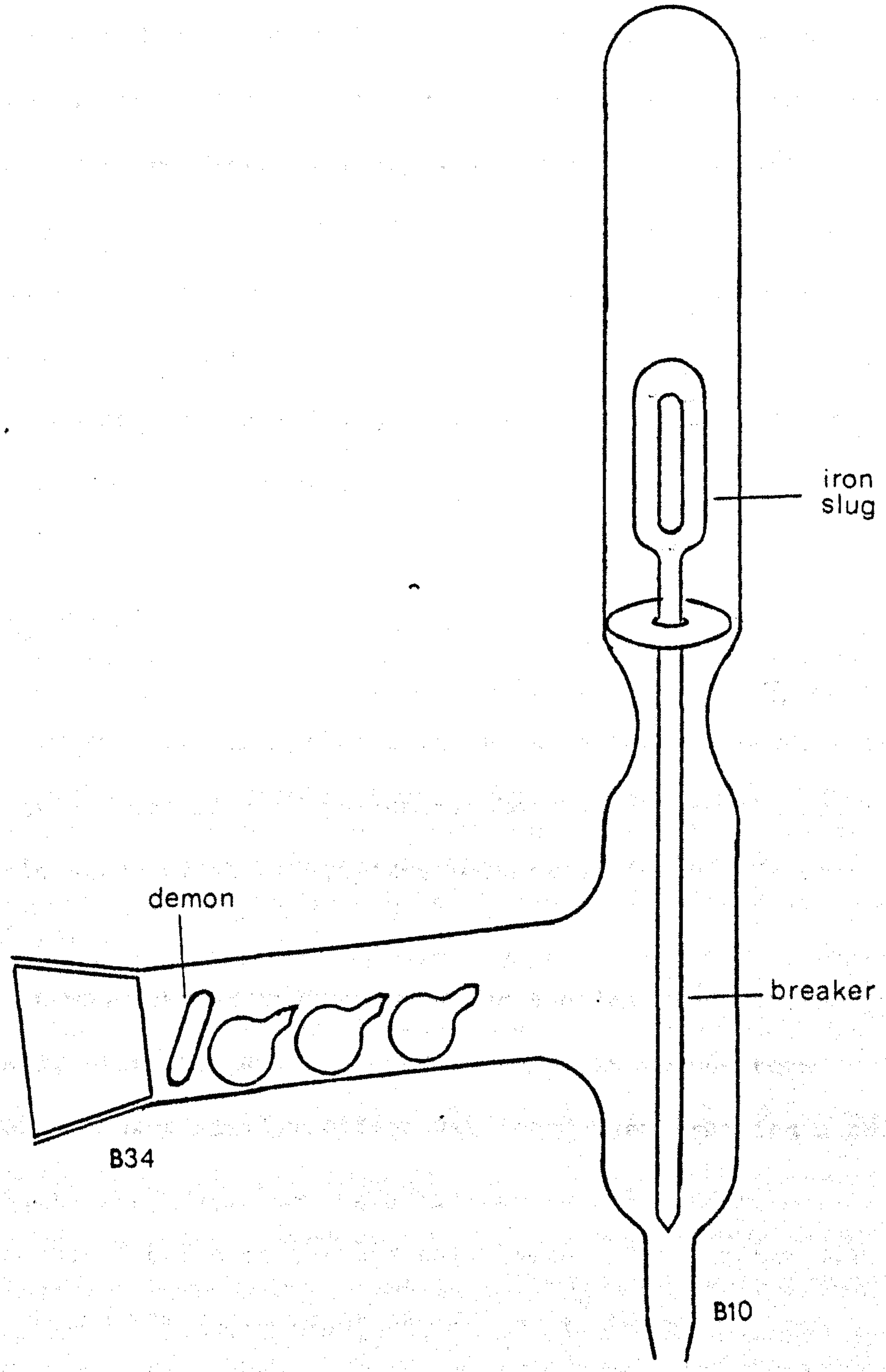
For each preparation one phial of salt solution was broken into a small flask and the solution divided into two. To one part of the solution a few drops of $AgNO_3$ in 95% ethanol were added. Lack of any precipitate was taken to indicate that no chloride was present.

To the other part of the solution a few drops of dilute HNO_3 and C_2H_5OH were added. The mixture was warmed and filtered. Then a few drops of aqueous NaCl were added to the filtrate. No precipitate formation was taken to indicate that no silver was present in the solution. (The results of these tests on the various salts are shown in Table 1.3.3.)

In addition, phials of CH_2Cl_2 solutions of II (prepared by method 1A), VII, VIII and IX were analysed by polarography.[45] For this experiment the phial storing and breaking apparatus shown in Fig.1.3.11 was used.

Only the solution of IX gave a polarographic wave indicative of silver in the solution and only the solution of II gave a wave for the carbocation.($E_{\frac{1}{2}} = +0.39V$ vs the S.C.E.)

Fig.1.3.11: Phial storing and breaking apparatus for use with the vacuum polarography cell.


iron
slug
demon
breaker
B34
B10

1.3.3.3: Analysis by G.L.C..

Lastly, the solutions of the two $C_2H_5CO^+$ salts prepared by the method 1C were analysed by gas chromatography in the following way: A phial of the salt solution was broken into a small flask and a few drops of water were added to the solution. After shaking the mixture it was flitered through a filter paper previously moistened with CH_2Cl_2. The filtrate was evaporated to approximately one tenth its volume and a sample injected into a gas chromatograph. The resulting trace indicated that only CH_2Cl_2 and C_2H_5COOH were present.

1.3.4: Unexplained phenomena.

Before concluding this section it is worth recording two rather strange and unexplained phenomena observed during the course of the kinetic study of acenaphthylene polymerisation by carbocation salt initiators.

It was noticed that on breaking a phial of $C_2H_5CO^+SbF_6^-$ in CH_2Cl_2 into $C_6H_5NO_2$ a slight increase in temperature was observed. A similar effect was noted when breaking a phial of $AgSbF_6$ (in $C_6H_5NO_2$) into $C_6H_5NO_2$. The latter effect was measured twice in the new calorimeter (See Chapter 4.) when the ΔH was found to be ca. 2.1×10^3 kJ mol^{-1} referred to the $AgSbF_6$. (A highly exothermic reaction was also observed by Mathias[50] when $HClO_4$ was added to $C_2H_5NO_2$.)

Since the addition of salt solution to $C_6H_5NO_2$ was always followed by addition of monomer, the solutions, at the end of the polymerisations, were deemed too "difficult" to be analysed with a view to elucidating the origin of the initial exotherm. Thus, no explanation is offered for these phenomena but they must certainly be due to some catalytic effect of the salts.

1.3.5: Conclusion.

From the results of the methods of preparation for carbocation salts described in Section 1.3.2 it should be apparent, and this is the view held by the author, that of all the methods tried the easiest and quickest technique is that developed in Łodz for the preparation of $C_6H_5CO^+SbF_6$. It remains to be seen whether the technique can be applied generally.

In retrospect, it is clear that the presence of silver in the salt solutions is not only undesirable, from the point of view of a clean polymerisation system, but it is probably a contributing factor in the instability of the salt solutions. The direct combination reaction eliminates the possibility of residual silver in the salt solution.

Table 1.4.1.

A Summary of the Polymerisation Tests.

T = 190 K

Salt	Formula	Polymer yield (in % referred to initial weight of isobutylene.)		
		Oligomers	Precipitated Polymer	Total
I	$Ph_3C^+SbF_6^-$	0	0	0
II	$Ph_2HC^+SbF_6^-$	0-5	90	90-95
III	$C_6H_5CO^+SbF_6^-$	10	70	80
V	$p\text{-}ClC_6H_4CO^+SbF_6^-$	20	50	70
VI	$CH_3CH_2CO^+PF_6^-$	30-40	20-30	50-60
VII	$CH_3CH_2CO^+SbF_6^-$	30-40	20-30	50-60

1.4: Polymerisation tests.

Since the initial aim of the work was to study the polymerisation of isobutylene with carbocation salt initiators most of the salts prepared in this work were tested with this reaction.

The apparatus used for such tests is shown in Fig.1.4.1. The procedure was as follows: The phial of salt solution was placed in the side arm of the apparatus, the apparatus was fused to the vacuum line and thoroughly evacuated and flamed for several hours. Isobutylene (1.0 ml) and CH_2Cl_2 (20 ml) were distilled into the apparatus which was then sealed off from the vacuum line. Then, having tipped the initiator phial into the isobutylene solution, the central tube was immersed in a cold bath for ca. 10 min ($T = 190$ K) after which time the initiator phial was broken, the contents mixed with the bulk solution and the tube replaced in the cold bath for a further 10 min. The reaction was stopped by opening the apparatus and pouring the contents into ca. 100 ml of methylated spirits. Any precipitated polymer was then filtered off and the remaining solution was analysed by G.L.C. for low oligomers and residual isobutylene. The solution was then evaporated to recover the low oligomers. A summary of the results obtained is given in Table 1.4.1.

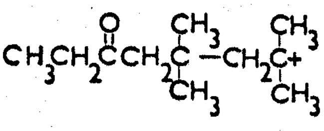
In addition to the information presented in Table 1.4.1 it was noted that salts VI and VII did not produce a rapid polymerisation of isobutylene. For the other four salts, since only I was stable enough to allow a concentration analysis, there was little point in analysing the polymers produced and the only conclusion that can be drawn is that except for I all these salts do polymerise isobutylene.

Since VI and VII could be prepared as stable solutions in

CH_2Cl_2 it seemed worthwhile to try to elucidate why they did not produce a rapid and complete polymerisation of isobutylene.

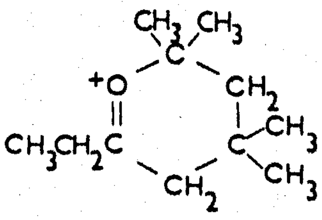
A further test experiment was carried out with each of these salts using 50 ml of salt solution and 1.0 ml (ca. 0.7 g) of isobutylene at 190 K, under vacuum. Both reactions were terminated with methylated spirits and the solution evaporated yielding 0.4 g of a colourless oil. The I.R. analysis of these oils showed no absorption between 1600 and 1800 cm^{-1}, but they did have strong absorption maxima at 1110 cm^{-1}. The inference that the oils contained no carbonyl groups was corroborated by our failure to prepare a 2,4-DNP derivative from them. In addition, G.L.C. suggested that up to 10% of the oils consisted of molecules made up of 3,4 or 5 units of isobutylene. Although an attempt was made to identify these compounds by G.C./Mass Spec. the low resolution of the readily available machine meant that identification was not conclusive. It should be noted that isobutylene and $C_2H_5CO^+$ have molecular weights of 56 and 57 respectively. At this stage it was decided to abandon further analysis of this system but it is interesting to speculate on a possible explanation for the above results.

After addition of two units of isobutylene to $C_2H_5CO^+$, ion X would be produced which could cyclise as shown in Eq.1.4.1 to produce ion XI.



$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2\underset{CH_3}{\overset{CH_3}{C}}-CH_2\underset{CH_3}{\overset{CH_3}{C}}+$

(X)

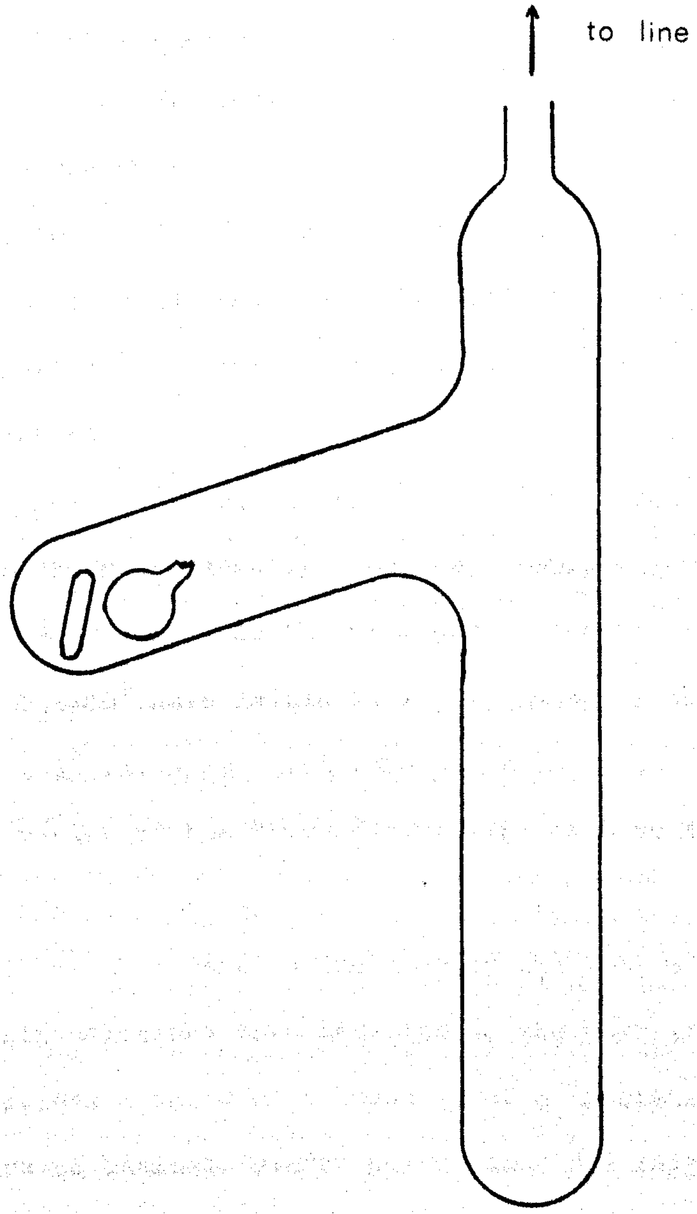


(XI)

Eq.1.4.1

Ion XI is significantly less reactive than X with respect to electrophilic attack on the monomer, and its likely neutralistion products contain no carbonyl group. Several reactions can be envisaged by which ion XI might be neutralised, but without additional evidence that this type of cyclic ion is present in the system, further speculation would be futile.

Fig.1.4.1: Apparatus for polymerisation tests on carbocation salts with isobutylene.


to line

1.5: Summary.

In this chapter a theoretical approach to the understanding of a relationship between molecular structure and the desirable properties of an ideal cationic initiator have been elucidated. Thus, the choice of an initiator for a kinetic study of an olefinic monomer can now be made systematically, provided that the necessary thermodynamic data are available.

In addition, the study of several methods of preparation for stable carbocation salts has been described and it is suggested that the direct combination of an organic halide and a metal halide is the most convenient method.

Our results show that, even if the initiation reaction of the polymerisation is thermodynamically possible, complications may arise during the early stages of the propagation reaction. (For example with the $C_2H_5CO^+$ salt initiation.) In addition, the testing of $(C_6H_5)_2HC^+$ salts as initiators has allowed the practical corroboration of the thermodynamic approach to the initiation reaction.

The difficulties that were encountered by the author in the preparation of salt solutions have thus led to the work in this chapter which provides a basic understanding of a theoretical and practical approach to cationic olefin polymerisations initiated by stable carbocation salts.

1.6: Suggestions for further work.

If the time available had allowed it, the author would have attempted the preparation of $(p\text{-}ClC_6H_4)_3C^+SbF_6^-$ by the direct combination method or by method 1A. This salt should be a useful initiator for a kinetic study of the polymerisation of isobutylene and thus the initial aim of the work could have been achieved.

During the course of the work described in this chapter it became apparent that the whole field of B.I.E. of the organic halide + metal halide systems is very poorly studied and fundamental work on these systems is necessary for a complete understanding of cationic polymerisations involving complex metal halide anions.

In addition, several gaps in the thermodynamic data with reference to these systems have been exposed. Particularly, the terms relating to the addition of a halide ion to a metal halide and a number of ionization potentials for halogen substituted organic halides.

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1.7.1: Equilibrium data for alkyl halide + metal halide systems.

$$RX + MtX_n \overset{K_i}{\rightleftharpoons} R^+MtX^-_{n+1} \overset{K_D}{\rightleftharpoons} R^+ + MtX_{n+1}$$

System	Solvent	K_i/l mol^{-1}	K_D/mol l^{-1}	$\Delta H^\ominus_6$/kJ mol^{-1}	$\Delta S^\ominus_6$/J mol^{-1} K^{-1}
$\phi_3CCl+HgCl_2$	CH_3NO_2	1.5×10^3	1.3×10^{-6}	0.84	-50.1
$\phi_3CCl+HgCl_2$	$C_2H_4Cl_2$	0.43	1.3×10^{-4}		
$\phi_3CF+AsF_5$	CH_2Cl_2		1.9×10^{-4}	-9.2	-105.0
$\phi_3CF+SbF_5$	CH_2Cl_2		2.4×10^{-4}	-9.2	-103.0
$\phi_3CCl+SbCl_5$	CH_2Cl_2		1.85×10^{-4}	-3.4	-83.7
$\phi_3CCl+SbCl_5$	CH_2Cl_2		3.1×10^{-4}	-8.4	-96.0
$CH_3COF+SbF_5$	CH_2Cl_2		1.2×10^{-4}	-2.6	-84.6
$\phi_3CBr+SnBr_4$	C_2H_5Br	8.6	1.6×10^{-4}		
				$\Delta G^\ominus_6$/kJ mol^{-1}	
$(p-Cl\phi)\phi_2CCl+HgCl_2$	CH_3NO_2	4.9×10^2	1.3×10^{-6}	4.2	
$(p-Me\phi)\phi_2CCl+HgCl_2$	CH_3NO_2	2.1×10^4	3.9×10^{-6}	1.7	
$(p-Cl\phi)_3CCl+HgCl_2$	CH_3NO_2	3.0×10^1	8.0×10^{-6}	4.9	

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1.7.2: Equilibrium data for the ionization and dissociation of alkyl halides.

$$RX \xrightarrow{K_i} R^+ + X^- \qquad \Delta H_i^\ominus,\ \Delta S_i^\ominus$$

System	Solvent	T/K	K_i/ mol l^{-1}	$\Delta H_i^\ominus$/ kJ mol^{-1}	$\Delta S_i^\ominus$/ J mol^{-1} K^{-1}	Ref.
$(C_6H_5)_3CCl$	$MeNO_2$	289	4.4×10^{-4}	9.83	-30.5	1
$(C_6H_5)_3CCl$	m-cresol	291	0.56	-12.6	-48.1	2
$(C_6H_5)_3CBr$	m-cresol	291	2.12	-10.4	-28.9	2
$(p\text{-}MeC_6H_4)_3CCl$	$MeNO_2$	289	1.7×10^{-1}	-2.72	-23.9	3
$(p\text{-}MeC_6H_4)_3CCl$	CH_2ClCH_2Cl	293	3.3×10^{-4}			4
$(p\text{-}MeC_6H_4)_2\ CCl$	"	293	2.7×10^{-4}			4
$(p\text{-}MeC_6H_4)\ _2CCl$	"	293	3.3×10^{-5}			4

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1.7.3: Reorganisation energies*. (E_r/ kJ mol^{-1})

Metal/Halide	F	Cl	Br	I
B	202.0	126.7	109.6	
Al		132.2	116.7	78.2

* The earlier data of Eley & Watts[2] have not been included. All the figures are taken from Cotton & Leto.[1]

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1.7.4a: Gas phase halide affinities for metal halides.

		Ref.
$WF_5 + F^- \longrightarrow WF_6^-$	;$A_{X^-} = -447$ kJ mol^{-1}	1
$BF_3 + F^- \longrightarrow BF_4^-$	;$A_{X^-} = -259$ kJ mol^{-1}	4

$$MtX_n + 2X^- \longrightarrow MtX_{n+2}^{2-} \qquad ;{-A_{2X^-}}$$

MtX_n	X	$-A_{2X^-}$/kJ mol^{-1}	Ref.
WCl_4	Cl	176	2
WBr_4	Br	-50	2
$TiCl_4$	Cl	76	3
$SnCl_4$	Cl	192	3
$NbCl_4$	Cl	171	3
$TaCl_4$	Cl	222	3
$MoCl_4$	Cl	163	3

1.7.4b: Electron Affinities of metal halides (E_a/ kJ mol^{-1})

		Ref.
$BF_4(g) + e^-(g) \longrightarrow BF_4^-(g)$	$E_a = -391$	4
$WF_6(g) + e^-(g) \longrightarrow WF_6^-(g)$	$E_a = -502$	5
$WCl_6(g) + 2e^-(g) \longrightarrow WCl_6^{2-}(g)$	$E_{2a} = -498$	2
$WBr_6(g) + 2e^-(g) \longrightarrow WBr_6^{2-}(g)$	$E_{2a} = -456$	2

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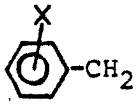
1.7.5: Ionization potentials of some organic radicals./eV

$R^{\cdot}$	$I(R^{\cdot})$	Ref.	$R^{\cdot}$	$I(R^{\cdot})$	Ref.
			ϕ_3C	6.82	5
X=			ϕ_2CH	7.32	2
m-CN	8.58	1	ϕCH_2	7.73	4
m-NO_2	8.56	1	CH_3	9.84	3
p-CN	8.36	1	C_2H_5	8.51	3
m-Cl	7.95	1	$(CH_3)_3C$	6.93	3
p-F	7.78	1	CCl_3	8.78	4
m-F	7.76	1	CF_3	9.95	4
m-CH_3	7.65	1	CH_2Cl	9.32	6
p-CH_3	7.46	1	CH_2F	9.35	4
p-iPr	7.42	1	CH_3CO	10.3	4
p-CH_3O	6.82	1			

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1.7.6: Bond dissociation energies. D(R-X)/ kJ mol^{-1}.

R=/X=	F	Cl	Br	I	H
CH_3	455.8	351.3	296.5	234.2	439.9
C_2H_5	443.3	338.7	284.4	221.6	409.8
$CH_3C=O$	497.7	338.7	280.2	209.1	359.7
CCl_3	426.6	305.3	230.0		401.5
CF_3	543.7	359.7	292.7	225.8	443.3
$C_6H_5C=O$		307.8	238.5[2]		
$C_6H_5CH_2$		284.5	213.4	167.4	347.3[3]
$(C_6H_5)_2CH$		234.3[3]			
$(C_6H_5)_3C$		200.8[3]			
$(CH_3)_3C$		330.4	263.5	196.7[3]	

Micellaneous.

X=	CH_3	C_2H_5	nC_3H_7	$CH_2C_6H_5$
$C_6H_5CH_2$	265.7	240.58	272.0	196.7

$D((C_6H_5)_3C\text{-}C(C_6H_5)_3) = 173.3$[4]

n.b. All data from reference 1 unless specified.

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1.7.7a: Average bond dissociation energies. $\bar{D}(Mt-X)$ / kJ mol^{-1}

Mt/X	F	Cl	Br	I
Sn(IV)		319[1]	266[4]	
Ta(V)	604[5]	429[5]	362[5]	
Al(III)	486[4]	308[4]	255[4]	
B(III)	581[2]	393[2]	309[2]	
P(V)	461[5]	260[5]		
P(III)		326[5]	263[5]	184[5]
Sb(V)		253[4]		
Sb(III)		314.7[4]		
As(III)	464[3]	292[3]	242[3]	180[3]
W(V)		356[4]	328[4]	
W(VI)	507[4]	349[5]	292[5]	
Ti(IV)	588[5]	427[5]	367[5]	
Mo(VI)	448[4]	314[4]		
Hg(II)	304[1]	337[1]	295[1]	250[1]
Fe(III)	390[1]	217[1]	195[1]	144[1]

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5. F.A.Adedeji, K.J.Cavell, J.A.Conner, A.Pilcher, H.A.Skinner & M.H. Zafarani-Moattar, 1978,

1.7.7b: Variation of average bond energy, $\bar{D}$(Mt-Cl)/ kJ mol^{-1} with formal oxidation state of the metal.[1]

d^n	Nb	Ta	Mo	W
n= 0	406	431	314	349
1	439	456	360	376
2	477		385	423

First dissociation energy, $D_1(Cl_{n-1}Mt-Cl)$/ kJ mol^{-1} compared with the mean dissociation energy, $\bar{D}$(Mt-Cl)/ kJ mol^{-1} of MtCl.[1]

Mt	n	$\bar{D}$	D_1	$\Delta = \bar{D} - D_1$
Ti	4	430	343	87
Nb	5	406	272	134
Ta	5	430	322	108
Mo	6	314	113	192
W	6	347	201	146

Reference.

1. J.A.Connor, Topics in Current Chemistry, 1977, <u>71</u>, 71.

1.7.8: Enthalpies of sublimation and vaporization* for various metal halides./ kJ mol^{-1}

Mt / X	F	Cl	Br	I
Sn(IV)			63	
Al(III)	312	60	45	64
B(III)			$30^{*,2}$	
P(V)		69	60	
Sb(V)		$89.3^{*,3}$		
W(V)	31.2^{2}	100^{2}	98.3^{2}	
Ti(IV)	95	52	68	46
Hg(II)	129	83	86	91
Mo(VI)	33			
Fe(III)		146	144	

n.b. All data from reference 1 unless specified.

References.

1. G.H.Aylward & T.J.V.Findlay, S.I.Chemical Data. J.Wiley & Sons Ltd. London, 1974.

2. J.A.N.E.F. Thermochemical Tables. 2nd Ed. NSRDS-NBS 37, 1975.

3. N.B.S. Technical Note., 270-1, 1965.

1.7.9: Data for calculation of crystal radii of ions.

$AlCl_4^-$ from $Li^+AlCl_4^-$: Al-Cl = 213.9 pm

Cl-Al-Cl = 108.6°

G.Mairesse, P.Barbier, J.P.Vignacourt & F.Baert, Cryst.Struct.Chem., 1977, <u>6</u>, 15.

AlF_4^- from $K^+AlF_4^-$: Al-F = 169 pm

F-Al-F = 109°

V.P.Spiridonov, E.V.Erokhin, Russ.J.Inorg.Chem., 1969, <u>14</u>, 332.

AsF_6^- from $SnF^+AsF_6^-$: As-F = 171.5 pm

F-As-F = 90°

L.Golic & I.Leban, Acta. Cryst., 1977, <u>B33</u>, 232.

SbF_6^- from $K^+SbF_6^-$: Sb-F = 184.5 pm

F-Sb-F = 90°

G.J.Kruger, C.W.F.T.Pisterius, A.M.Heyns, Acta.Cryst., 1976, <u>B32</u>, 2916.

BF_4^- from $K^+BF_4^-$: B-F = 138.5 pm

F-B-F = 109°

G.Brunten, Acta.Cryst., 1969, <u>B25</u>, 2161.

BCl_4^- from $NS_2Cl_2^+BCl_4^-$: B-Cl = 185.6 pm

Cl-B-Cl = 109°

O.Glemser, B.Krebs, J.Wegener, E.Kindler, Angew.Chem., 1969, <u>81</u>, 568.

Section 1.7.10: $\Delta H^{\ominus}_{vap}$ of some organic halides. / kJ mol^{-1}

R/X	F	Cl	Br	I
CH_3CO	24.8	30.1[2]	47.9	
C_2H_5	23.0	26.4	28.4	33.0
CH_3	16.7	22.5	24.8	27.9
CCl_3	26.9	32.0		
CF_3	12.6	16.7		
C_6H_5CO		47.9	50.5	

All data from reference 1 unless otherwise stated.

References:

1. *Handbook of Chemistry* and Physics. 56th. Ed. 1975-6.
2. D.R.Stull, E.F.Westrum & G.C.Sinke, The Chemical Thermodynamics of Organic Compounds. J.Wiley & Sons. N.Y. 1969.

1.7.11:

The general equation devised by Abraham et al.[1] is:

$$\Delta G_s^{\ominus} = \Delta G_e^{\ominus} + \Delta G_n^{\ominus}$$

$$= 69.4z^2((1/e_1)-1)((1/a)-(1/b)) + 69.4z^2((1/e_o)-1)(1/b) + \Delta G_n^{\ominus}$$

Where: $e_1 = 2$, a = the ionic crystal radius in nm, and $b = (a+r)$ where: r = solvent radius in nm; z = charge on the ion. The overall $\Delta G_s^{\ominus}$ is in kJ mol^{-1}.

For CH_2Cl_2: $e_o = 8.93$ at 298 K and $r = 0.2375$ nm so that:

$$\Delta G_s^{\ominus} = -34.7((1/a)-(1/b)) - 61.6(1/b) + \Delta G_n^{\ominus}$$

In addition, for ions with $a < 0.3$ nm, $\Delta G_n^{\ominus}$ can be calculated by:

$$\Delta G_n^{\ominus} = -128.4a + 41.68 \quad / \text{ kJ mol}^{-1}.$$

For larger ions a suitable model solute for which $\Delta G_n^{\ominus}$ is known must be used. It should be noted that the equations given above are for the process: ion(1 atm) ⟶ ion(sol, unit mol fraction). For the process: ion(1 atm) ⟶ ion(sol, 1 mol l^{-1}) a correction must be made:

$$\Delta G_s^{\ominus} = \Delta G_e^{\ominus} + \Delta G_n^{\ominus} - 6.65 \quad / \text{ kJ mol}^{-1}$$

Where: the correction factor is $RT\ln(1000V_m)$ where; V_m is the molar volume of the solvent.

---

[1] This is an extract from a private communication from M.Abraham to Prof. P.H.Plesch, 1979.

Chapter 2: A Short Study of the Kinetics of Acenapthylene. Polymerisation by Carbocation Salt Initiators.

2.1: Introduction.

The cationic polymerisation of acenaphthylene has been studied by numerous people both under high vacuum[1] and under nitrogen[2] using a variety of initiators and solvents.[3,4,5,] However, no reliable k_p^+ values have yet been established.

As a continuation of the earlier work of Kingston[6] in this laboratory it was decided to attempt to obtain some more kinetic data for the polymerisation of acenaphthylene in $C_6H_5NO_2$ with stable carbocation salt initiators.

Initial results showed serious descrepancies between this work and the earlier study. The results are therefore presented as they stand and some attempt will then be made to explain the differences between the two sets of results.

In the present work, in addition to dilatometry and spectroscopy, reaction-calorimetry has been used for several kinetic experiments to examine the effect of considerably higher initiator concentrations which produce reaction rates too great to be measured dilatometrically.

Despite the simplifications resulting from the use of a highly polar solvent and carbocation salt initiators, the system remains complicated. However a value for the rate constant of free ion propagation (k_p^+) has been obtained and some explanation of the complexities will be put forward.

2.2: Experimental.

2.2.1: Materials.

Nitrobenzene (Analar B.D.H.), was fractionally crystallised three times by placing five litres in a cold room (273 K) overnight and then decanting off the remaining liquid in the morning. By this procedure the volume was reduced by half. The $C_6H_5NO_2$ was then poured onto freshly baked alumina and degassed on the vacuum line by the conventional freeze-pump-thaw technique. It was then distilled off the alumina into a blackened flask under vacuum. A splash head between the two flasks ensured that no alumina was carried over during the distillation. The $C_6H_5NO_2$ was gravity-fed to the reaction vessel.[6] The final product was almost colourless and had a conductivity of 1.0×10^{-8} S cm^{-1}.

Acenaphthylene (B.D.H.Ltd.), unless specified otherwise in Table 2.2.1, was zone-refined in sealed tubes (water pump vacuum) and then recrystallised from hexane to yield fine, canary yellow, platelets. m.p. 366 K (Lit.[7] 366 K). Recrystallisation is essential since during the zone-refining process some polymerisation occurs even in sealed tubes. After recrystallisation the product was put into the apparatus shown in Fig.2.2.1, the apparatus evacuated and the joint sealed off at E. The acenaphthylene was then sublimed in vacuo from A to B (Fig.2.2.1) until ca. 20% of the original amount remained in A. This was then sealed off at C and 20 ml of $C_6H_5NO_2$ run into B. The apparatus was then sealed off from the vacuum line at D and turned upside down so that the vacuum phials were filled with the solution of acenaphthylene in $C_6H_5NO_2$.

The phials were then sealed off in the usual way[8] and the concentration of the solution in the phials was determined by measuring the U.V. absorption at 465 nm for two phials from each batch. The remaining phials were stored in the dark until use.

Diphenyl methyl chloride (dityl chloride) (Kodak/Eastman) was prepared as described in Section 1.3.1. Solutions of $(C_6H_5)_2HCCl$ in $C_6H_5NO_2$ were made in the apparatus shown in Fig.2.2.2.

Silver Hexafluoroantimonate (Fluorochem Ltd.) was used as supplied. It was dried by continuous pumping in vacuo for 24 h before $C_6H_5NO_2$ solutions were made using the device shown in Fig.2.2.2.

Propionyl hexafluorophosphate was prepared as described (Section 1.3.2.4). It was stored and used as a CH_2Cl_2 solution. Such solutions were colourless and did not form any precipitate even after storage at room temperature, in the dark, for nine months.

Table 2.2.1.

Experimental Details of Kinetic Experiments.

Exp.	Pumping Time /h	Monomer Source	Apparatus	Comments
SPAN4	22	+	‡	
5	16	+	‡	
6	16	+	‡	
8	18	+	‡	
11	18	As supplied: Unopened bottle	‡	
12	4		As used by K.[6]	
9	16	+	‡	
10	17	+	‡	
14	24	As used by K.[6]	‡	No colour
16	16	+	Calorimeter	
17	2	As used by K.[6]	As used by K.[6]	No colour
18	16	+	Calorimeter	
19	18	+	‡	Killed before colour developed.
20	18	+	‡	
22	18	+	‡	

+ Monomer for these experiments was purified as described in the text.

‡ Tap dilatometer (Fig.2.2.3)

N.B. All dilatometer experiments were carried out with the dilatometer in a water bath thermostated to 298 ± 0.1 K.

2.2.2: Methods.

Table 2.2.1 gives details of the experimental methods and the source of monomer for the kinetic experiments. For most of the dilatometric experiments it was found convenient to use a dilatometer containing a tap (Fig.2.2.3). This design circumvents the problems encountered when trying to fill the more usual design of vacuum dilatometer (e.g. ref. 6) with a $C_6H_5NO_2$ solution, and provided that reasonable care is taken when closing the tap, the volume of the dilatometer remains essentially constant for all experiments. The general procedure for the dilatometer experiments was as follows: The monomer and initiator phials were put into the main tube (A,Fig.2.2.3) and the apparatus sealed onto the vacuum line at B. The apparatus was then pumped and flamed out for the required time after which 20 ml of $C_6H_5NO_2$ was run into the apparatus which was then sealed off from the line at B. The whole apparatus was then immersed in a constant temperature bath at 298 +0.2 K, for 30 min. The apparatus was then removed from the bath and the monomer and initiator phials broken as rapidly as possible with the magnetic "demon". Having mixed the resulting solution in A, the tap was opened until the dilatometer filled to the desired level at which stage the tap was closed and the apparatus returned to the constant temperature bath ready for the first cathetometer reading. Generally, the first cathetometer reading was taken after 2 min of the apparatus being removed from the bath.

The calorimeter used for experiments SPAN 16 and 18 is described in Chapter 4 of this thesis.

Most of the experiments were terminated by addition of methanol to the reaction mixture. Experiments SPAN 4 and 5 were killed with 1,1-diphenyl ethene, but this method was abandoned for later experiments since the absorption maximum of the resulting cation is at a shorter wavelength than the solvent cut-off. All polymer solutions were then treated in the following manner: The polymer was precipitated in methylated spirits, filtered, dissolved in toluene, filtered, precipitated in metylated spirits, filtered, washed twice with 20 ml of cold hexane and vacuum dried 24 h. The second hexane washing was examined by G.L.C. for $C_6H_5NO_2$. Less than 0.01% by weight of $C_6H_5NO_2$, referred to the resulting polymer, was present in these second washings. The use of two successive precipitations was initially to remove the AgCl which was present in those reaction mixtures for which $(C_6H_5)_2HC^+SbF_6^-$ had been used as the initiator, since AgCl is slightly soluble in $C_6H_5NO_2$. The method was subsequently used for all experiments since it also ensured more complete removal of $C_6H_5NO_2$ from the polymer.

Molecular Weights were measured in chloroform solution with a Mechrolab 301 vapour pressure osmometer.

Fig.2.2.3: A "tap dilatometer".

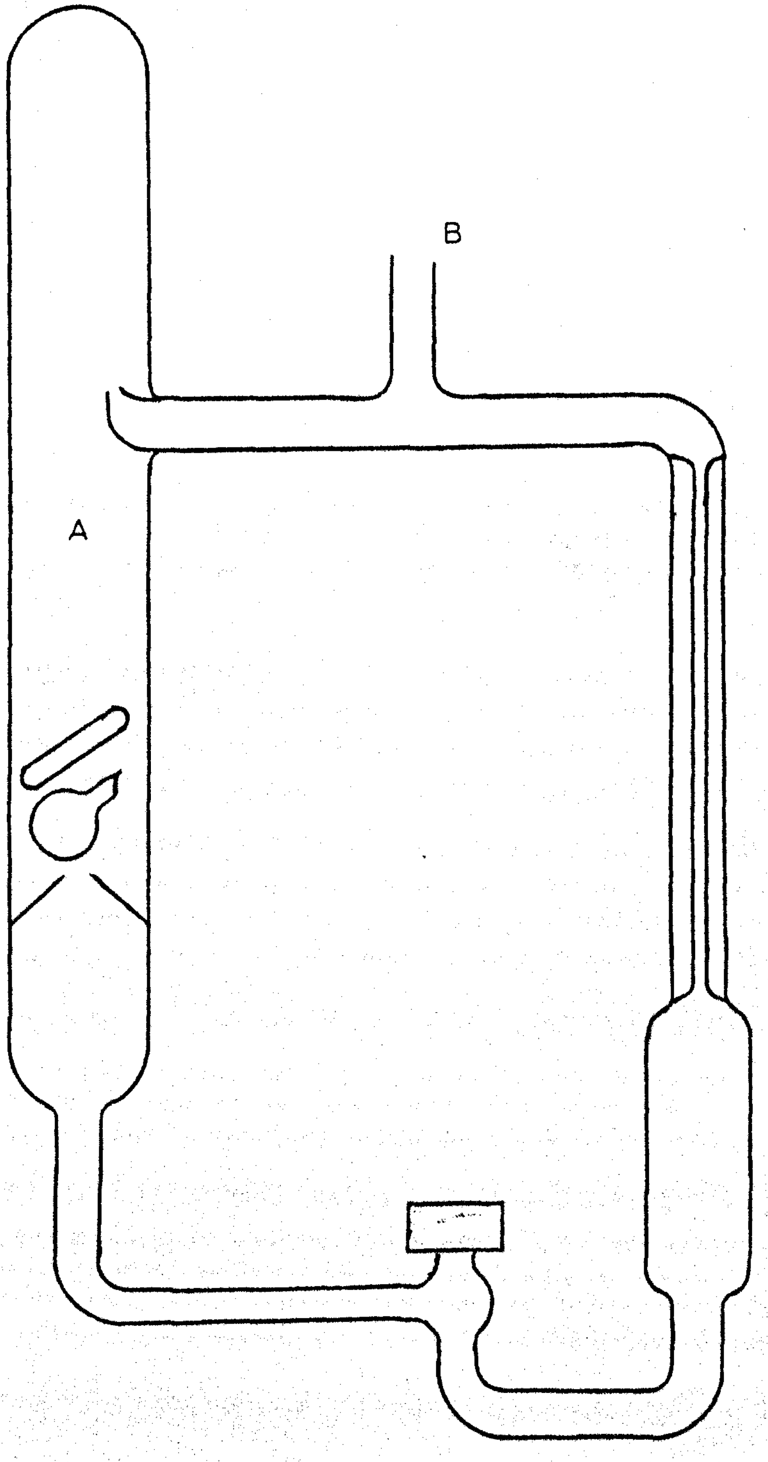
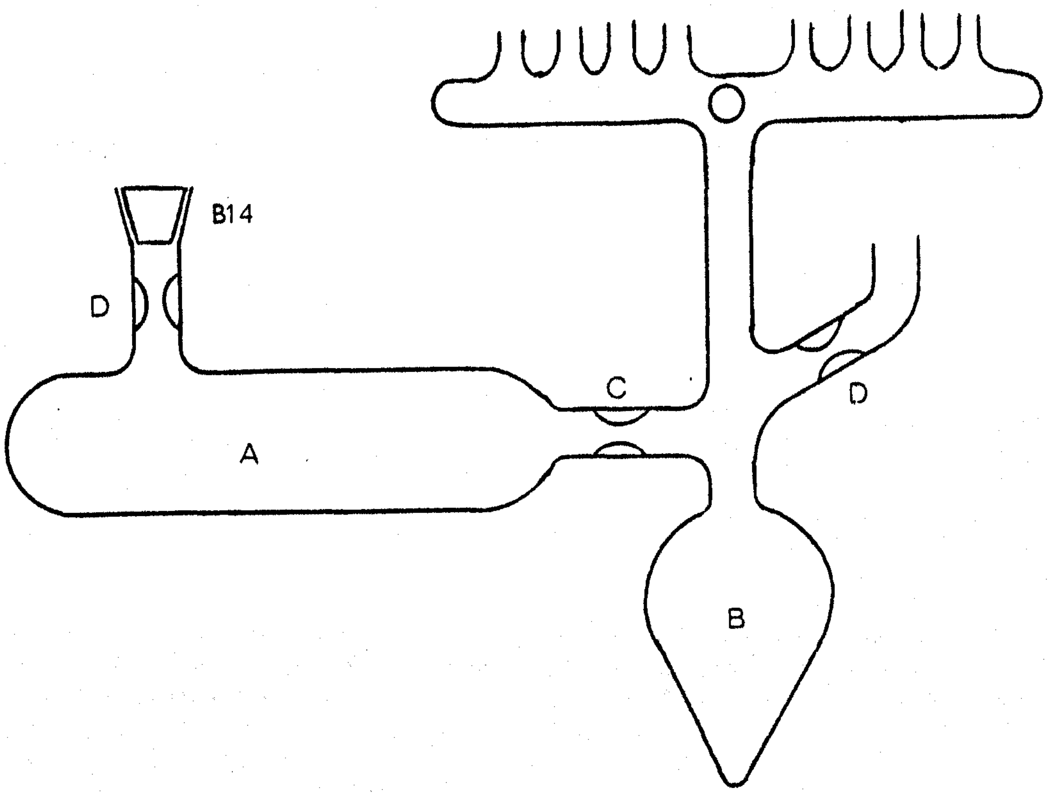

B
A

Fig.2.2.1: Device for vacuum sublimation of acenaphthylene and subsequent preparation of phials of $C_6H_5NO_2$ solutions of the sublimate.

Fig.2.2.2: Tipping device for preparation of dilute solutions from a phial of reagent.


B14
D
C
A
D
B

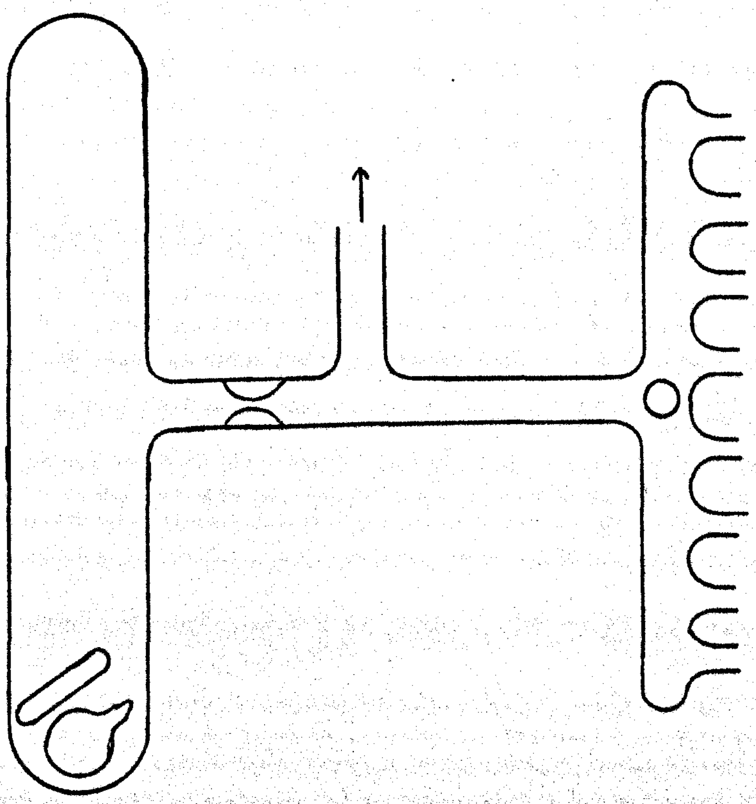


Table 2.3.1.

Summary of Data from Kinetic Experiments.

Exp.	10^4c_o/M	m_o/M	$10^3k_1/s^{-1}$	Yield/%	D.P.
Initiator $C_2H_5CO^+PF_6^-$					
SPAN4	4.5	0.2	10.2	>90%	
5	2.4	0.22	2.8	>90%	6.6
6	2.3	0.37	1.32	>90%	11.2
8	3.9	0.27	3.32	>90%	5.6
11	3.7	0.20	4.65	>90%	6.8
12	2.0	0.23	3.41	70%	
Initiator $(C_6H_5)_2HC^+SbF_6^-$					
9	2.8	0.29	3.33	>90%	
10	5.4	0.22	8.23	>90%	
14	6.6	0.20	4.45	60%	
16	27.2	0.12	61.9	>90%	
17	5.0	0.21	1.41	60%	
18	26.4	0.11	55.7	>90%	
19	3.8	0.37	4.45	60%	
20	2.0	0.39	1.42	60%	
22	2.1	0.14	5.23	80%	

2.3: Results and discussion.

The results of the kinetic experiments are summarised in Table 2.3.1. Fig 2.3.1 shows typical first order plots of the data from SPAN 4 and 5 from which it can be seen that there is a well defined point after which the reaction deviates from first-order behaviour with respect to monomer. This break point occurred simultaneously with the development of a strong colour in the solutions and was also the point after which further data caused the computer programme, used to analyse the data by Moore's method,[10] to enter into a non-terminating loop. For these reasons the results are presented here only in terms of the first ca. 70% of reaction. Attempts to fit the data to zero- and second-order expressions were not successful, neither were efforts to fit the data to two consecutive first-order expressions, since no consistent pattern could be found in the results for the later stages of the reaction. For this reason experiments SPAN 19-22 were terminated before any colour developed in the solution by tipping the contents of the dilatometer into methylated spirits. Yields of polymers from those experiments which were allowed to run to completion (See Table 2.3.1.) were generally greater than 80%, although difficulty in filtering the semi-colloidal solutions means that the gravimetrically determined yields are unreliable. A better measure of the extent of reaction was obtained from the absorption at 465 nm (characteristic of the monomer) in the filtrate from the first polymer isolation. The results are shown in Table 2.3.1.

If, for the polymerisation of acenaphthylene initiated bv carbocation salts, the initiation step is effectively instantaneous compared to propagation, then the rate-determing step is the

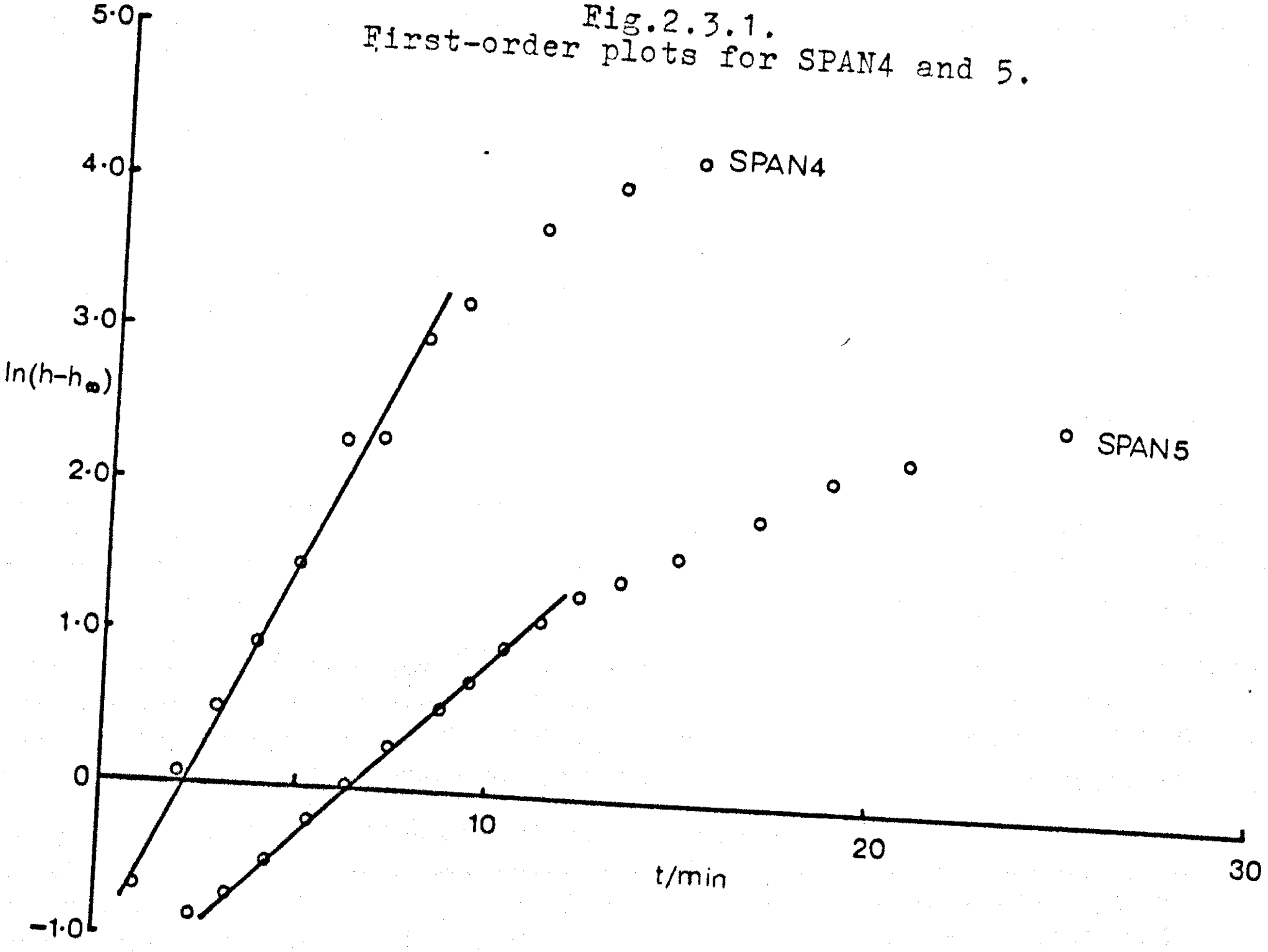


Fig.2.3.1.
First-order plots for SPAN4 and 5.

Fig.2.3.2.
Plot of k_1 vs c_0 for all data shown in Table 2.3.1.

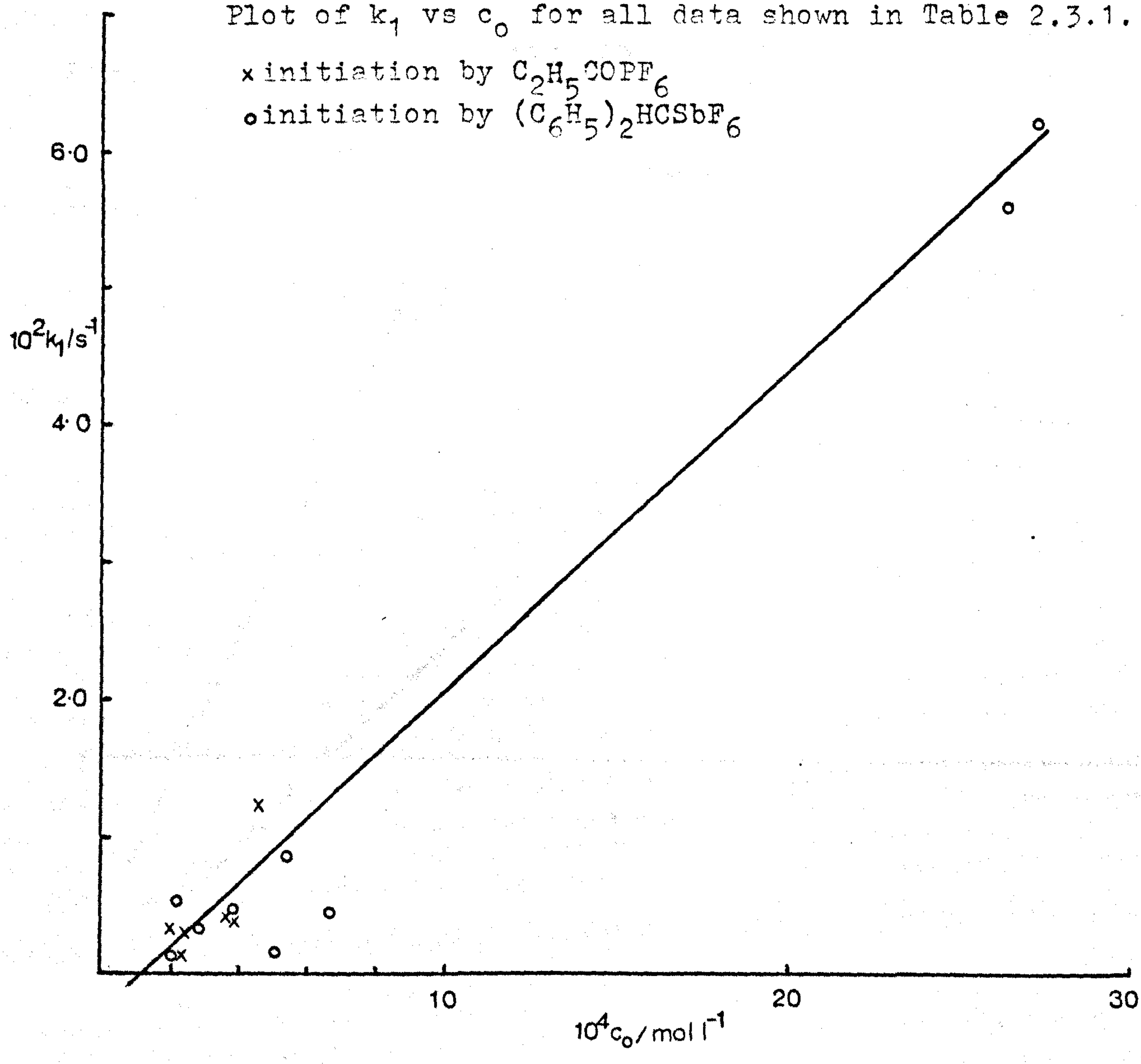
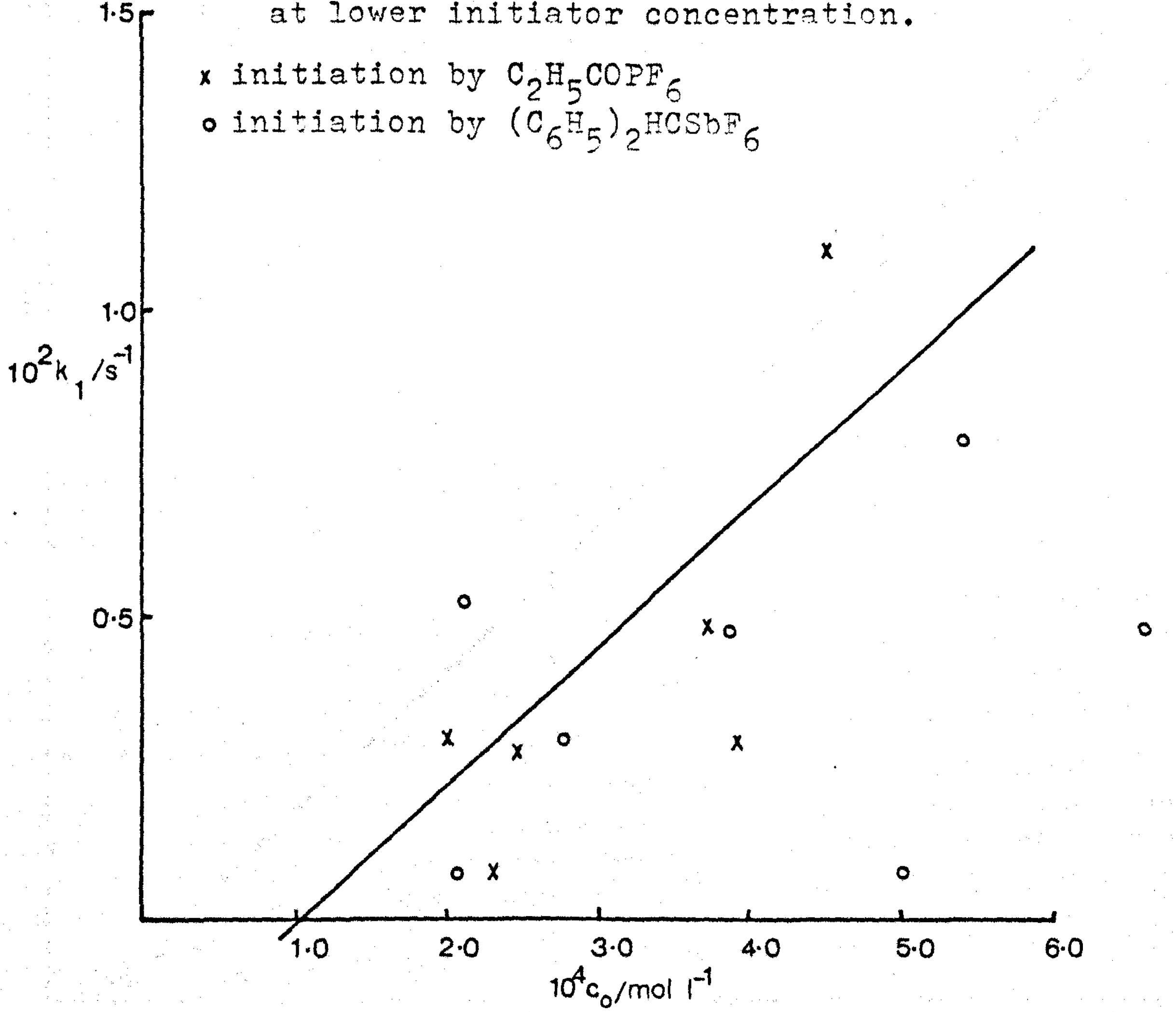


Fig. 2.3.3.
Detail of Fig.2.3.2 showing data
at lower initiator concentration.



bimolecular reaction:

$$P_n^+ + M \longrightarrow P_{n+1}^+ \qquad \text{Eq.2.3.1}$$

and: $$-dm/dt = k_p[P_n^+]m \qquad \text{Eq.2.3.2}$$

where m = [M]

For as long as the concentration of growing ends remains constant, equation 2.3.2 can be reduced to a first-order expression with respect to monomer (Eq.2.3.3):

$$-dm/dt = k_1 m \qquad \text{Eq.2.3.3}$$

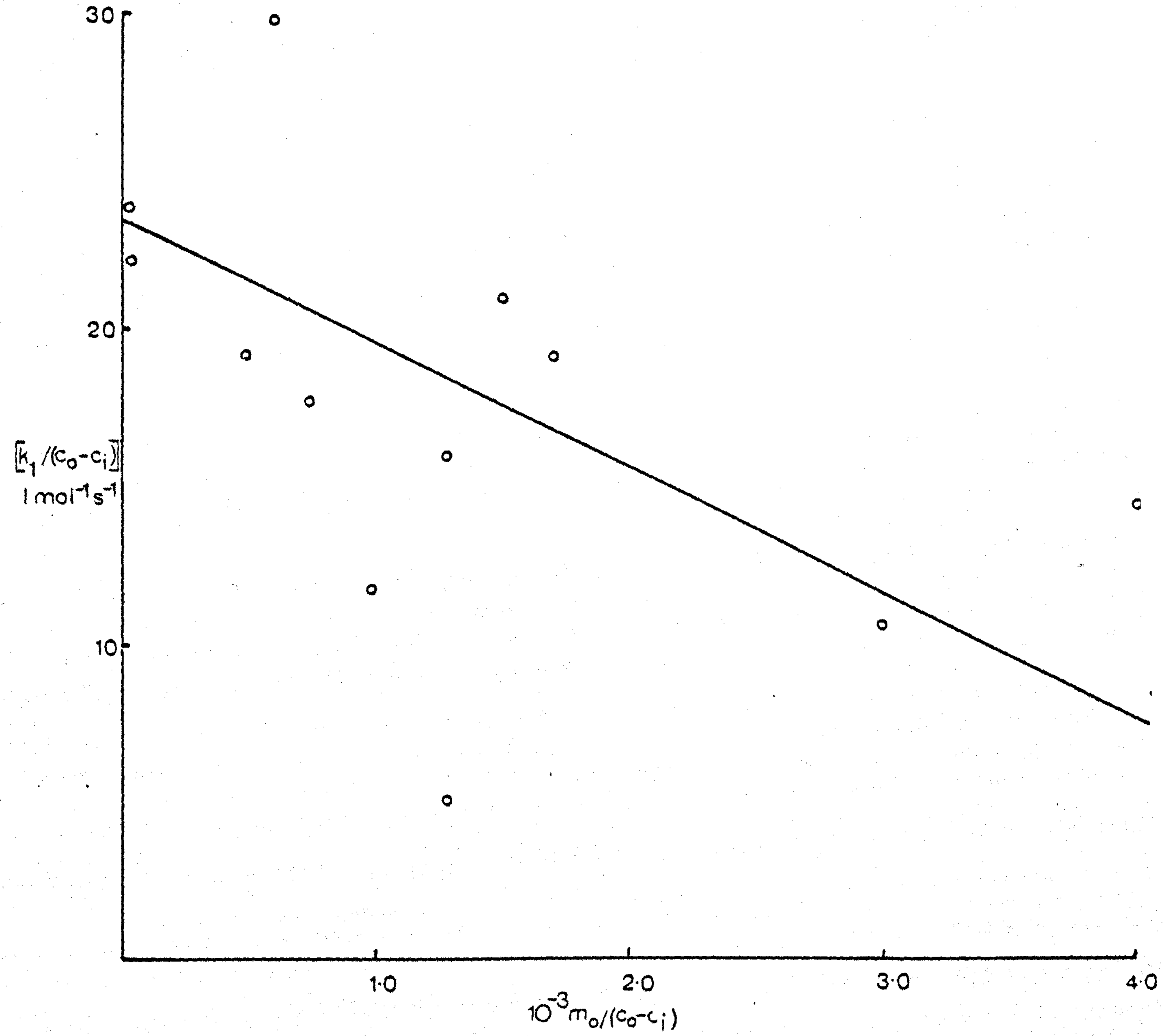
Our experiments conform to such an expression for the first ca.70% of reaction . In addition, if the initiation is quantitative, and there is no termination:

$$[P_n^+] = c_o \qquad \text{Eq.2.3.4}$$

where· c_o is the starting initiator concentration.

From equations 2.3.2, .3 and .4 it can be seen that a plot of k_1 against c_o should yield a straight line with a slope equal to k_p. Such a plot for all the data in Table 2.3.1 is shown in Fig.2.3.2 and a detail of this graph is shown in Fig.2.3.3. It can be seen that except for the data from experiments SPAN 14 and 17, a single straight line fits all the data, regardless of the type of initiator used. Thus, it is reasonable to assume that the k_p value ob+ained from this line is indeed k_p^+: 22.9 $\pm$0.06 l mol^{-1}s^{-1}. It is worth noting also that whether the monomer was rigorously

Fig.2.3.4.
Plot of $k_1/(c_o-c_i)$ against $m_o/(c_o-c_i)$.



purified as described in Section 2.2.1 or whether it came directly from an unopened bottle did not affect the kinetic results significantly. However, the monomer prepared by Kingston[6] did give significantly lower rates of polymerisation.

The intercept of the plot in Fig.2.3.2 gives a measure of the residual impurities in the system, $c_i = 1.26\ (\pm 0.3) \times 10^{-4}$ mol l^{-1}.

Since some of the initiator is effectively neutralised by these residual impurities, the relationship between k_1, k_p^+ and c_o is given more precisely by equation 2.3.5:

$$k_1 = k_p^+(c_o - c_i) \qquad \text{Eq.2.3.5}$$

If there is any residual impurity in the monomer which effectively neutralises the initiator, equation 2.3.5 becomes:

$$k_1 = k_p^+(c_o - c_i - \beta m_o) \qquad \text{Eq.2.3.6}$$

where: m_o is the concentration of the residual impurities in the monomer. Equation 2.3.6 can be rewritten in the more useful form of equation 2.3.7:

$$k_1/(c_o - c_i) = k_p^+ - k_p^+ \beta m_o/(c_o - c_i) \qquad \text{Eq.2.3.7}$$

A plot of $k_1/(c_o-c_i)$ against $m_o/(c_o-c_i)$, using the value of c_i obtained from Fig.2.3.2 and the data from Table 2.2.1 is shown in Fig.2.3.4. (The data from experiments SPAN 14 and 17 have been omitted.) The value of k_p^+ obtained from the intercept of this plot, 23.3(±3.7) l $mol^{-1}s^{-1}$, is in excellent agreement with that obtained from Fig.2.3.2, but the wide scatter in the data makes the exact value of β, $1.8(\pm 0.9) \times 10^{-4}$, less reliable. However, the order of magnitude suggests that in the reaction mixtures the concentration of effective impurities derived from the monomer is ca. 10^{-5} mol l^{-1}; thus, ca. 10% of the initiator is neutralised by an impurity which is not removed by our purification procedure. From equation 2.3.7 and our k_p^+ and c_i values it follows that β for the monomer prepared by Kingston is ca. 1.7×10^{-3}, which is an order of magnitude greater than for our monomer. The data from SPAN 17 are unlikely to give a reasonable result for β by this treatment since c_i almost certainly depends on pumping time[6] which was unusually short for that experiment. Although the evidence from one experiment is inconclusive, it is not unreasonable to suppose that Kingston's monomer was much less pure than ours. This might explain why Kingston's k_p^+ values were much smaller than ours.

For a polymerisation initiated by a carbocation salt in a medium of high polarity only free ion reactions need to be considered and the reaction scheme has therefore been simplified to:[11]

$$P_n^+ + M \xrightarrow{k_p^+} P_{n+1}^+ \qquad \text{Eq.2.3.8}$$

$$P_n^+ + M \xrightarrow{k_{trm}^+} P_n + P_1^+ \qquad \text{Eq.2.3.9}$$

$$P_n^+ + MtX_{n+1}^- \xrightarrow{k_t^+} P_nX + MtX_n \qquad \text{Eq.2.3.10}$$

For free ions the "self-termination" reaction, (Eq.2.3.10) is of second-order with respect to the growing end concentration since, $[P_n^+] = [MtX_{n+1}^-]$.

Therefore, the Mayo equation for this simple scheme is:

$$1/DP = (k_{trm}^+/k_p^+) + (k_t^+[P_n^+]/k_p^+m) \qquad \text{Eq.2.3.11}$$

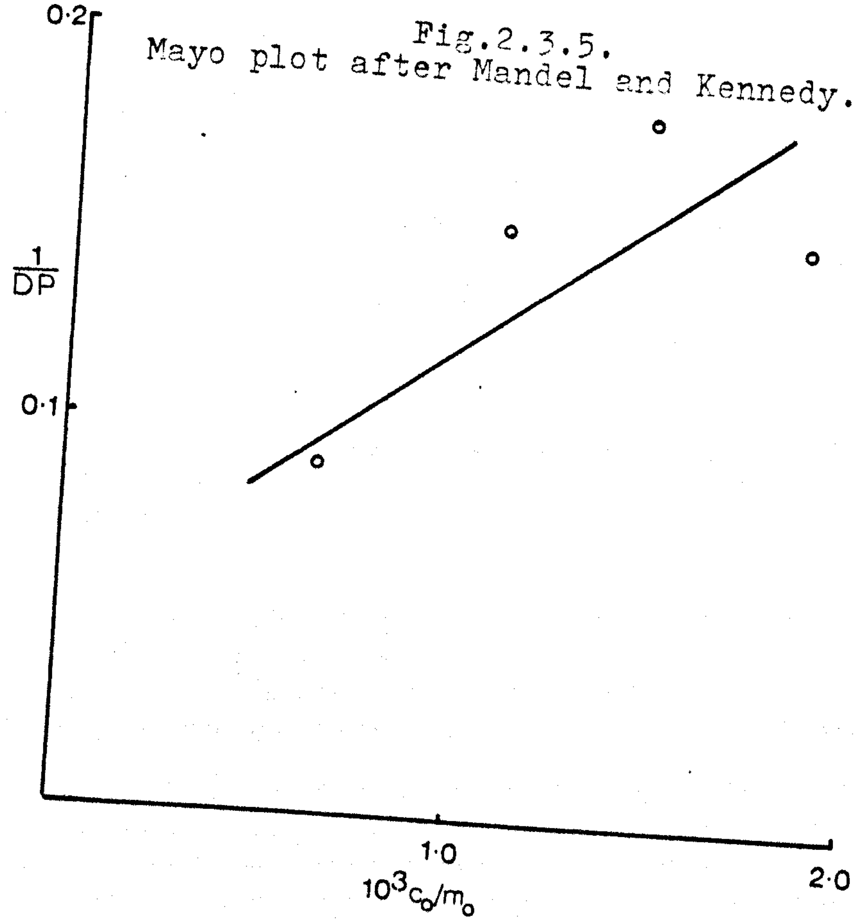
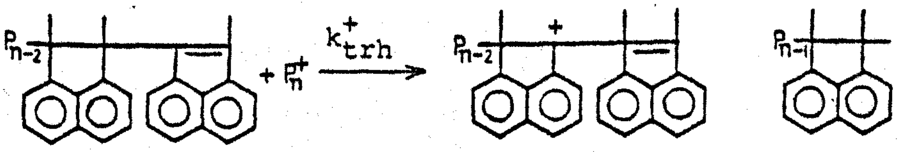


Fig.2.3.5.
Mayo plot after Mandel and Kennedy.

Fig.2.3.5 shows the plot of 1/DP against c_o/m (Since $c_o = [P_n^+]$) which despite the paucity of data, suggests that both transfer to monomer and a termination reaction, such as that in equation 2.3.10, are present. However, the situation is not as simple as this scheme suggests: It is reasonable to assume, by analogy with other cationic olefin polymerisations, (provided that no rearrangement occurs) that a β-proton transfer from a polymeric ion to a monomer molecule produces a polymer chain terminated by a double bond I. For the polymerisation of acenaphthylene this species may then react, by hydride transfer, with another carbenium ion to produce one chain terminated by an alkane moiety III, and one terminated by an allylic ion II .(Eq.2.3.12)



Eq.2.3.12.

(I) (II) (III)

Such allylic ions are unlikely to give rise to further polymerisation since they are significantly more stable than the acenaphthenium ion. (See Chapter 3 and also ref 12 and references therein.)

The presence of such a termination step in the reaction scheme will add a further term to the Mayo equation such that it becomes:

$$1/DP = (k_{trm}^+/k_p^+) + (k_t^+ [P_n^+] + k_{trh}^+[P_n])/k_p^+m \qquad \text{Eq.2.3.13}$$

Since the concentration of dead polymer chains, terminated by a double bond ($[P_n]$) will change during the course of the reaction, equation 2.3.13 is not amenable to simple graphical analysis.

That allylic ions are formed during the polymerisation of

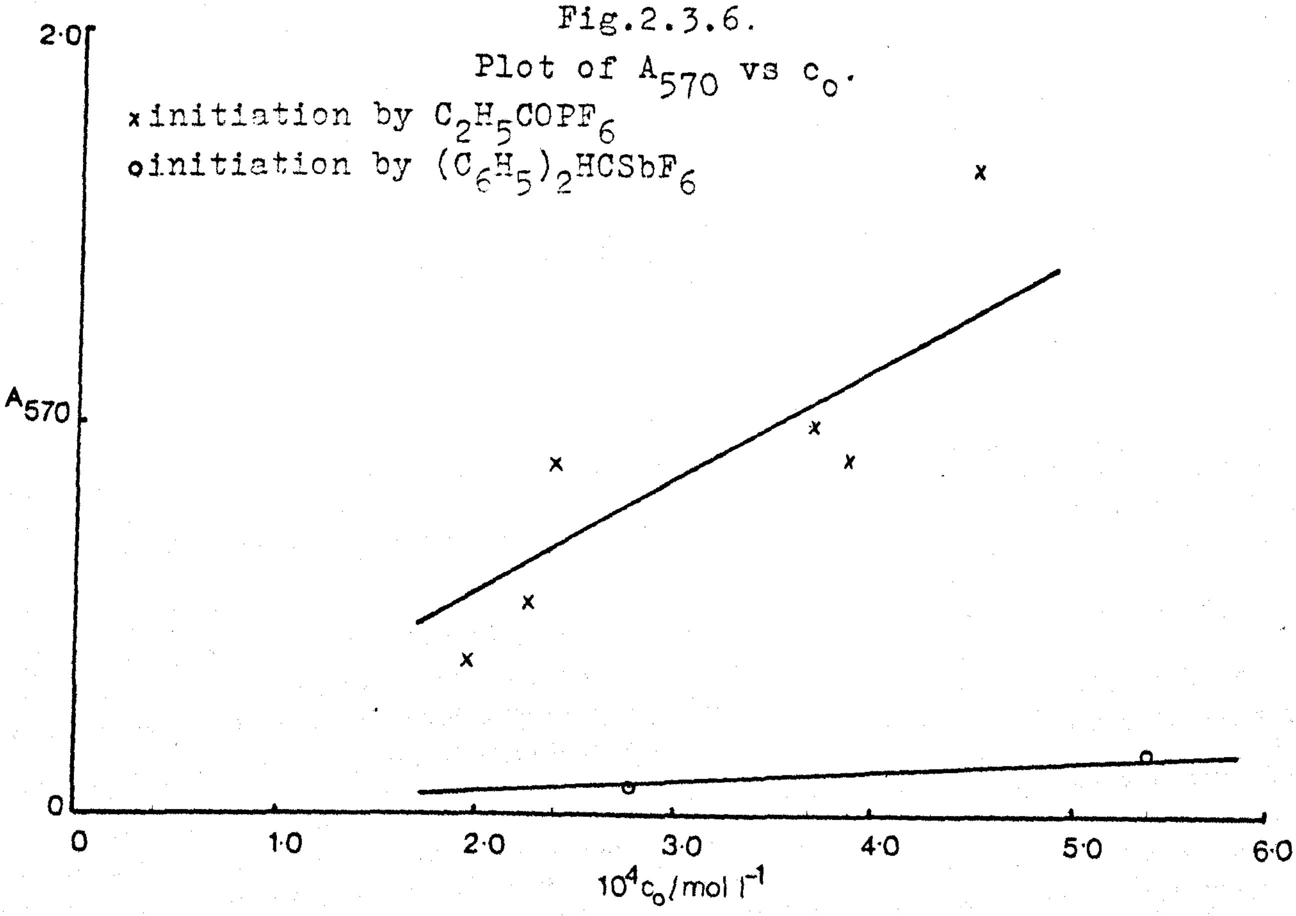


Fig.2.3.6.

Plot of A_{570} vs c_o.

acenaphthylene is corroborated by the oberved absorption maximum at 570 nm and the strong colour development towards the end of the polymerisation. (See Chapter 3) However, despite the absorbance at the maximum being proportional to the starting concentration of initiator, (see Fig.2.3.6.), it also depends on the type of initiator used, which suggests that the reaction is more complicated than the simple scheme presented here.

Infra-red spectra were run on a representative sample of polymers initiated by both $(C_6H_5)_2HC^+$ and $C_2H_5CO^+$ salts, and although the evidence is not very clear, it is possible to infer the presence of a carbonyl end-group for the polymers initiated by $C_2H_5CO^+$ salts. For comparison, Fig.2.3.7 shows the infra red spectra of the polymers initiated by both $(C_6H_5)_2HC^+$ (SPAN 19) and $C_2H_5CO^+$ (SPAN 4) salts and in addition those of Kingston's polymers initiated by both $C_2H_5CO^+$ (SK 135) and NO_2^+ (SK 154) salts. All these spectra were recorded by the present author.

No attempt was made during the course of this study to confirm the nature of the other end group of the polymers by either U.V or NMR methods, since in the short time remaining for this project it was not felt that this area would rapidly provide useful information additional to that already given in the earlier work.[6]

In addition to the possibility that the monomer used by Kingston contained more impurities than that used in this work, there is an alternative explanation of the difference between Kingston's results and ours.

Fig.2.3.8 shows the computer fitted least squares lines obtained from the data of Kingston[6] for different pumping times and also the straight line from Fig.2.3.2 of this work where

Fig.2.3.7: Infra-red spectra for comparison of polyacenaphthylene initiated by $C_2H_5CO^+$ (SPAN4 and SK135), NO_2^+ (SK154) and $(C_6H_5)_2HC^+$ (SPAN19) salts.

Note: 1720 cm^{-1} band can be assigned to -CO group and the bands at 1450,1585 and 1660 can be assigned to $-NO_2$ group.

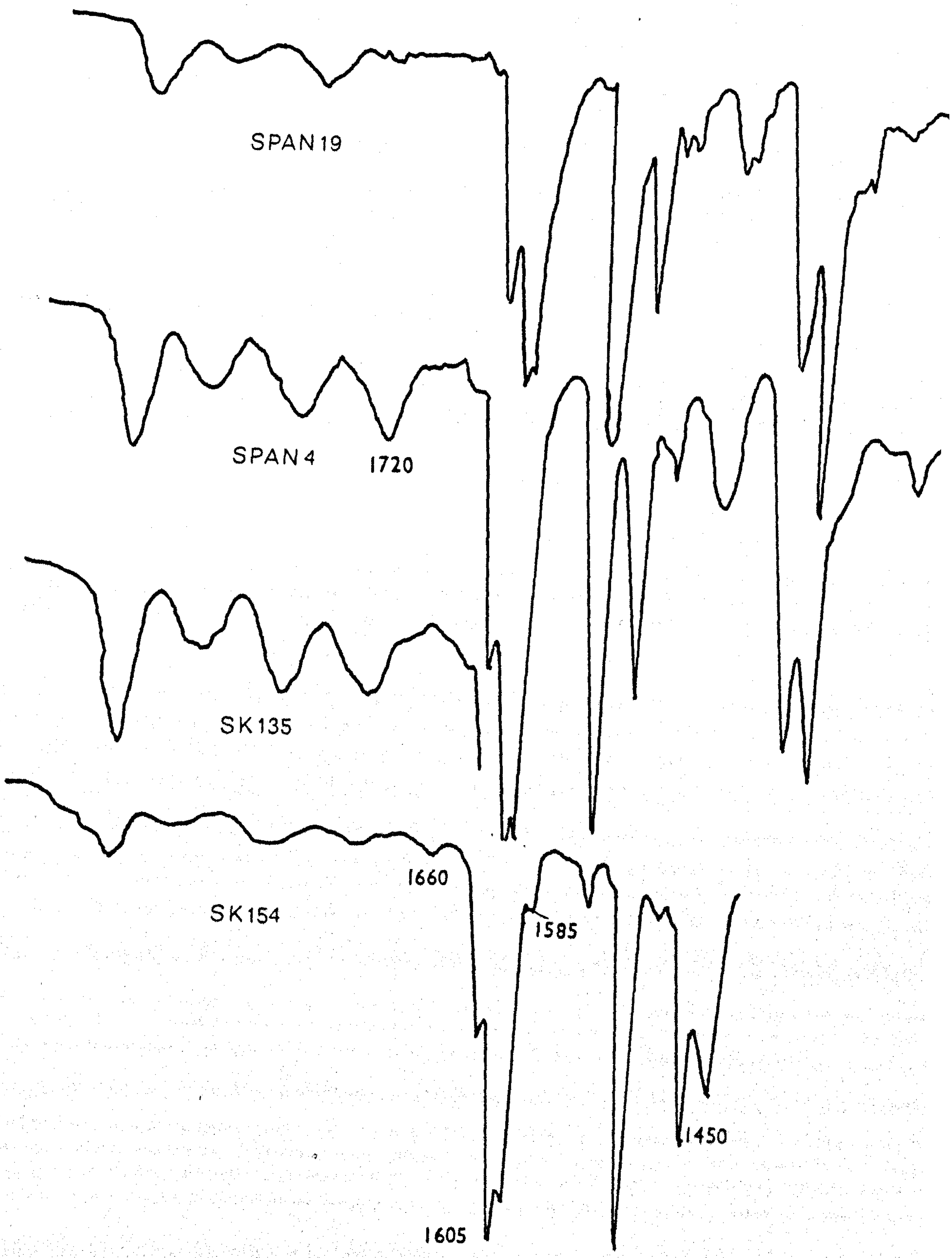
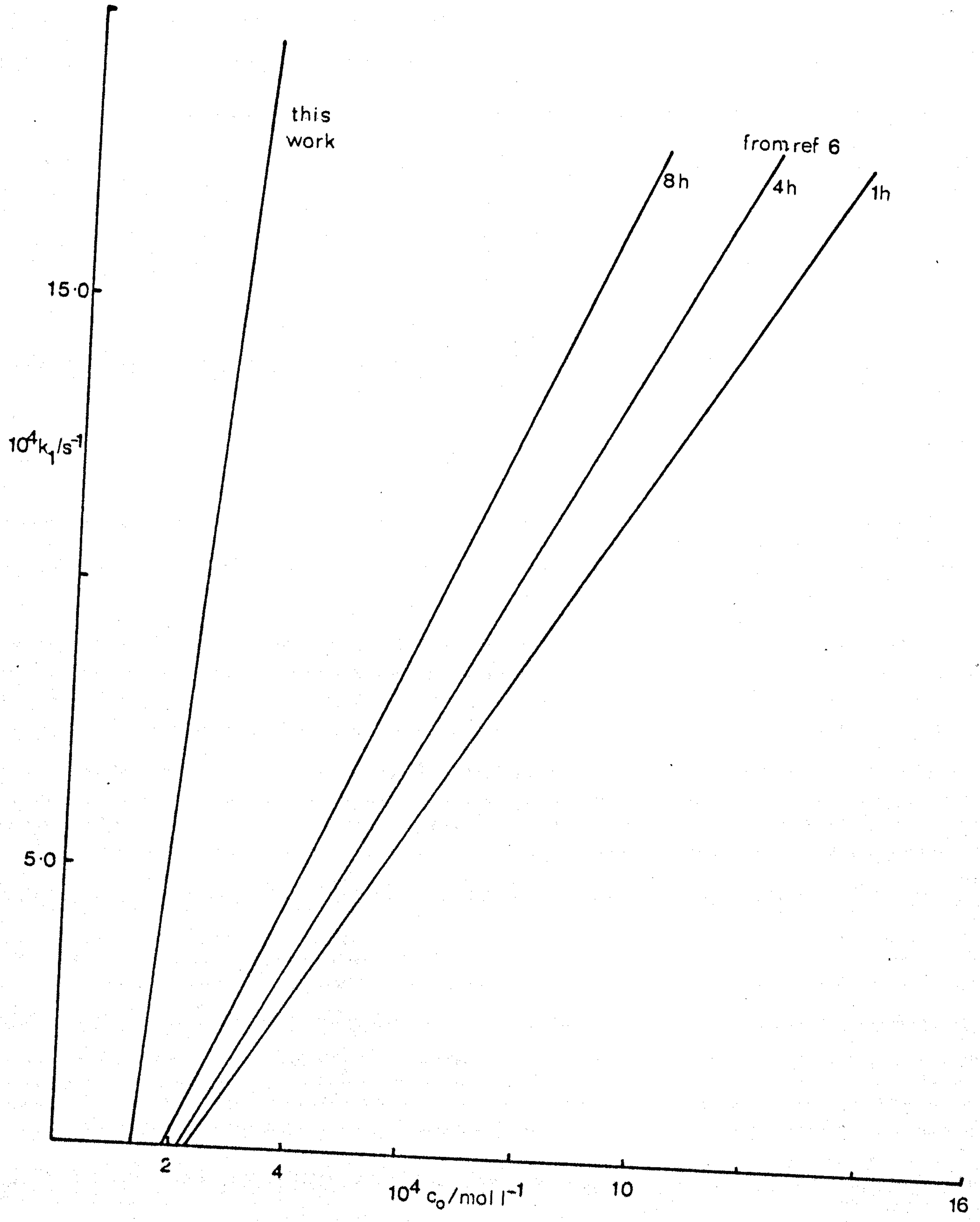

SPAN 19
SPAN 4
1720
SK 135
SK 154
1660
1585
1450
1605

Fig.2.3.8.
Summary of data from this work and ref.6 for comparison.



pumping time was generally greater than 16 h. It can be seen that increasing the length of the pumping time not only decreases c_i but also increases the slope of the line, which implies that k_p^+ increases with pumping time. A possible explanation of this effect can be drawn from the recent evidence obtained by polarography[13]. It has been shown that oxygen complexes with some carbocations in CH_2Cl_2 and that the resulting ions have a less negative $E_{\frac{1}{2}}$ than the uncomplexed carbocations. From this it may be inferred that the k_p^+ of the carbocation + oxygen complex will be smaller than that of the uncomplexed ion. Thus, as the concentration of oxygen is reduced by longer pumping the proportion of carbocations which are complexed with oxygen will decrease and the observed rate-constant will increase.

2.4: Conclusion.

Although the work did not achieve the initial aim of corroborating Kingston's results, it has been successful in that a value of $k_p^+ = 22.9 \pm 0.1$ l $mol^{-1}s^{-1}$, T = 298 K has been established for the polymerisation of acenaphthylene in $C_6H_5NO_2$. The work has also presented some possible answers to the enigma of the colour development in the polymerising mixtures and the deviation from first-order behaviour shown by this reaction. The work has also offered some tentative explanations for the differences between the results presented here and those of Kingston[6]. Most important is the evidence that the rate of propagation is independent of both the anion and the cation of the salt initiator which confirms the basic tenet that in $C_6H_5NO_2$ solution the polymerisation is propagated by a free cation, at least for the first 70% of reaction

2.5: Suggestions for further work.

The first problem which has to be answered for this system is what is the impurity in the monomer that neutralises the initiator, and how can it be removed.

It is clear too, that there remain several problems with regard to the nature of the termination reactions which need to be explored further. Indeed, the U.V. work presented in Chapter 3 might prove a starting point for such work.

Another interesting approach might be to examine more precisely the effect of oxygen on the kinetics of the system.

Finally, once these three problems had been examined, a full kinetic analysis with a range of carbocation salt initiators would be appropriate.

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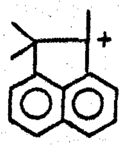
Chapter 3:The Ultra Violet Spectrum Of The Acenaphthenium Ion.

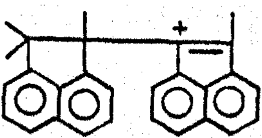
3.1.1: Introduction.

During the short study of the cationic polymerisation of acenaphthylene in nitrobenzene it was noticed that the development of intense colour was not coincidental with initiation of the polymerisation. Indeed Kingston[1] observed no colour development when the polymerisation was initiated by $CH_3CH_2CO^+SbF_6$. In view of the kinetic evidence in Chapter 2 these observations suggest that either the growing acenaphthenium ion is not coloured or that for the major part of the polymerisation the propagation was due to some species other than the acenaphthenium ion.

Gandini and Plesch[2] suggested that the spectrum of the acenaphthenium ion (I) has a maximum at 640 nm. Young[3] disputed this and assigned the absorption at 570 nm to ion (I) and that at 640 nm to ion (II).



(I)



(II)

The aim of the work described in this chapter was to find out whether any of the absorption maxima from 555 nm to 650 nm are due to ion (I) and to show definitely where the absorption maximum of ion (I) is. The methods adopted were developed from those of Bertoli.[4]

3.2: Experimental.

3.2.1: Materials.

Acenaphthylene (B.D.H.Ltd.) was purified as described in Chapter two.

Sulphuric Acid (Analar,B.D.H.Ltd.) was used as supplied, as were glacial acetic acid (M.& B.Ltd.), chlorosulphonic acid (B.D.H.Ltd.) and trifluoromethane sulphonic acid (3M Co.Ltd.).

Dichloromethane was purified as already described in Chapter one.

Nitromethane (B.D.H.Ltd.) was distilled under reduced pressure and stored over calcium sulphate.

Acetoxyacenaphthene was prepared as described by Flowers,[5] the only modification to the method being that the product was purified by column chromatography using alumina (Activity 4) with toluene as the eluent. Yield: 60%, b.p.439K/5mm Hg. (Lit.[6]:439-441K/5mm Hg.) The structure was confirmed by ^{13}C and ^{1}H NMR.

Acenaphthenol was prepared from acetoxyacenaphthene by the method described by Cason.[6] Toluene was used instead of benzene. Yield: 76%, m.p.416-7K.(Lit.[6]:417-8K)

1-Bromoacenaphthene was prepared as described by Julia and Baillarge.[7] It should be noted that this material decomposes very rapidly and for use in the following experiments it was prepared immediately before use. No attempt was made to confirm the structure.

All other reagents were used as supplied and were of standard laboratory grade.

Fig.3.2.1: Spectrum of acenaphthylene in H_2SO_4.

Solid line = ca. 5 min after mixing.

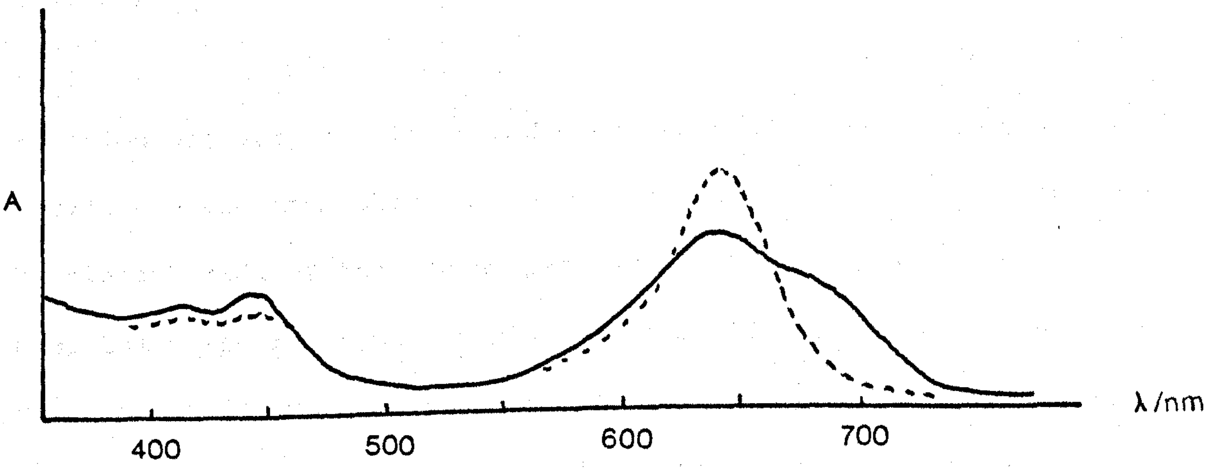
Dotted line = 24h after mixing.

Fig.3.2.2: Spectrum of acenaphthylene and $HClO_4$ in CH_2Cl_2

Fig.3.2.3: Spectrum of acenaphthylene in $ClSO_3H$.

Solid line = ca. 5 min after mixing.

Dotted line = 24 h after mixing.


A
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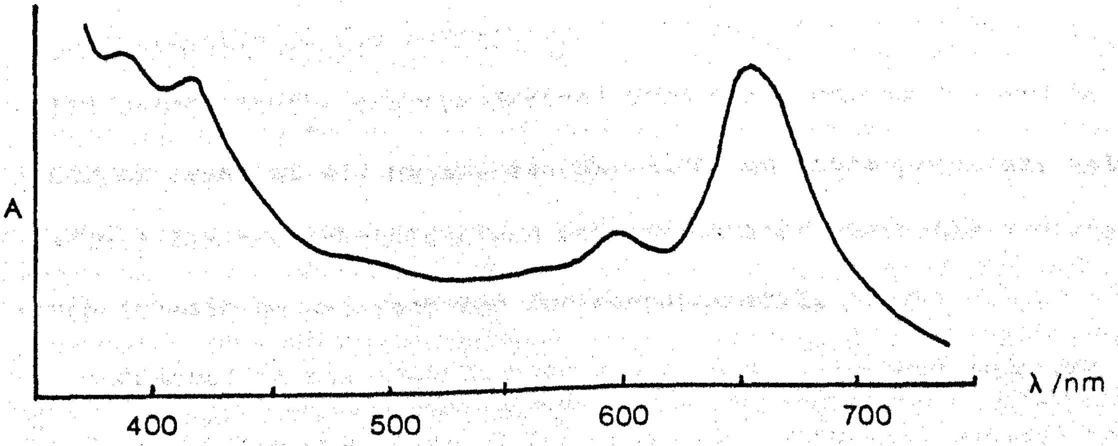
λ/nm


A
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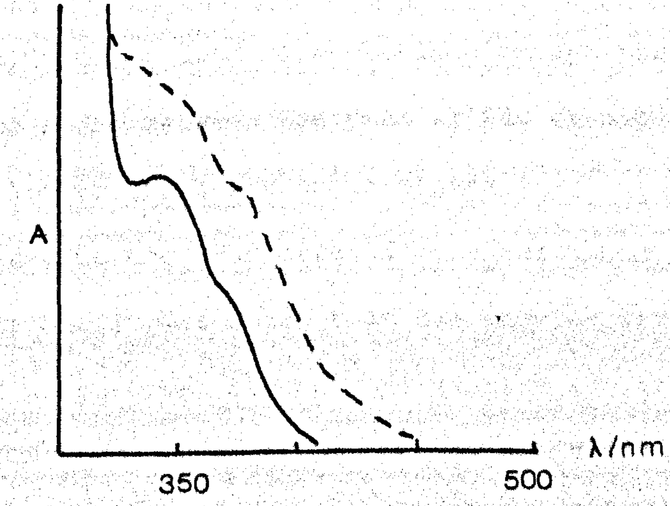
700
λ/nm


A
350
500
λ/nm

3.2.2: Methods and Results.

Fig.3.2.1 shows the spectra obtained from a solution prepared by adding, slowly, a 10^{-4}M solution of acenaphthylene in glacial acetic acid via a fine capilliary to ice cold, vigorously stirred, sulphuric acid. The mixture initially appeared blue but before addition was complete it turned deep, emerald, green. In order to obtain the spectrum showing the well developed shoulder on the long wavelength side of the 640 nm peak it was found to be important to keep the temperature of the mixture below 273 K. It can be seen that the peak at 640 nm also has a shoulder on the short wavelength side which dis-appears with time. Initially the absorbance at 640 nm was ca. 0.7 but after 24 h. this had increased to ca. 1.2. (Concentration of acenaphthylene in solution: ca. 1×10^{-5}M, cell length 1.0 cm.) Similar spectra were obtained by substituting acetoxyacenaphthene and acenaphthenol for acenaphthylene in the above procedure. The differences in the spectra derived from these compounds were in the pair of peaks at 412 nm and 438 nm. Although these peaks are well defined for acenaphthylene and acetoxyacenaphthene, only a plateau from 400-450 nm was recorded for acenaphthenol.

Changes in the spectra over a period of time were recorded when using all three compounds. The spectra were then extrapolated to zero time. No extra, useful, data were obtained except that no isosbestic point was found between the peak at 640 nm and the longer or the shorter wavelength shoulders to this peak.

Addition of water to the concentrated acid solutions caused a rapid loss of colour but it was noted that the shorter wavelength shoulder to the 640 nm peak was the most persistent and if 60% H_2SO_4 rather than concentrated acid was used at the mixing stage two clear peaks were seen: one at 640 nm and a stronger peak at 575 nm. However, neither of these peaks had an absorption greater than 0.1 but the peaks at 412 and 438 nm were just as well developed in this solution as they were in the concentrated acid solution.

In order to determine the nature of the species giving rise to the spectra preparative scale (0.1 g) recovery experiments were attempted: 0.1 g of the test material was dissolved in 2.0 ml glacial acetic acid.This solution was then added via a capillary into 5.0 ml H_2SO_4 at 272 K while the mixture was vigorously stirred. When the addition was complete the mixture was added slowly and with vigorous stirring to saturated aqueous NaOH The resulting aqueous solution was then extracted with CH_2Cl_2 and evaporated.

With acenaphthylene the CH_2Cl_2 extractions yielded no involatile material and the aqueous layer retained a brown fluorescence. Despite attempts to modify the procedure by extracting a CH_2Cl_2 solution of acenaphthylene into H_2SO_4 and then neutralising with methanolic NaOH at lower temperatures, only water soluble products, possibly ring substituted sulphuric acid derivatives of acenaphthylene, could be obtained.

From acetoxyacenaphthene the above procedure yielded 0.03 g of a viscous yellow oil, the T.L.C. and NMR of which indicated that it contained at least three compounds: acenaphthylene (40-50%), acenaphthenol (20-30%) and 20-30% of an unknown compound which was strongly fluorescent and had an R_f value which was lower than that of the other two compounds. This could be biacene. 0.5 g of polymeric material was also recovered.

Fig.3.2.2 shows the spectrum obtained from a solution prepared by adding 50 ml of a CH_2Cl_2 solution of acenaphthylene (0.01 M) to 100 ml of a CH_2Cl_2 solution of $HClO_4$, (0.01 M) in the manner already described. No blue colour was observed at any stage; the mixture appearing green after the first drop of the acenaphthylene solution had been added. It should be noted that the A_{662} when compared with that produced in H_2SO_4 at much lower concentration is very small and also that the peaks from 400 - 450 nm are relatively well developed. Neutralisation of this solution with methanol led to an immediate loss of colour and the formation of white precipitate which was shown to be polymeric by T.L.C. and NMR. The yield of this material was 85% referred to the initial amount of acenaphthylene.

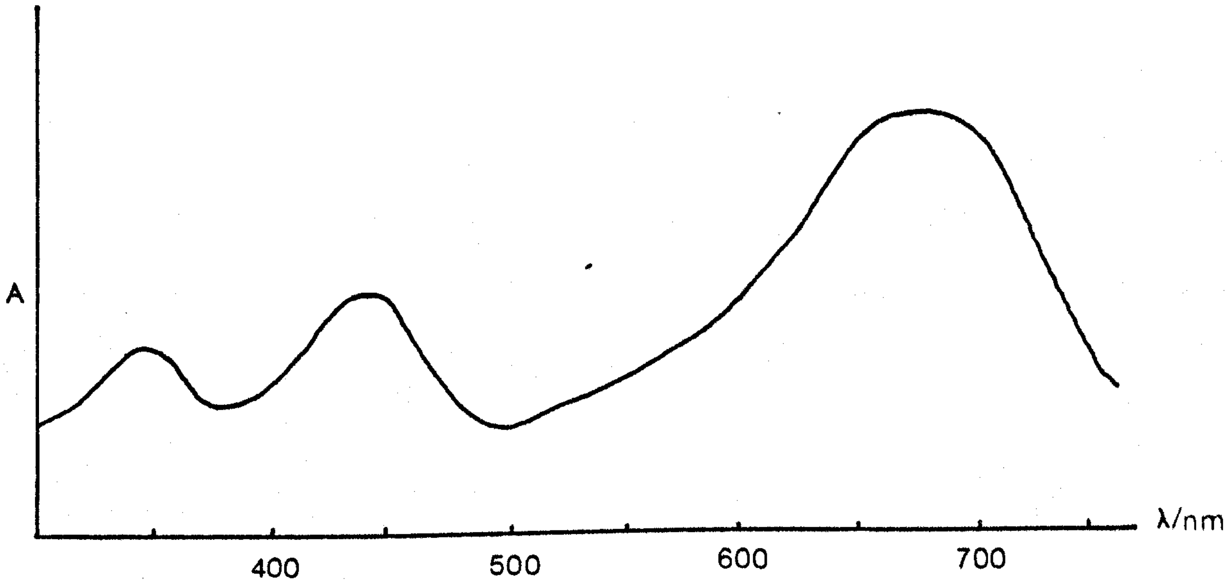
Fig.3.2.3 shows the spectrum obtained from a solution prepared by adding a 10^{-3}M solution of acenaphthylene in glacial acetic acid in the usual way to H_2SO_4. No colour was observed even after two days. A larger scale, preparative experiment involving an extraction from CCl_4 into H_2SO_4 produced a deep green colour in the acid layer. Neutralisation of the resulting mixture with both aqueous and methanolic NaOH proved very dangerous and it was extremely difficult to keep the mixture at low temperature. Finally the neutralisation was achieved by first diluting the mixture with glacial acetic acid four fold. However only polymeric material was isolated. Repeating the experiment with acetoxyacenaphthene gave similar results.

Fig.3.2.4 shows the spectrum obtained from a solution prepared, in the manner described, from acetoxyacenaphthene (10^{-3}M) and trifluoromethane sulphonic acid. The solution remained blue-green for several hours. A preparative scale experiment with a CH_2Cl_2 solution of acetoxyacenaphthene, after treatment with aqueous NaOH and extraction of the aqueous layer with CH_2Cl_2, yielded an orange viscous oil whose T.L.C. showed only two spots. The major component was acenaphthene. The other component, whose R_f value was greater than that acenaphthene, was not identified but was highly fluorescent.

Fig.3.2.4: Spectrum of acetoxy-acenaphthene in CF_3SO_3H.

Fig.3.2.5: Spectrum of acenaphthylene in CH_2Cl_2 after addition of $AlCl_3$.

Fig.3.2.6: Spectrum of acetoxy-acenaphthene in 80% (v/v) H_2SO_4.


A
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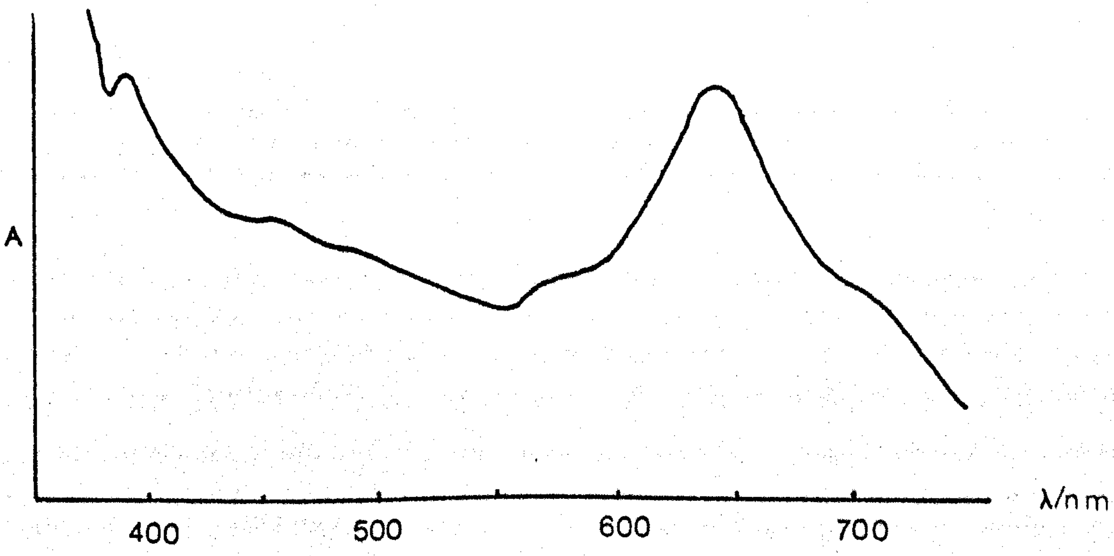
A
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λ/nm

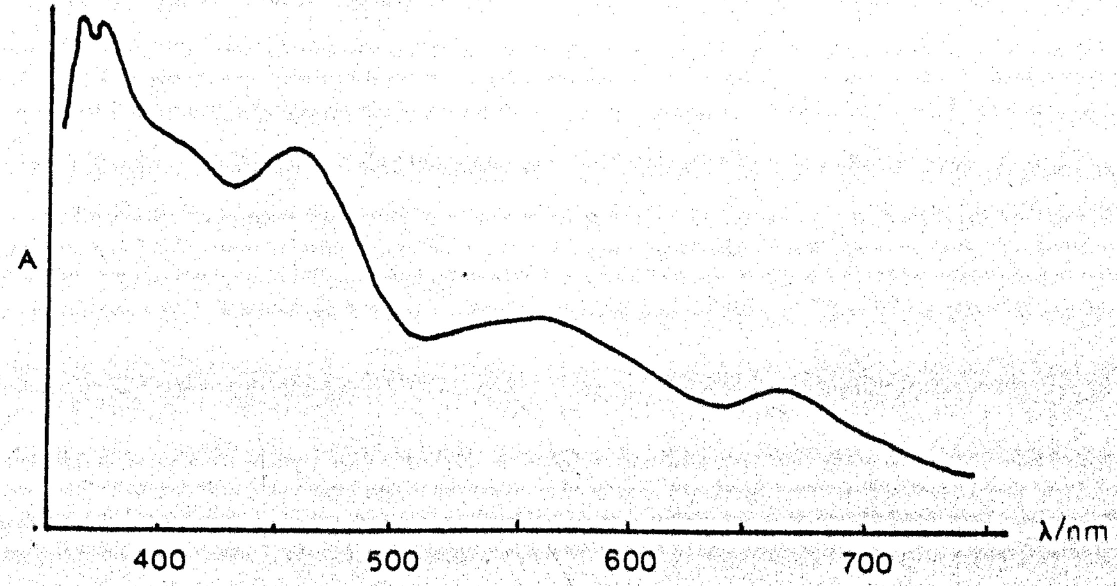
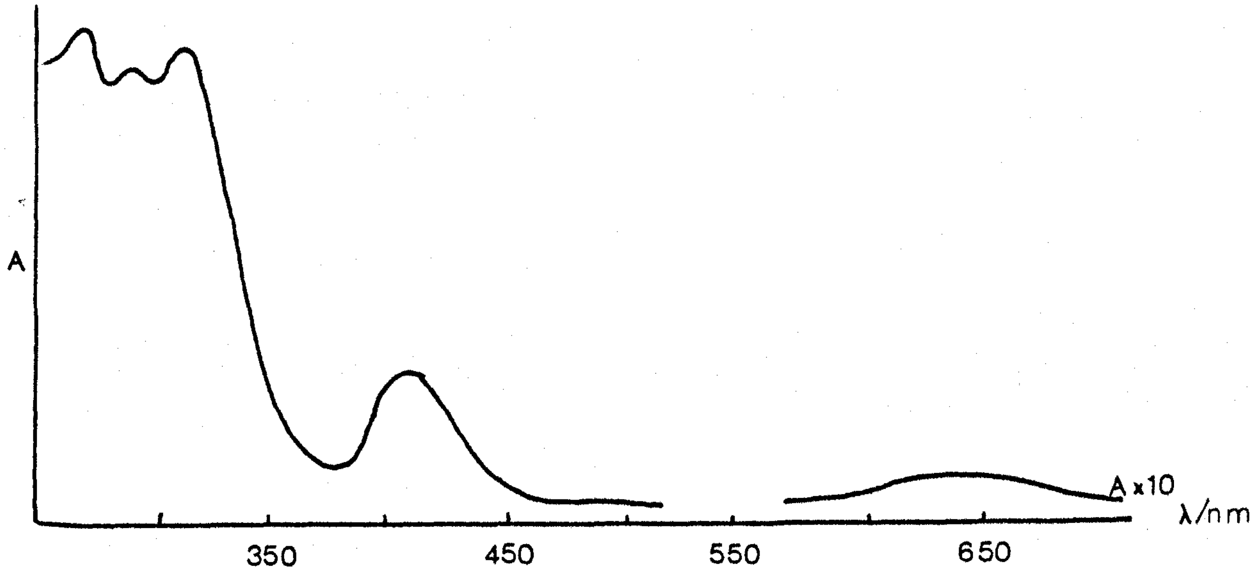
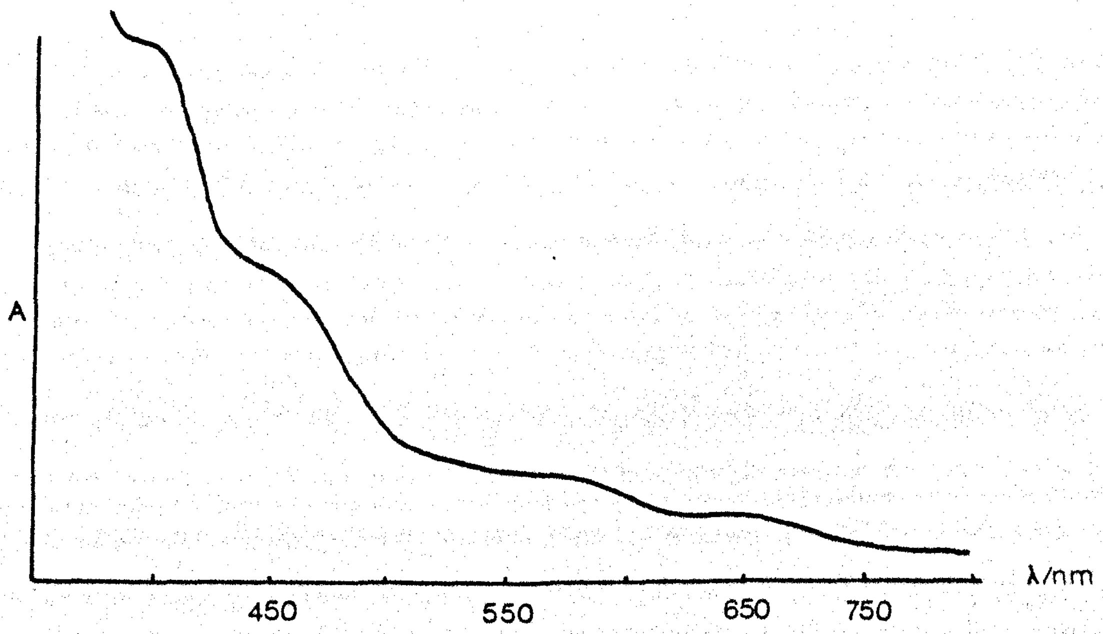

A
400
500
600
700
λ/nm

Fig.3.2.7: Spectrum of acenaphthene in H_2SO_4.

Fig.3.2.8: Spectrum of 1-bromoacenaphthene in $CH_3NO_2 + H_2SO_4$.


A
A x10
λ/nm
350
450
550
650


A
λ/nm
450
550
650
750

Preparative experiments were tried with both $AlCl_3$ and $TiCl_4$ in CH_2Cl_2 at ca. 268 K. The spectrum from the reaction of $AlCl_3$ with acenaphthylene, after dilution with CH_2Cl_2, is shown in Fig.3.2.5. The spectrum obtained from the reaction of $TiCl_4$ and acenaphthylene was almost identical. Neutralisation of these solutions with both aqueous and methanolic NaOH yielded only polymeric material. However, on one occasion small amounts of acenaphthene, identified by NMR and T.L.C. were isolated although this experiment could not be repeated.

Addition of H_2SO_4 to a glacial acetic acid solution of acetoxyacenaphthene (10^{-3}M) until the mixture was 80% v/v H_2SO_4 yielded the spectrum shown in Fig.3.2.6.

Acenaphthene in glacial acetic acid (10^{-2}M) when slowly added to H_2SO_4, in the usual way, yielded the spectrum shown in Fig.3.2.7.

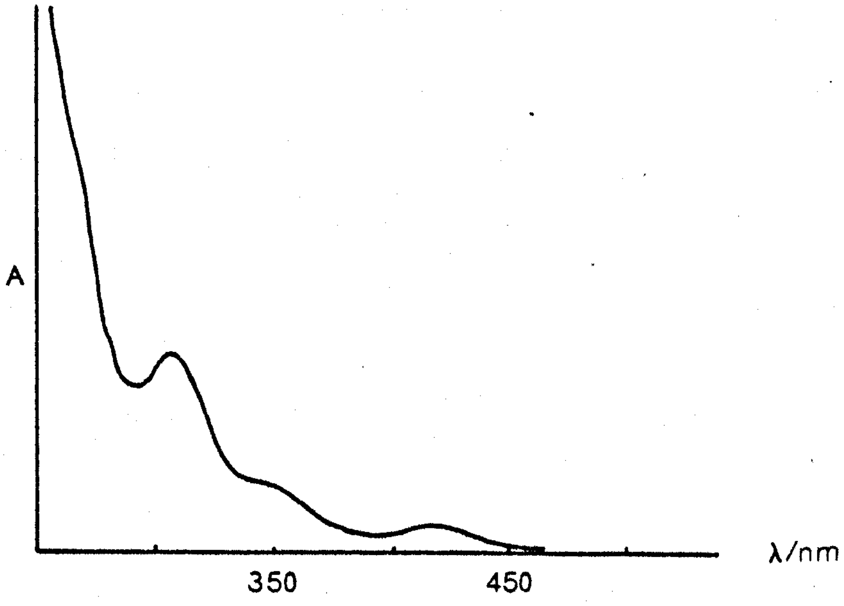
When $HgBr_2$ was added to a fresh solution (10^{-3}M) of 1-bromoacenaphthene in CH_3NO_2 no maxima were observed above the U.V. cut off of the solvent; 390 nm. To another 10 ml portion of the same solution 1 ml of H_2SO_4 was added. The spectrum is shown in Fig.3.2.8.

In an attempt to obtain a clean spectrum of ion I, 1-naphthylene methanol was dissolved in glacial acetic acid (10^{-3}M) and added to H_2SO_4 in the usual way. No colour was observed and the spectrum was very similar to that of the benzotropylium ion which is an isomeric form of the 1-napthyl methyl cation. Attempts to extract the ion from CH_2Cl_2 solution (10% w/v) into

H_2SO_4 were unsuccessful. Even with very slow addition of the CH_2Cl_2 solution to a well stirred acid at 247 K the droplets of CH_2Cl_2 became deep green-blue and an insoluble precipitate formed. After leaving overnight the acid layer became pale-blue . The spectrum of the acid solution is shown in Fig.3.2.10. The polymeric material was not analysed as it proved to be insoluble in all common organic solvents and in water. Attempts to recover the absorbing species from the acid were unsuccessful. The T.L.C. plates of the CH_2Cl_2 extractions from the neutralised acid layer gave only one spot which would not move even with ethyl acetate as the eluent.

Fig.3.2.9: Spectrum of 1-naphthylene methanol in H_2SO_4.

Fig.3.2.10: Spectrum of H_2SO_4 extraction from CH_2Cl_2 solution of 1-naphthylene methanol.


A
λ/nm
350
450

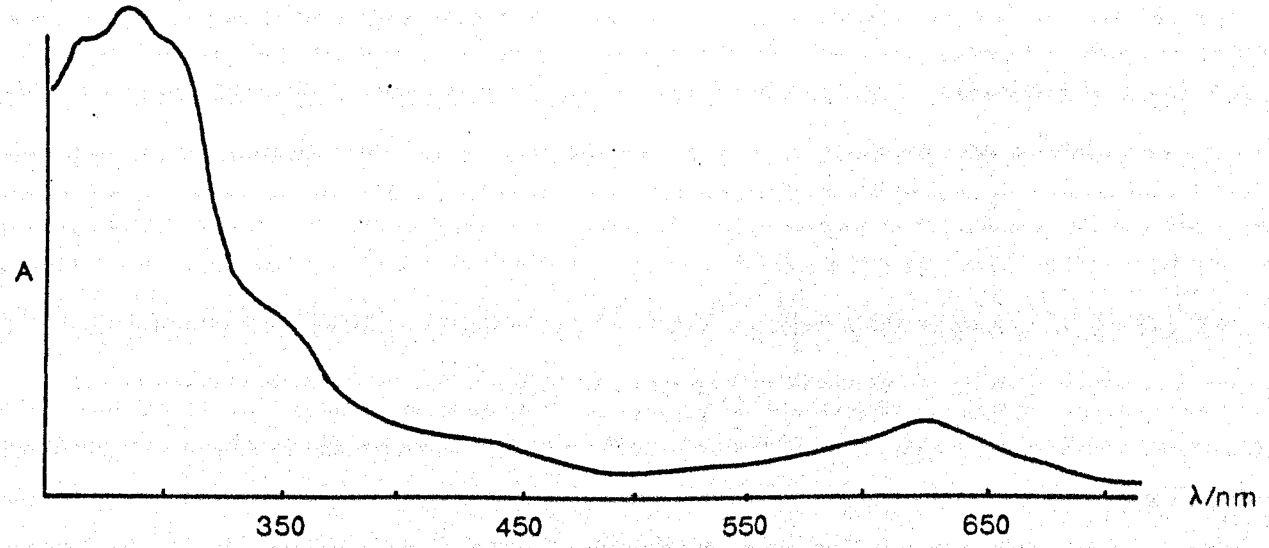

A
λ/nm
350
450
550
650

Table 3.3.1.

The Calculated Absorption Spectra of Ions III and IV.

(Oscillator strengths are given in parentheses)

Ion III

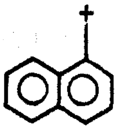
λ_{568} (0.024), λ_{435} (0.355), λ_{293} (0.338).

Ion IV

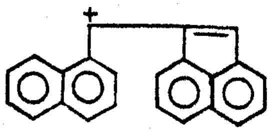
λ_{626} (0.047), λ_{550} (1.675), λ_{498} (0.005), λ_{411} (0.063), λ_{379} (0.045), λ_{337} (0.545), λ_{295} (0.173).

3.3: Molecular Orbital Calculations.

In addition to the experimental work it was thought useful to calculate by S.C.F. methods with configuration interaction[8] the spectra of the two ions, III and IV. These calculations were performed by computer with the help of Dr.H.H.Greenwood.



III



IV

The results from the calculations for these ions are given in Table 3.3.1 which gives the oscillator strengths for those transitions with an energy greater than 4.955 eV (λ = 250 nm).

For both ions the band at the longest wavelength is very sensitive to the core integral value. The major, β, band at slightly shorter wavelength is very insensitive to this parameter. It should be noted that these calculations tend to present an upper limit for the λ_{max} values.

3.4: Discussion.

It is clear that although the spectra show some considerable similarity despite the use of a variety of techniques and starting materials in our attempts to generate the acenaphthenium ion the numerical reproducibility is poor.

Before drawing any tentative conclusions it is important to review the other qualitative information available from the kinetic experiments reported in Chapter 2 and also to examine some information from the literature.

During the kinetic work the U.V. spectra recorded after the end of the kinetic runs, not in vacuo, always showed a strong absorption at 575 nm and often showed a weaker absorption at ca. 650 nm. In those kinetic runs for which the initiator was $(C_6H_5)_2HC^+SbF_6^-$ the solutions almost always developed a green colour whereas those solutions in which the initiator was $C_2H_5CO^+PF_6^-$ the colour which developed was a burgandy red. In addition, in two experiments in which the system was thought to be wetter than normal the dityl-initiated polymerisation mixture developed a deep red colour, not qualitatively the same as the colour for the propionyl initiated mixtures. On opening the polymerising mixtures to the atmosphere both the green and red solutions became dark brown.

Lastly it is important to note that despite the evidence from the kinetic work that the polymerisation is of a cationic type in which the propagating species would be, in terms of the absorption spectrum, the acenaphthenium ion, no colour developed until the reactions ceased to be of first-order with respect to monomer.

It is difficult in the light of the results presented here; the spectral, the kinetic and the molecular orbital calculations, to assign the peak at 570 nm to the acenaphthenium ion.

It is interesting to examine the evidence of Mackor et al.[9] who have used more sophisticated experimental techniques to obtain the spectra of conjugate acids of several polycyclic aromatic systems and have found good correlation between the calculated (S.C.F.C.I.) and experimental results. A major feature of that work is that the conjugate acids of pyrene and benzopyrene which have a perinaphthenium ion base structure, a higher homologue of the acenaphthenium ion, absorb between 400 and 500 nm. It seems unlikely that the lower homologue, with fewer electrons, will absorb at considerably longer wavelengths.

Finally, it is interesting to quote Reid's[10] observation with respect to the pyrene, HF, BF_3 system: " Absorption bands appeared in the red and infra-red [which] bore no consistent relationship to the absorption band around 400 nm".

Several points of crucial importance can be extracted from the experimental work described here despite the variability of the spectra obtained: Firstly, for those experiments where monomeric material was recovered from the acid solutions an absorption maximum at 440 ±10 nm was observed. (Fig.3.2.1, 4 and 5.) Secondly, the peaks at 560 ± 10, 640 ± 10 and 700 ± 10 nm are very variable, in position, persistence and relative size. Lastly under the mild conditions used to obtain the spectra in Fig.3.2.6 and 8 the peak at 440 ± 10 nm is considerably larger than those peaks at longer wavelengths.

In the light of the experimental evidence summarised above and the molecular orbital calculations it is felt that the absorption maximum at 440 ± 10 nm is the major absorption of the acenaphthenium ion (I) above 300 nm. The absorption maximum at 560 ± 10 nm probably arises from the ρ-band of the acenapthenium ion (I) and the β-band of the dimeric ion II and thus the exact position and intensity of this absorption band vary with the proportions of these two species in the solution. The maximum at 640 ± 10 nm is probably due to the dimeric ion II although both this band and that at longer wavelengths must also, in part be due to other, as yet unidentified species.

3.5: Suggestions for further work.

Although it now seems clear from the work described in this Chapter that the acenaphthenium ion absorbs at ca. 440 nm, no clean spectra of this ion have been obtained. This must certainly be the first target of further experimental work.

This work also leaves open the identity of the absorbing species responsible for the absorption maxima at ca. 700 nm and clarification of this should also be the aim of further work.

It is possible that both these goals might be achieved by doing experiments in superacid media using the techniques of Mackor et al.[9]

The molecular orbital calculations and the literature survey which accompanied this work revealed that the theoretical aspects of the acenaphthenium and similar ions are of considerable interest and could well reward further, more intensive, study than the present author had time for.

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Chapter 4: Adiabatic Reaction Calorimetry

4.1: Introduction concerning the theory.

For many years adiabatic reaction calorimetry has provided a powerful technique for studying the kinetics of cationic polymerisations of various monomers. From the early designs of Plesch[1] the Biddulph-Plesch calorimeter[2,3] (B.P.C.) was developed after some ten years of continuous research. That the B.P.C. is a very successful design is clear from the number of years for which it has been used both at Keele and elsewhere without major modification[4,5]. Nevertheless, some of its imperfections are clear from those modifications which have been made to the basic design (e.g. ref. 6) and also from the use of very different designs of calorimeter for similar work. (e.g. ref. 7 & 8)

A conventionally stirred reaction calorimeter, for example the B.P.C., with careful experimental design and operation, can effectively measure the kinetics of reactions with half-lives from several seconds to several minutes. The lower limit depends on a number of variables, but especially on the efficiency of mixing of the reagents and the response time of the temperature measuring device. The upper limit depends on the overall thermal characteristics of the apparatus. In addition to being applicable over a useful range of reaction rates, reaction calorimetry can be applied to a wide range of monomers and over a wide, flexible, temperature range. It is especially useful for studying the polymerisation of alkenes, for example isobutylene, which do not exhibit a U.V. absorption maximum. A further advantage of reaction calorimetry as a technique for studying the kinetics of any ionic polymerisation is that, with reasonable experimental dexterity it can be operated under high vacuum conditions without considerable expense.

With the development of stable carbocation salts for the polymerisation of vinyl monomers, especially isobutylene, there arose several problems with respect to the use of the well established B.P.C.. It was decided therefore to reassess all the features of the old calorimeter, and to try to develop a new calorimeter which could fulfill a similar task, but would also be useful with the new initiators and would have fewer limitations.

4.2: A critical assessment of the Biddulph-Plesch calorimeter.

A full description of the operating procedure for the B.P.C. is given in Panton's Thesis[3] and only those details of the method which are of immediate interest will be discussed here.

The addition of initiator to a monomer solution in the B.P.C. is normally effected by breaking vacuum phials (See Chapter 7) of initiator with the magnetically controlled glass breaker.(Fig.4.2.1) For both the models of the B.P.C. presently in use at Keele the maximum number of phials that can be broken is three. The limit is controlled both by the number of "stops" (See Fig.4.2.1) built into the breaking mechanism and also by the requirement that the phials must be broken at, or beneath the surface of the liquid. For some experiments, for example where sequential addition of initiator is desirable and a killing reagent is to be added via a vacuum phial, more than three phials need to be used. Thus, the first improvement concerned a facility for adding a larger number of phials to the system. In addition to the well defined problem regarding the number of phials which can be used for any single experiment, there are two, more nebulous, problems with the phial carrier in the B.P.C.. Firstly, the apparatus is very fragile and, being a part of the calorimeter which suffers considerable mechanical shock during normal operation, it is a frequent site of repair. Secondly, unless the phials are carefully secured into position with platinum wire the second and third phials have a tendency to jump free of the carrier when the first phial is broken.

Having considered the phial storing and breaking mechanism in the B.P.C. it was apparent that a radically different device was needed.

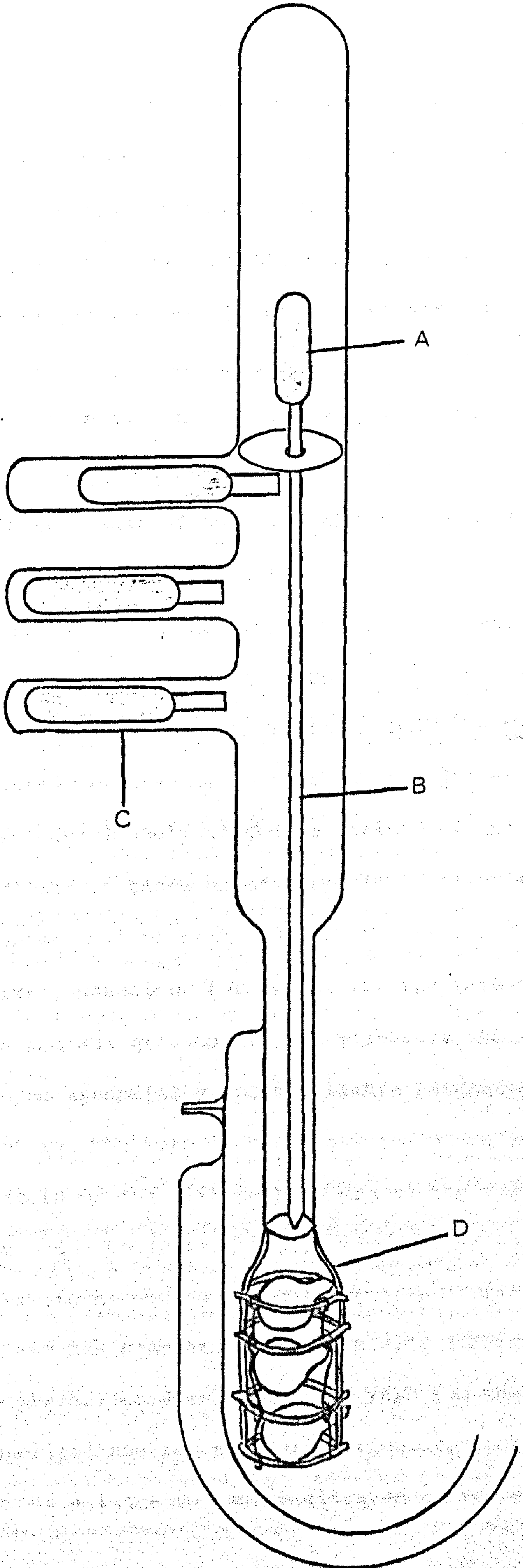
Fig.4.2.1: The phial breaking mechanism of the Biddulph-Plesch calorimeter.

Key: A= glass enclosed iron slug.

B= the glass rod breaker.

C= the "breaker stop" and glass enclosed metal slug.

D= the phial carrier showing the phials sitting in the carrier on glass "riders" and secured by platinum wire.


A
B
C
D

Krummenacher's[7] apparatus, which was "bequeathed" to Prof. Plesch, was modified during the work described in Chapter 5 of this thesis to allow the sequential addition of several phials (See Fig. 5.2.). In Krummenacher's design the unbroken phial is not in contact with the reaction mixture so that its contents are not in thermal equilibrium with the reaction mixture and also some of the contents may remain adhering to the phial fragments above the reaction mixture. These problems are easily remedied by increasing the length of the tube holding the phial ready for breaking so that the phial floats on the reaction mixture in the end of this tube. Several holes in the walls of the tube allow the contents of the phial to be efficiently mixed with the reaction solution. With these modifications the mechanism is both robust and reliable.

Cooling the reactants in the B.P.C. is a simple and convenient process: a cooling bath is raised around the reaction vessel until the desired temperature is reached, the jacket is then evacuated to achieve approximately adiabatic conitions. The conditions are, in fact, closer to those of an isoperibole calorimeter since heat input is balanced against heat loss to achieve a stable, ideally isothermal, baseline. For the B.P.C. the rate of heat input, largely via the thermal gradient in the glassware above the calorimeter, depends on essentially uncontrollable parameters such as the ambient temperature. The rate of heat loss is controlled by the height and temperature of the cooling bath around the reaction vessel.

In order to achieve better temperature stability it is necessary to have more effective thermal isolation of the reaction vessel and its contents. For the B.P.C. difficulties arise because of the thermal gradient above the reaction vessel. In the Paris laboratories[6] the reactants in the calorimeter are cooled on the surface of a large condenser situated above the reaction vessel

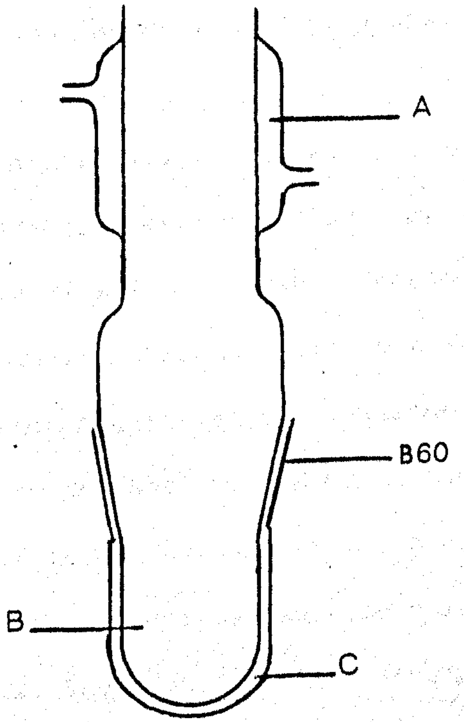
Fig.4.2.2: The basic design of the Paris Reaction vessel. The sketch shows the large overhead condenser, A, and the reaction vessel, B, and Dewer space, C, constructed from a B60 cone and socket.

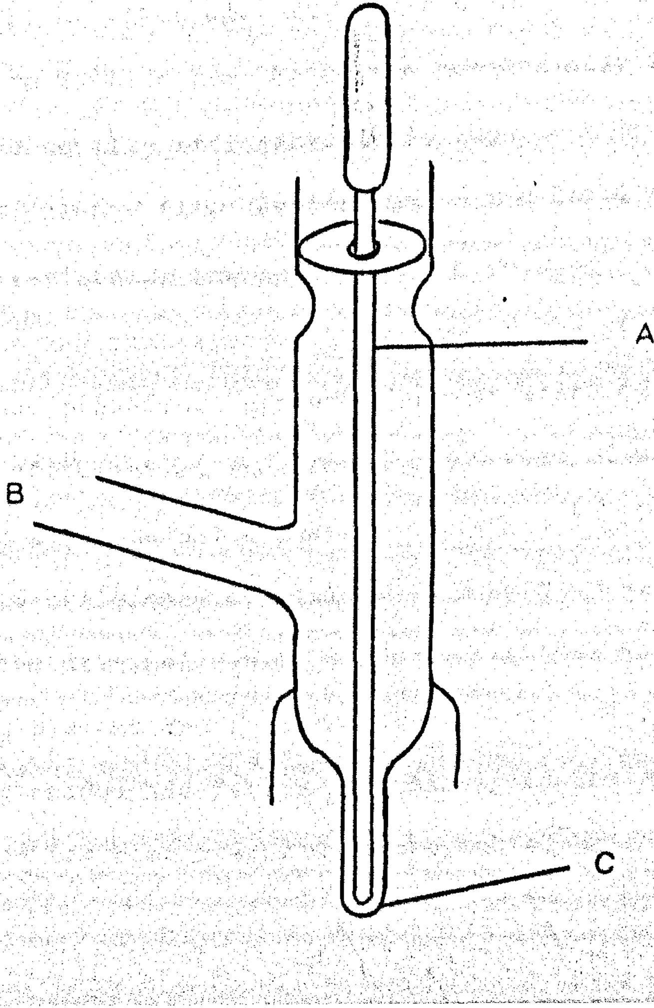
Fig.4.2.3: Device for addition of known large volumes of reagents to vacuum systems .

Key: A= magnetically controlled glass breaker.

B= connection to a burette containing initiator solution.

C= fragile end to tube to allow easy breaking.


A
B60
B
C


A
B
C

(Fig.4.2.2), so that all the glassware below the condenser, provided that it is well insulated, is in thermal equilibrium with the reactants. A simple vacuum jacket around the reaction vessel then maintains reasonable thermal stability. Additionally, with such an arrangement, the vacuum jacket can be permanently, and therefore more thoroughly, evacuated.

The stirrer of the B.P.C. is, because of the method of cooling, driven from above through a magnetic clutch by a rotating horseshoe magnet. One of the undesirable features of the B.P.C. is the considerable vibration arising from the slightly eccentric motion of the horseshoe magnet and the considerable length of the stirrer itself. If the contents of the new calorimeter could be cooled by an overhead condenser, the stirring could be achieved from below by a conventional plate type magnetic stirrer with a magnetic "demon". In the B.P.C. the most efficient stirring has been shown to be produced by a paddle type stirrer. This is also the design favoured by Arnett et al.[9] for their calorimeter. However, with stirring controlled from below the commercially available "star" stirrer is equally efficient. It is important too, to notice that in the B.P.C. planar flow develops above the level of the former of the platinum resistance thermometer under certain, rather ill defined, conditions and that although the site of the stirrer, below the temperature probe does produce the best stirring, the glass former prevents efficient mixing. For any new type of calorimeter the design of the internal glassware needed to be tested carefully with respect to efficiency of mixing. (See Section 4.3)

In the original B.P.C. the same platinum wire operated as both a heating element and a thermometer. Since the original self-balancing bridge has fallen into disrepair the change in the resistance has been measured as the out of balance current in a conventional Wheatstone bridge with the platinum resistance ($R_{Pt}+R_1$) in one arm and a set of dummy leads (R_1) in the other. Provided that the temperature change does not produce more than ca. 1Ω change in the resistance, the method is reasonably accurate but it must be realised that the out of balance current is not linearly related to the change in R_{Pt}[10].(See also Eq.4.4.1.)

In the B.P.C. it is not possible to measure the temperature in the calorimeter while electrical heating is applied. Thus, the effective rate of heat transfer from the heater cannot be monitored. Furthermore, when switching from the heating to the temperature sensing mode the galvanometer becomes temporarily overloaded by feedback. Both these problems are overcome by including a separate heater in the calorimeter design. This arrangement has the added advantage that the thermal mixing of the reaction mixture can also be monitored.

Although the problem of hysteresis and non-linearity of response of thermistors can be overcome, the speed of response, ease of construction and sensitivity of the platinum resistance thermometer make the latter the preferred temperature sensor for vacuum calorimeters.

In addition to those problems already outlined, the major difficulty in using the B.P.C. for kinetic experiments with carbocation salts as initiators arose because the size of the reaction vessel is unsuitable if the initiator is to be added in solution. The minimum volume of reaction mixture that can be used in the B.P.C. is ca. 200 ml. Under optimum conditions the concentration of water, the major effective impurity, can be reduced to ca. 10^{-5} mol l^{-1}. In order for this to be ca. 1% of the initiator concentration, the minimum concentration of initiator in the reaction mixture needs to be 10^{-3} mol l^{-1}. If two 1 ml phials can be broken simultaneously, the minimum concentration required is ca. 10^{-1} mol l^{-1}. However, this is near the solubility limit, at ambient temperatures, for many of the salts considered in this work. (See Chapter 1)

The problem could be solved by adding more initiator solution, for example by breaking the end of a tube containing a known volume of solution; the apparatus for this is shown in Fig.4.2.3. However, for larger volumes of initiator solution the problems of thermal equilibrium and efficient mixing become more acute. An alternative solution to the problem is to reduce the overall volume of the reaction vessel by about a factor of ten.

One feature of the B.P.C. for which no improvements could be envisaged,is the conductivity electrodes. Since this work involved ionic propagating species, conductivity could provide useful information.

Finally, the emptying and cleaning of the B.P.C. is one of the most convenient aspects of the apparatus.[3] However, the flange joint, sealed with Apiezon Q compound, is a frequent site of leaks and increases the length of pumping time required to reach a good working vacuum (10^{-4} to 10^{-5} mm Hg) and to reduce the level of water to an acceptable level. Both the Paris calorimeter (Fig.4.2.2) and the Krummenacher reaction vessel have no greased or waxed joints on the reaction vessel, which eliminates a source of leaks, reduces the necessary pumping time and increases the overall reproducibility of the results.

It follows therefore, that there are several ways in which the B.P.C. can be developed and improved: 1) A new phial breaking mechanism similar in design to that of Krummenacher's. 2) The facility for multiple phial storage in a side arm. 3) Overhead cooling on the surface of a large condenser or cold finger. 4) A permanently evacuated vacuum jacket for the reaction vessel. 5) Stirring operated from below by a conventional plate type magnetic stirrer and, 6) the inclusion of a separate heating probe.

It is clear that the new design should have temperature and conductivity probes similar in design to those in the B.P.C. and that all these considerations must be included into a design which has a reaction volume of ca. 30 ml, some ten times smaller than the B.P.C.

Fig.4.3.1: Outline sketch of the new calorimeter.

Key: A= cold finger.

B= magnetically controlled glass breaker.

C= the phial magazine

D= the resistance thermometer and dummy leads.

E= the conductivity leads.

F= the heater leads.

G= "star stirrer".

H= vacuum jacket.

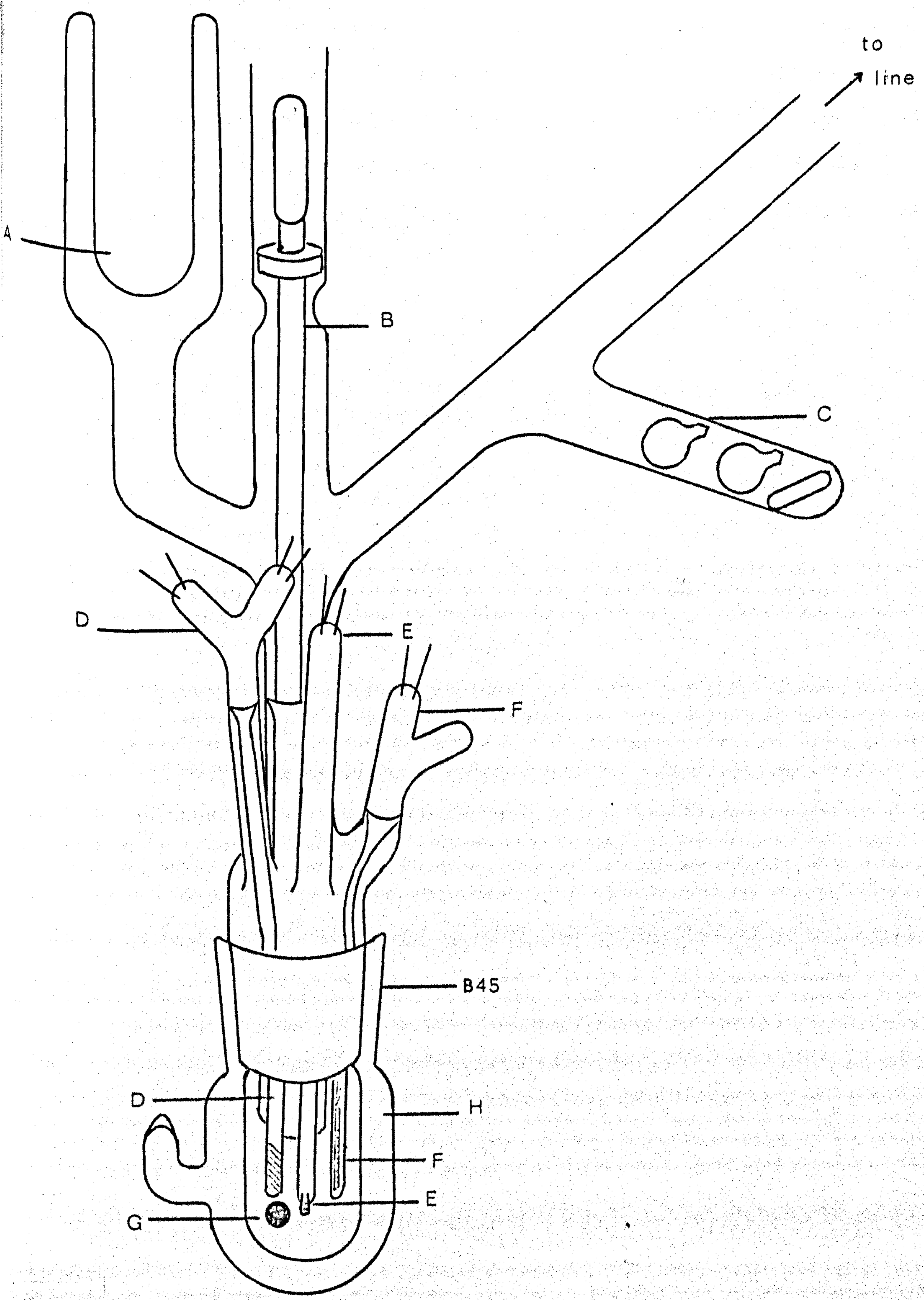
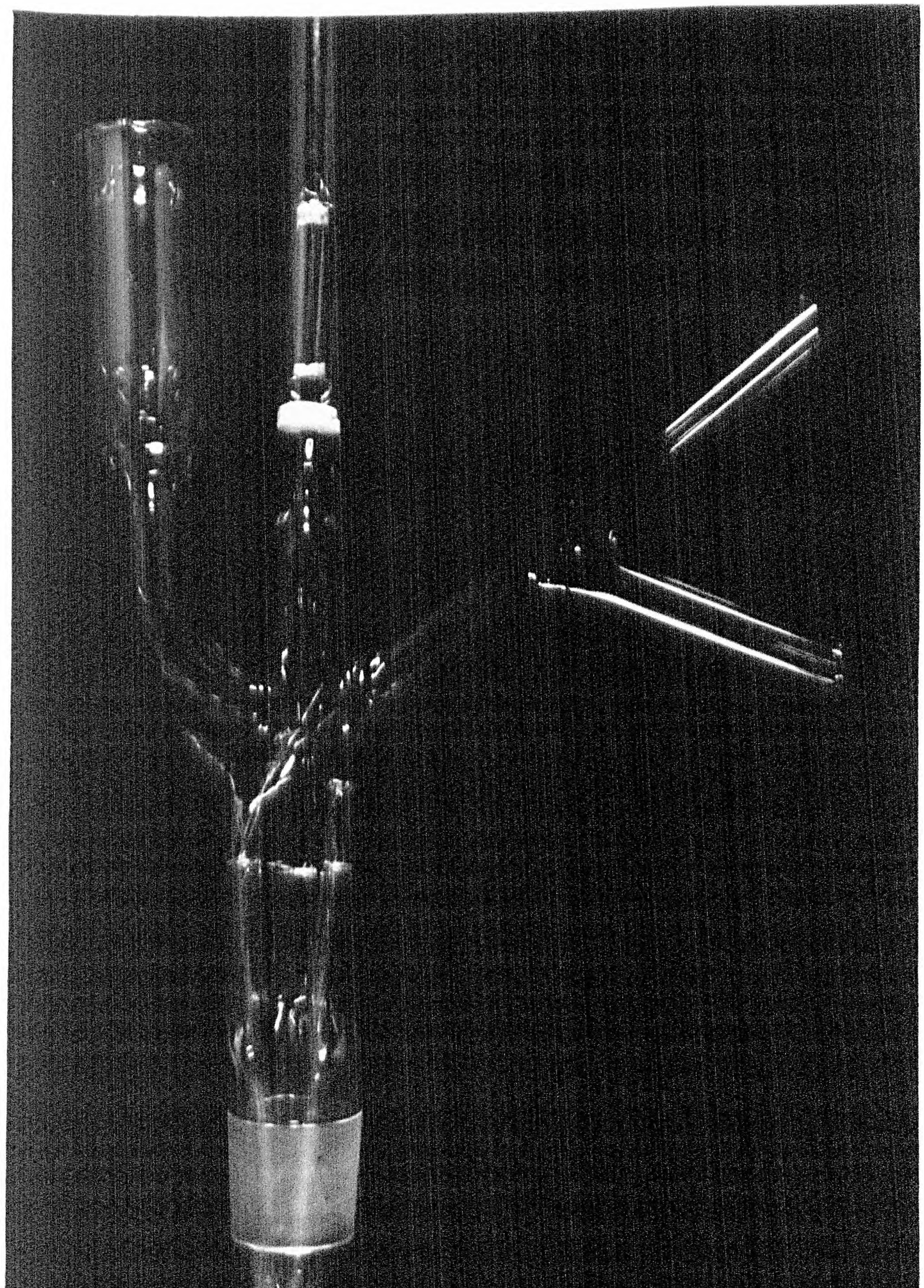

to
line
A
B
C
D
E
F
B45
D
H
F
E
G

Fig.4.3.2: An early model of the new calorimeter without the vacuum jacket or the heating element.



4.3: A new adiabatic calorimeter.

The most difficult problem with the new design was to reduce the operating volume to one tenth that of the B.P.C. and at the same time retain all the necessary fittings. Fig.4.3.1 shows how the suggestions made in Section 4.2 have been realised. The accompanying photograph, Fig.4.3.2, shows the model of the calorimeter before assembly and before addition of the heating element.

In Fig.4.3.1 the modified, Krummenacher type, phial storing/breaking mechanism is shown. The phials are pushed out of the magazine with a magnetic "demon" and then fall into the main tube. The bottom of the main tube is slighly restricted and holds the phial at the surface of the liquid until the phial is broken. Six holes in the walls of the main tube where the phial is held, allow the reaction mixture to wash over the phial and so achieve thermal equilibrium and efficient mixing. Despite these holes the structure remains quite robust. The phial magazine can store six phials but a simple modification could allow a greater number to be used.

The solvent (and monomer, if it is not added from a phial) can be distilled into the apparatus via the cold finger (A, Fiq.4.3.1) which is also used to cool the reaction mixture. With a dry ice/acetone mixture in A the reaction solution can be cooled to ca. 200 K, provided that all the glassware up to the level of A is lagged with thick glass rope. At 200 K the rate of temperature rise after cooling had been stopped (by removal of the cooling mixture from the cold finger) was found to be < 0.1 K min^{-1}. To test the speed with which the contents of the phial achieve thermal equilibrium with the bulk solution, phials of solvent were broken at

Fig.4.3.3: Section across the top of the B45 cone on the new calorimeter.

Key: A= the main tube.

B= Pt resistance thermometer.

C= conductivity electrodes.

D= heater.

Fig.4.3.4: Section c-d on Fig 4.3.3.

Key: A-D as above.

E= 4 mm O.D. Pyrex tube.

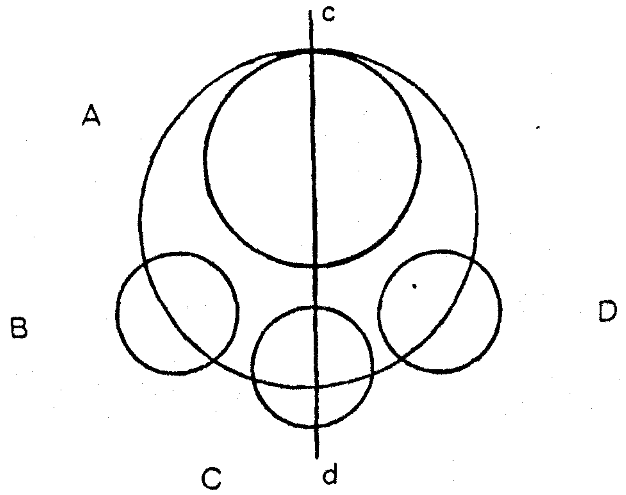
F= Pyrex/Soda graded seal.

G= B45 cone.

H= 4 mm O.D. Soda glass tube.

I= insulated copper leads.

J= Pt wire silver soldered to the copper wire and the lead glass bead which maintains the cell dimensions.


c
A
B
D
C
d

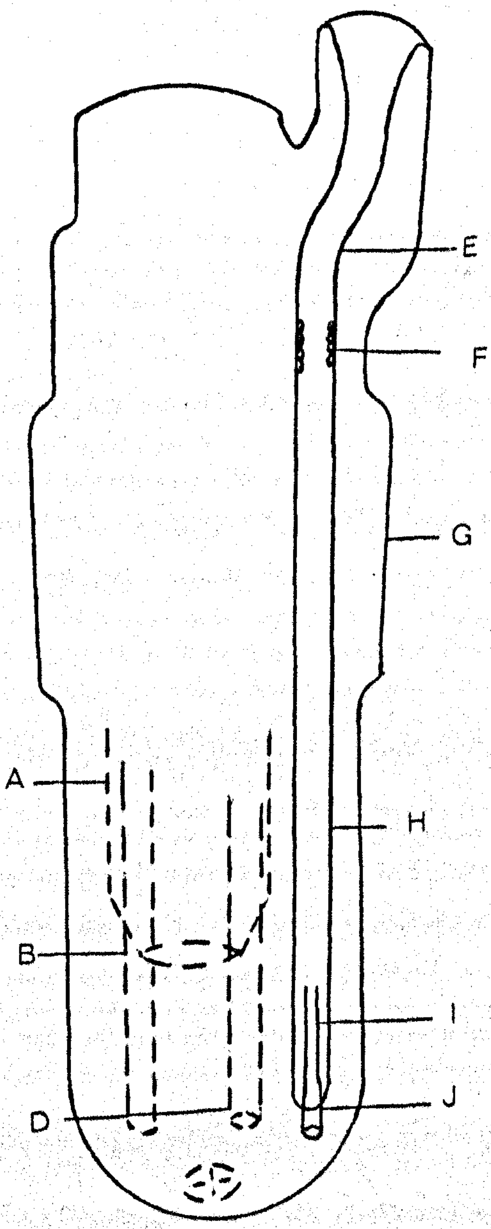

E
F
G
A
H
B
I
J
D

Fig.4.3.5: The platinum resistance thermometer probe for the new calorimeter.

Key: A= resistance thermometer leads

B= dummy leads.

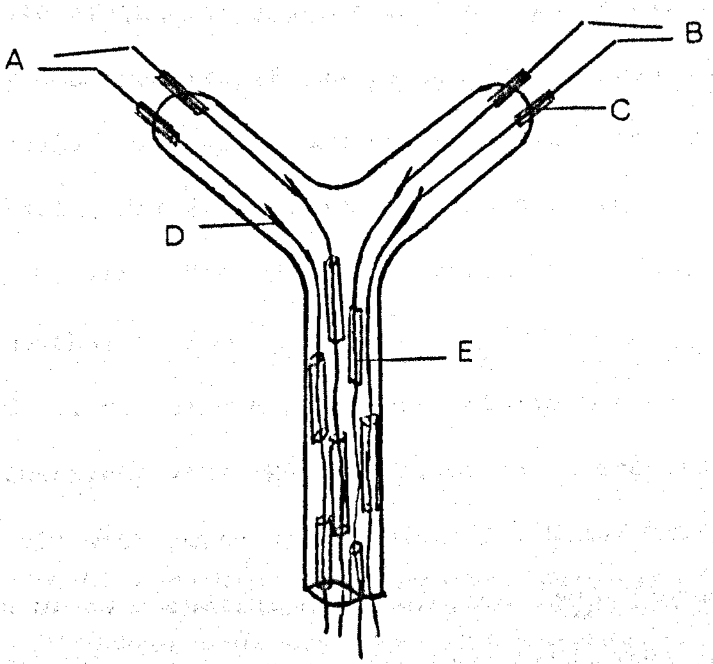
C= tungsten through glass seal.

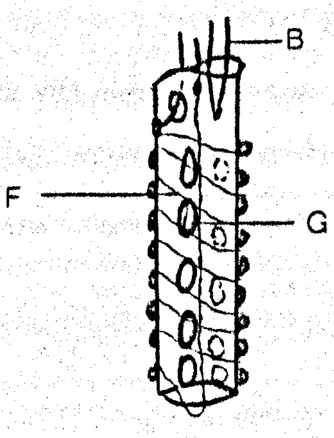
D= tungsten to platinum silver soldered joint.

E= fine glas capillary insulation for leads.

F= 0.1 mm diam. Pt wire of the resistance thermometer.

G= holes in the glass former to allow efficient mixing and heat transfer.


A
B
C
D
E


B
F
G

200 K after being held in position for 2, 5 and 10 min. Only the 2 min test showed any temperature jump when the phial was broken. Provided that the glass breaker is kept as far down the calorimeter as possible at all times the temperature jump due to dropping the breaker is always less thn 0.01 K.

The base of the calorimeter is made from a B45 cone which allows easy construction of the vacuum jacket from a B45 socket. The joint was sealed with black wax and then evacuated by pumping with frequent flaming for 24 h before sealing off from the vacuum line. The vacuum was still "black" to a powerful Tesla coil discharge after six months.

The efficiency of mixing in the calorimeter was tested in two ways: qualitatively with $KMnO_4$ solutions in acetone and quantitatively with aqueous KCl solutions. Using $KMnO_4$, either as crystals or as a concentrated solution the movement of the phial contents after breaking can be observed. This gives useful information with respect to the various devices in the calorimeter - and the amount of obstruction that these present to efficient mixing. With aqueous KCl solutions the conductivity can be monitored and the length of time taken to achieve a level trace can be measured. For the final model of the calorimeter in which a "star demon" (S.G.L.) did the stirring, the time taken to achieve constant conductivity was ca. 0.5 s.

The platinum resistance thermometer and the conductivity electrodes proved to be relatively simple to reduce in size. The precise designs of these two probes are shown in the diagrams of Fig.4.3.3-5. The major problem with these probes was providing efficient, robust insulation for the individual wires. This was finally achieved by threading the wires through fine glass capillaries before assembly. In contrast to the B.P.C. the dummy leads for the thermometer are in the same tube as the actual leads of the thermometer which is simpler and more efficient. The holes down the length of the glass former of the resistance thermometer reduce the obstruction that this probe presents to efficient mixing and also increases the sensitivity of the thermometer. The conductivity and resistance thermometer probes are shown in the photograph of Fig.4.3.5.

The design of the heater was not so straightforward and numerous designs were tested before a satisfactory construction was found.(Fig.4.3.7) The heater needed to have a resistance of at least 30 Ω and at the same time it must be both mechanically strong and chemically inert.

The initial design incorporated the heater into the conductivity probe as shown in Fig.4.3.8. The first model of this design had a fine platinum wire (0.1 mm diam.) as the heating element but this suffered from two disadvantages: Firstly, it was mechanically very weak and tended to get broken by pieces of glass from spent phials, Secondly, local overheating of the wire, where it passed through the glass tubing caused the wire to snap and, on one occasion, the glass cracked. A second model of the same basic design had a stainless steel element (0.1 mm diam.) spot welded to 0.5 mm diameter platinum leads passing through the soda glass tube. The element and leads were gold plated to make them chemically inert. (See Section 4.4 for details.) Unfortunately, although apparently perfect plating was achieved (See Fig.4.3.9.) and the heater worked very well it was found that after several hours in CH_2Cl_2 the gold plate fell off the element. After this it was decided to use a glass enclosed heater similar to that used by Arnett et al..[9] (Fig.4.3.7) The glass tubing surrounding the actual heater is drawn from 4 mm O.D. tubing so that the walls are less than a millimeter thick.

Fig.4.3.6: Photograph showing the platinum resistance thermometer and the conductivity probes. (1.5 x actual size.)

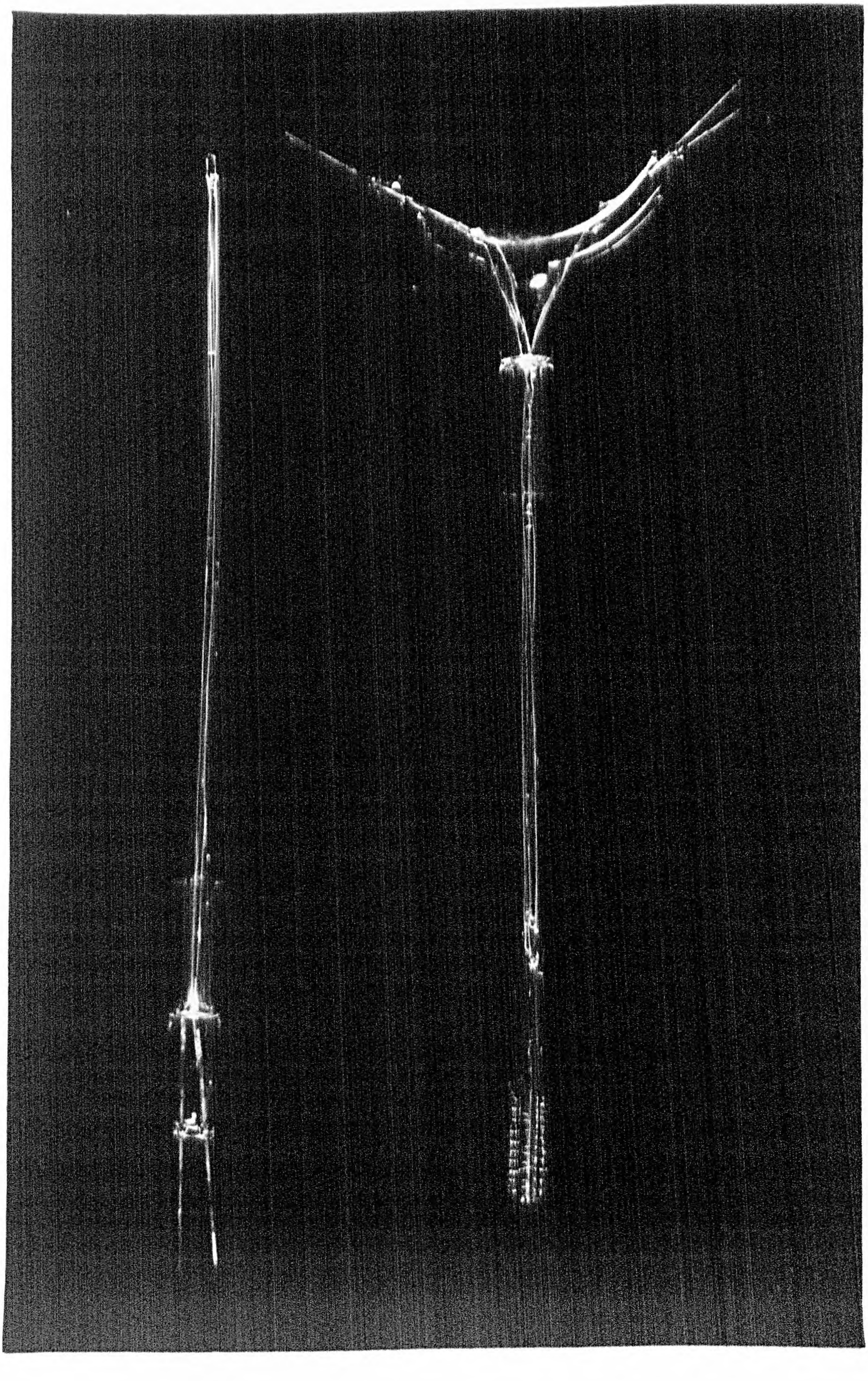


Fig.4.3.7: The final design for the heater probe.

Key: A= tungsten rod.

B= insulated copper leads.

C= manganin wire heater spot welded to copper leads.

D= the glass capillary former.

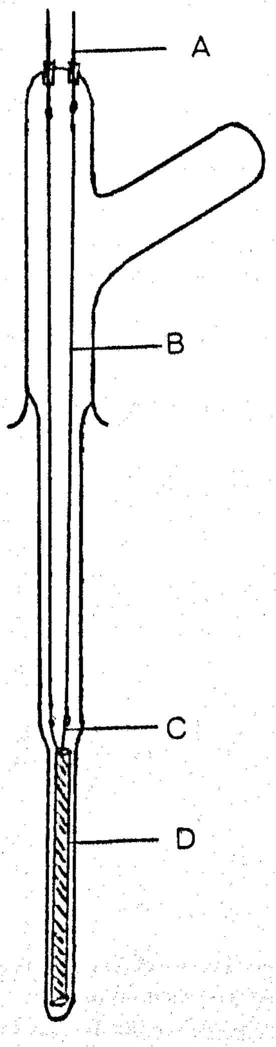
Fig.4.3.8: Heater design incorporating conductivity cell.

Key: A= 4.0 mm O.D. Pyrex tube.

B= Pyrex/Soda graded seal.

C= insulated copper leads silver soldered to platinum wires of the conductivity cell.

D= stainless steel heating element silver soldered to platinum wire (1.0 mm diam.)


A
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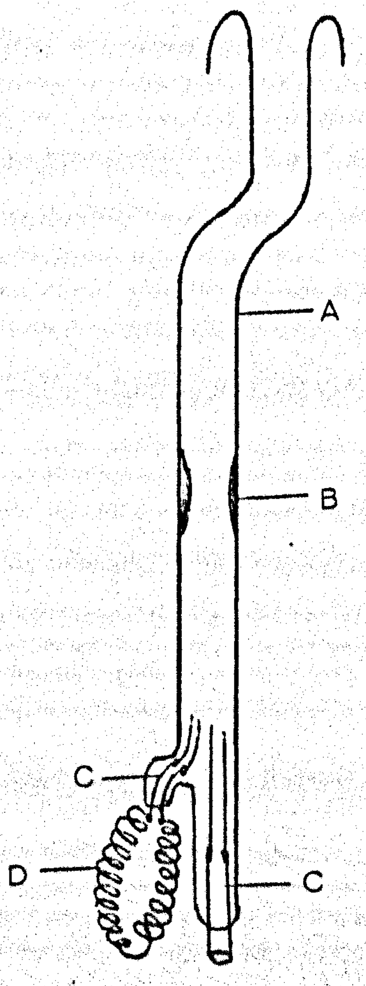
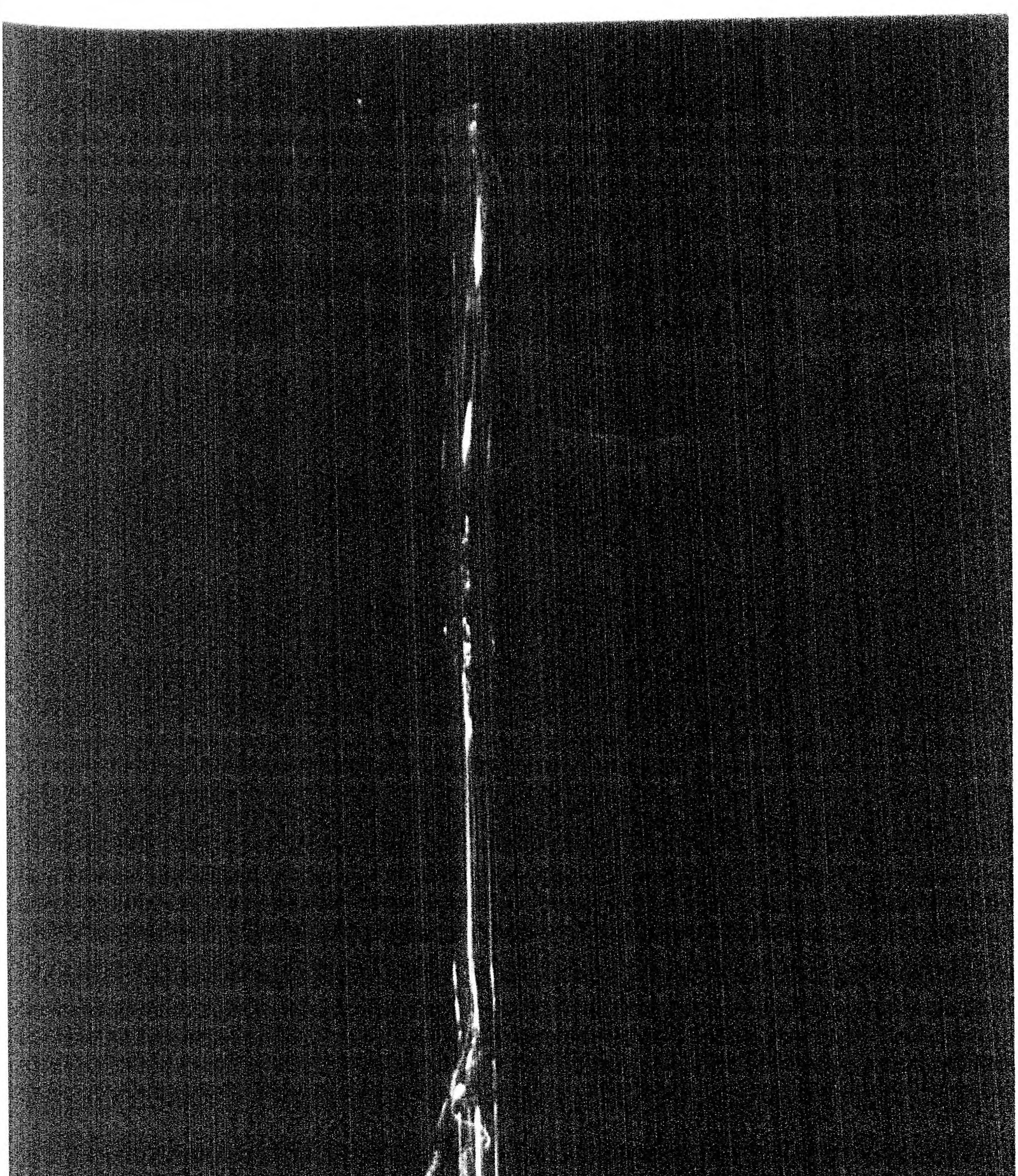

A
B
C
D
C

Fig.4.3.9: The conductivity probe incorporating a gold plated heater. (1.5 x actual size.)



Silicone oil was found to be the best heat transfer agent since its high boiling point allows the unit to be sealed under a water pump vacuum without any danger of the oil boiling during operation of the heater. It is advantageous to seal the heater probe since that stops loss or contamination of the heat transfer fluid. Although a glass enclosed heater (e.g.Fig.4.3.7) does show a greater time lag between elctrical switching and thermal equilibrium in the bulk solution than a bare wire heater (e.g.Fig.4.3.8) the increase, 0.1 s, is not significant. (For experimental details see Section 4.4.)

After an experiment the calorimeter is separated from the vacuum line and the contents removed by suction, either with a long syringe needle or a Nylon tube, attached via a trap, to a vacuum pump. The latter device also allows the small pieces of broken glass to be removed from the calorimeter. The calorimter is cleaned by filling it to the level of the cold finger with a suitable solvent and allowing it to stand for several hours. The solvent is then removed by suction and the apparatus dried in a stream of N_2 before reassembly for the next experiment.

4.4: Experimental methods.

4.4.1: Materials.

Solvents for the calibration of the platinum resistance thermometer were three times fractionally crystallised before use. All other materials were used as supplied and were of standard laboratory grade unless otherwise specified.

4.4.2: Glassblowing and miscellaneous techniques.

Although the final design of the calorimeter is solely due to the author it is the result of many fruitful hours of discusion with Prof.P.H.Plesch, Mr G.E.Holdcroft and many others.

The working model of the calorimeter is largely the result of the expert glassblowing of Mr C.Cork and the silver soldering of Mr P.Holbrook. Not withstanding this considerable assistance the original glass models of the calorimeter and the many separate parts used for testing were all made by the author.

4.4.3: Gold plating the heating element.

4.4.3.1:Introduction.

Several attempts were made to plate a stainless steel wire element (See Fig.4.3.8.) attached both by silver solder and spot welds to the platinum leads. Only two methods will be described here, the first because it demonstrates the considerable efforts that were applied to the problem of making an inert heating element and the second because it demonstrates that, in the opinion of the author, gold plating should be left to the experts since it is not strictly, a scientific operation , but rather an art.

4.4.3.2: Gold.

For both methods the starting material was a redundant gold filling supplied by Prof. P.H.Plesch. It was initially purified in the following way: One filling of moderate size (1.1 g) was cut into six pieces. Each piece was pressed into a flat disc, ca. 0.25mm thick, using an old I.R. KBr disc press. The discs were then placed in boiling nitric acid for 6 h. After this treatment the discs had lost ca. 20% of their initial weight. (Dental gold also contains Cu, Ag and a variety of other metals depending on the precise use.[12]) From the silver chloride precipitated during the preparation of $AuCl_3$ it is estimated that less than 1% by weight of the remaining disc was Ag.

4.4.3.3: Gold chloride.

Gold chloride was prepared after the method described by Mellor.[13] 0.13 g of Au (from above) was dissolved in 50 ml of aqua regia and the solution boiled until the volume was reduced to about 5 ml. The solution was then allowed to cool to ambient temperature, diluted with 40 ml of distilled water and left overnight. A fine white precipitate (AgCl) was then filtered off (0.0012 g) and the filtrate evaporated to about 5 ml over a Bunsen flame. The residue was then poured into a Petri dish and put in a vacuum desiccator over $CaCl_2$. After 6 h of constant pumping the residue had yielded a layer of canary yellow needle crystals which were very hygroscopic and rapidly formed a viscous solution in the open air.

4.4.3.4: "Cold plating".

A "cold plating" solution was made from gold chloride (prepared as above) as described by Henly.[14] Despite taking considerable care with the cleaning of the wires to be plated and following the prescription as exactly as possible no plating of either the platinum or the stainless steel wire was observed.

4.4.3.5: Electrical plating.

After several unsuccessful attempts to prepare nicely plated heating elements the following method was discovered.

The wire elements were first cleaned by soaking in boiling hexane for 30 min, then quickly dipping the wire successively into hot chromic acid, hot water, hot sodium hydroxide (20% w/v), cold water. The wires were then liberally rinsed with deionised water and immediately plated. The plating was most successful where the wire had been well wetted by the water after the cleaning process.

The plating solution consisted of 100 ml of deionised water saturated with KCN into which one of the gold discs (as described above) had been dissolved. The wire to be plated was then anodically stripped at a high voltage (60 V) with a platinum cathode. The polarity of the wire to be plated was then reversed, a gold anode placed in the solution and a voltage of 2.0 V applied. Within a few minutes a bright, coherent gold plate was achieved. (See Fig. 4.3.9.) The gold plate was not lifted by mechanical scratching but after a few hours in CH_2Cl_2 the gold plate separated from the wire.

A sample of stainless steel coated with gold plate prepared from Wet Gold[15] was put to the same tests with similar results.

No further experiments were carried out after this as the basic design of the heating probe was changed.

4.4.4: Calibration of the platinum resistance thermometer.

The leads to the thermometer, inside the calorimeter, were constructed from 1.0 mm diam. platinum wire. The thermometer was made from 0.1 mm diam. wire. Both wires were grade 4 platinum as supplied by Johnson Metals Ltd..

The circuit for measuring the resistance of the thermometer is shown in Fig.4.4.1. A Sefram Graphispot, type GR2VAD, was used as the galvanometer and the temperature/time recorder. By inserting a known resistance in the bridge to replace R_{Pt} the effect of 0.1Ω changes in R_{Pt} on the out of balance current was calibrated.

To calibrate the thermometer its resistance was measured at the freezing point of four solvents: C_6H_6 (278.71 K), CCl_4 (250.93 K), $CHCl_3$ (209.63 K), and $C_6H_5CH_3$ (178.19 K). For each solvent the cooling curves with respect to time were recorded, both while cooling and warming, until the resistance at the freezing point was the same for two successive runs.

The resistance thermometer was recalibrated whenever any modification to the thermometer probe was made. A typical calibration graph is shown in Fig. 4.4.2.

Fig.4.4.1: Circuit diagram of the Wheatstone bridge for measuring the resistance of the platinum thermometer.

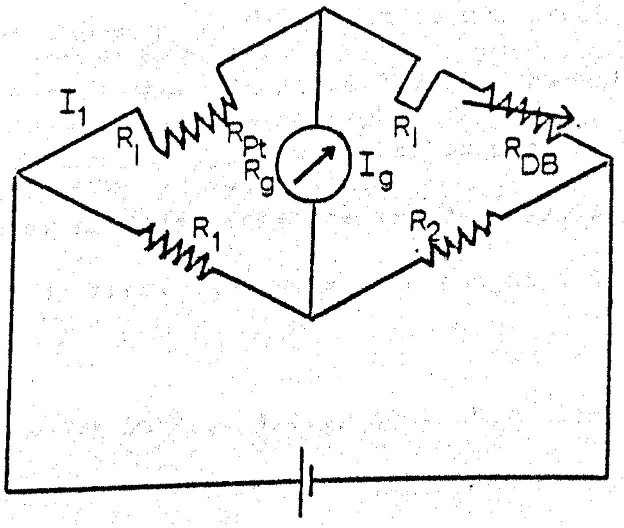
$$R_{Pt} = (I_g/I_1) \times (2R_g + ((1 + (R_{DB} + (R_1/R_2))) \times R_{DB})) \qquad \text{Eq.4.4.1.}$$

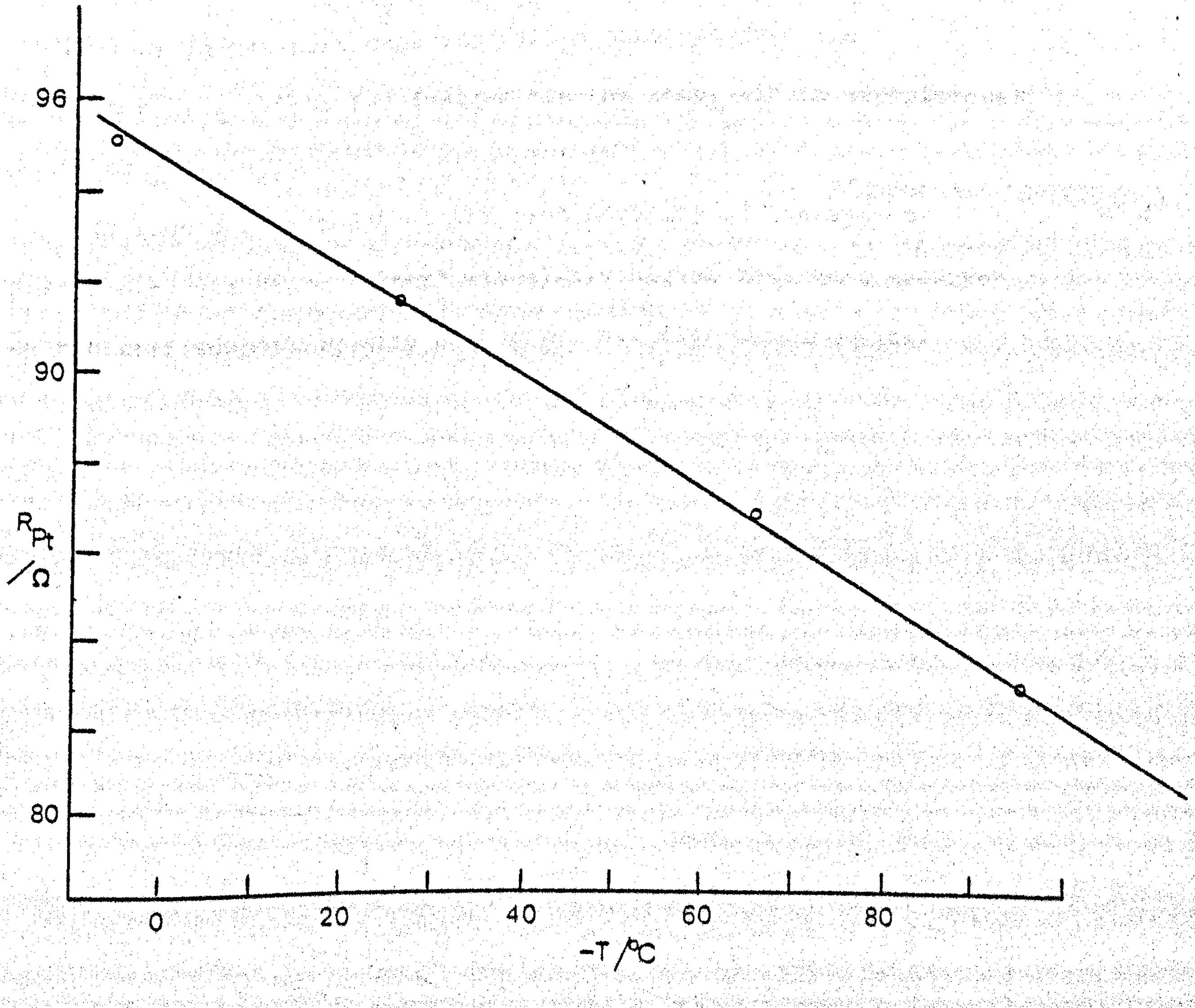
Fig.4.4.2: Calibration graph for the Pt resistance thermometer.

Slope = 0.1124 ΩK^{-1} (S.E. ± 1.7×10^{-4})

Intercept = 93.88 Ω (S.E. ± 1.02×10^{-2})

Correlation coefficient 0.99.


I_1
R_l
R_{Pt}
R_g
I_g
R_l
R_{DB}
R_1
R_2


96
90
80
R_{Pt} /Ω
0
20
40
60
80
−T /°C

4.4.5: Experiments to test the heater.

When it was realised that a self-supporting wire heater, shown in Fig. 4.3.8 was going to be difficult to construct in comparison with the "tube heater" shown in Fig.4.3.7 the thermal characteristics of the two types were tested with respect to time in a dummy calorimeter containg only the two heaters, a resistance thermometer and a stirrer. The tests were run at 273 K at atmospheric pressure.

The results shown in Fig. 4.4.3, show that although the time lag between electrical switching and consequent effect on the bulk solution is almost twice as long for the "tube heater", the difference in the heat capacity values obtained from the measurements with the two designs are the same, within experimental error of ±5%.

It should be noted that the heat capacity of the system (Calorimeter+25ml CH_2Cl_2) measured by the "tube heater" was always higher than that measured by the self-supporting wire heater for all five measurements.

Fig.4.4.3: Temperature/time curves for the two different heater designs.

A= self-supporting wire heater.(Fig.4.3.8)

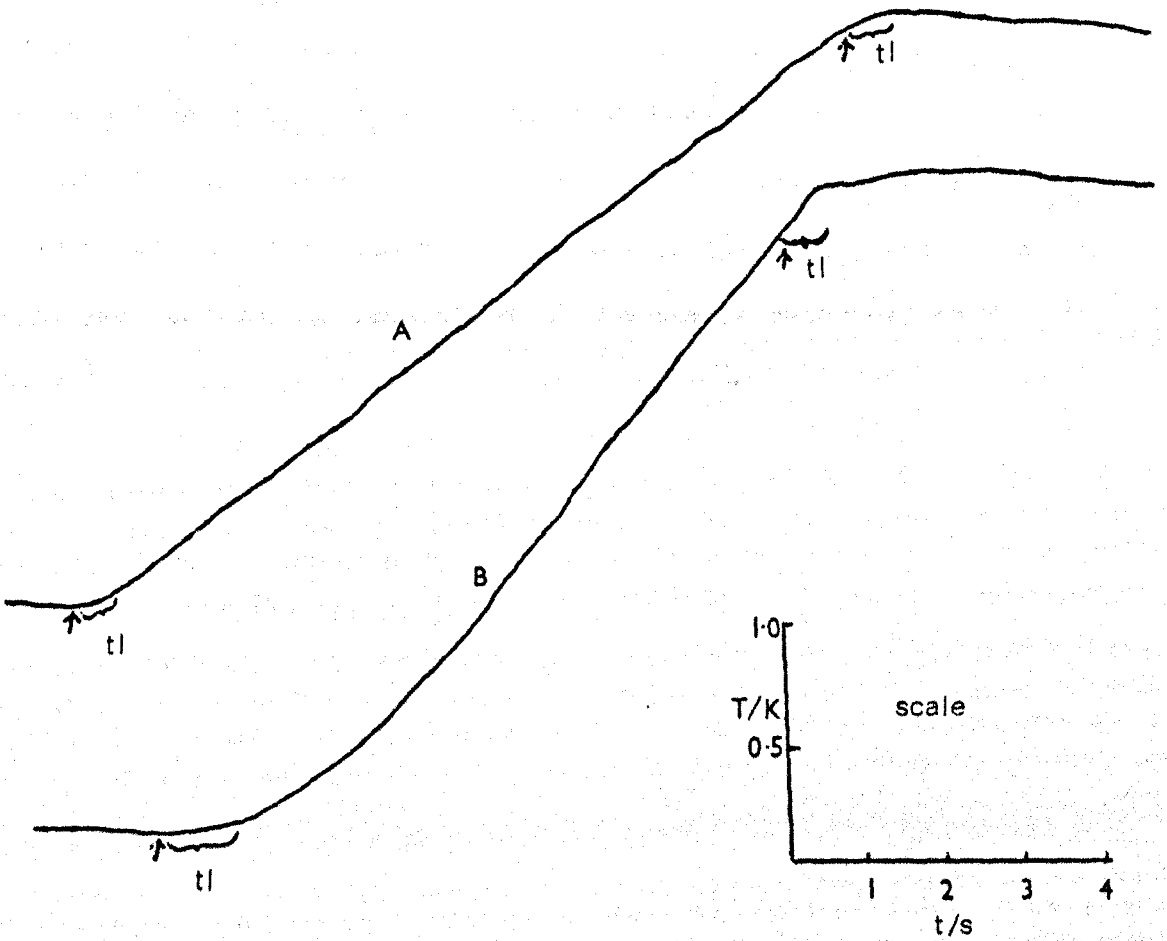
B= tube heater (Fig.4.3.7)

t.l. = time lag for electrical switching to have effect on temperature/time curve.

= electrical switching.

$C_p(A) = 62.76 \pm 3.5$ J/K

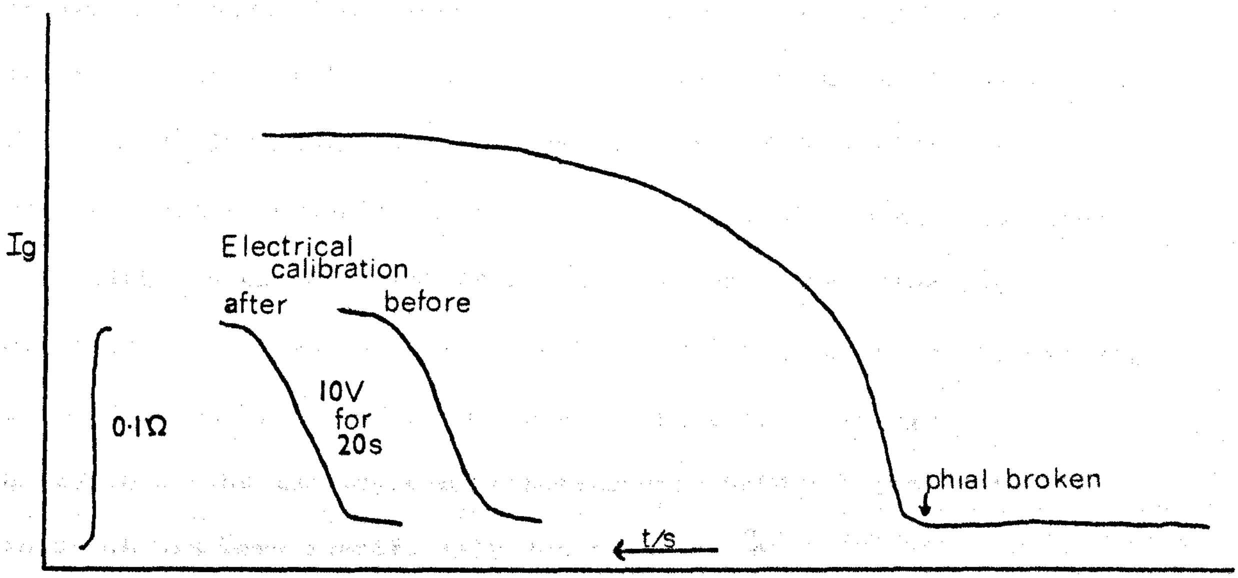
$C_p(B) = 66.23 \pm 4.1$ J/K


t1
t1
A
B
t1
t1
1·0
T/K
scale
0·5
1
2
3
4
t/s

4.4.6: Kinetic experiments.

As well as testing the calorimeter by electrical calibration and simple physical experiments it was used for several kinetic experiments. Unfortunately the complicated chemistry of the isobutylene/$C_2H_5CO^+SbF_6^-$/CH_2Cl_2 system meant that the early tests failed (See Chapter 1.4.), and no more experiments with isobutylene were done. However, towards the end of this work the calorimeter was used to measure the kinetics for the polymerisation of acenaphthylene in $C_6H_5NO_2$ with $(C_6H_5)_2HC^+SbF_6^-$ as the initiator at ambient temperature. A full galvanometer trace of one such experiment is shown in Fig. 4.4.4. The rate-constant for the polymerisation was determined in the manner described by Panton.[3]

Fig. 4.4.4: Galvanometer trace for SPAN 16.


Ig
Electrical calibration
after
before
0·1Ω
10V for 20s
phial broken
t/s

4.5: Conclusion.

At the start of this part of the work it was envisaged that the results would take the form of a modified B.P.C.. Instead, a new calorimeter has been designed and built which combines the better features of several different types of vacuum reaction vessel in use today. In addition to simply combining the best parts of the various designs the individual devices have been modified and diminished in size so that an overall reaction volume of 30 ml has been achieved.

Although the calorimeter has been shown to be effective in electrical and physical tests and for a few measurements, it has yet to be rigorously tested by being used for a full kinetic analysis of the isobutylene/carbocation salt/CH_2Cl_2 system for which it has been specifically designed.

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Chapter 5: Attempts at Synthesising and Polymerising 1- and 2- Halo Vinyl Ethers.

5.1: Proem.

Having developed a promising initiator/solvent system and proved its worth with a well known monomer there is the opportunity to try it out with new monomers. Thus, it can be argued, that systematically the following chapter on the possibility of producing polymers from 1- and 2- halo-vinyl ethers is in its correct place in this thesis. However, chronologically, this chapter should be at the beginning of the thesis, since the work was completed during the first year of the research described herein.

Because this chapter was written largely in the late summer of 1977 it has been revised more recently, and the literature has been surveyed to the end of 1979.

5.2: Introduction.

The cationic polymerisation of unsubstituted vinyl ethers has been well studied. 2-Halo-vinyl ethers have also been polymerised cationically.[1,2,3,4,] The literature on 1-halo-vinyl ethers is very sparse and as far as is known their polymerisability has not been studied.

The aim of this project was to find a simple, efficient and general synthesis for this group of compounds and to examine their polymerisability.

The project was, however, largely unsuccessful. No new, simple or general synthesis was found. The only 1-halo-vinyl ether which was made (1-chloro,1-ethoxy ethene (I)) could not be purified to a degree where cationic polymerisation was likely to be successful. The preparation which was thought to provide 1-halo vinyl ethers on a reasonably efficient scale was shown by ^{13}C NMR to produce 2-halo-vinyl ethers, a most unexpected product, at any rate at "first thought".

Much time was lost before the true structure of this product was elucidated and many unsuccessful attempts were made to polymerise the two 2-halo-vinyl ethers synthesised,(CHCl:CHOR; R = phenyl (II) & p-methoxy-phenyl (III)).

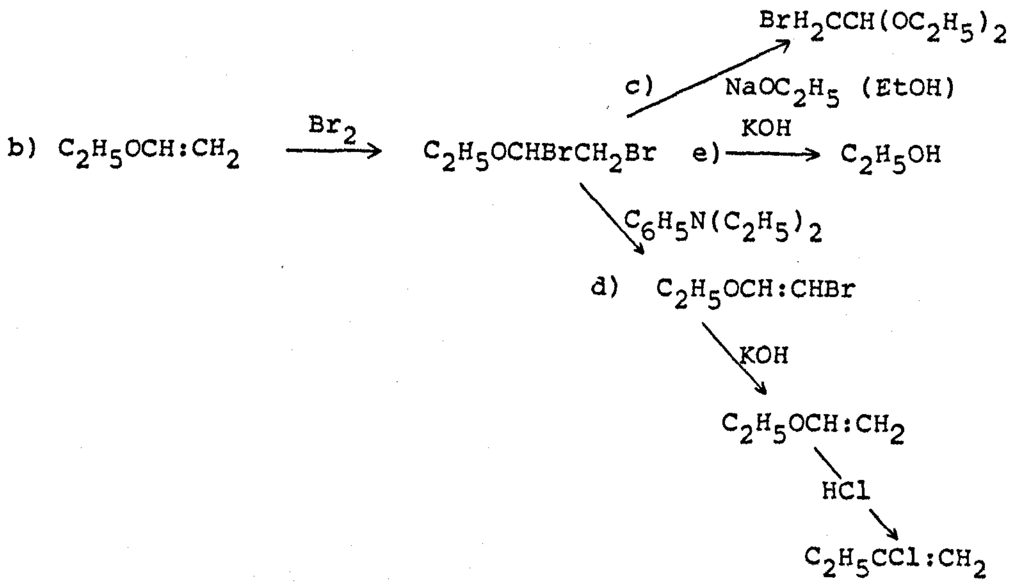
The stereochemistry of 2-halo-vinyl ethers has been studied by I.R., Raman, and NMR spectroscopy and although the cis/trans structures on the vinylic bond are now well characterised,[5] the stereochemistry about the oxygen atom is still in dispute.[6,7]

The evidence of NMR, which shows a considerable dependence of chemical shifts and coupling constants on both solvent type and concentration,[8] is somewhat ambiguous. The I.R. spectroscopy suggests that although for 2-chloro,1-methoxy ethene there are two rotational isomers for the trans form, for the cis form there are no such rotational isomers.[9]

That 2-halo-vinyl ethers do polymerise has been known since 1950 when Van Dorp et al.[10] noted that pure 2-chloro,1-ethoxy ethene polymerised spontaneously to a glassy solid. In the same year Shostakovskii and Sidel'kovskaya[1] recorded that 2-chloro-vinyl alkyl (Et,nBu,iPr) ethers will polymerise with $SnCl_4$ and $FeCl_3$ but not with Bz_2O_2. However, Price and Schwann[11] record that 2-chloro,1-ethoxy ethene does polymerise via a radical mechanism, albeit sluggishly and produces only oligomers. Apart from the patent literature[12,13] there are few references to the cationic polymerisation of 2-halo-vinyl ethers. Okuyama and Fueno[3] have copolymerised the two stereoisomers, and each of the isomers with vinyl isobutyl ether. They record that the cis-isomer is more reactive than the trans form by a factor of ca. 5 and that the cis form is less reactive than vinyl isobutyl ether by a factor of ca. 25. A similar cis/trans "reactivity ratio" is recorded more recently by Hirokawa et al..[4] Natta et al.[2] have studied this group of monomers to examine stereospecific polymerisation mechanisms. They concluded that both isomers propagate via a cis opening of the double bond to produce two different isomeric polymer structures; however, poly(cis,2-chloro,1-ethoxy ethene) has at least three different isomeric structures[4] and thus the conclusions of Natta et al.,[2] although seemingly correct for the trans isomer, are probably a simplification of the real situation.

Scheme 5.3.1.

a) $CH_2{:}CCl_2 + C_2H_5ONa \longrightarrow$ No products.



f) $C_2H_5OCOCH_3 \xrightarrow{PCl_5}$ No products.

5.3: Experimental.

5.3.1: Preparation of monomers, solvents and reagents.

All solvents for use in the preparation of monomers were dried and distilled in the usual manner[14,15] if appropriate. Other reagents were examined by G.L.C., NMR and I.R. before use and when necessary were purified according to the literature.[14] Vinylidene chloride was used as supplied by Koch Light, (Puriss.stab.)

1-chloro,1-ethoxy ethene.(I)

Scheme 5.3.1 shows the various ways in which we attempted to synthesise the title compound and summarises the results of these attempts. Short notes on the experiments are given below.

Notes to Scheme 5.3.1.

a) The reaction was done in $(C_2H_5)_2O$ at ambient and reflux temperatures under dry nitrogen. Kuryla and Leis[16] reported similar findings although no explanation is given as to why the reaction gives ketene acetals when "non-simple" alcohols, for example, 2-ethoxy-ethanol, are used.

b) The bromination of ethyl vinyl ether was carried out at ice/salt bath temperatures, (263 to 268 K).[17]

c) The crude brominated ether from b) was added to a solution of $NaOC_2H_5$ in abs. C_2H_5OH at ambient temperature. When all the ether had been added the mixture was refluxed for two hours before being fractionally distilled. McElvain and Fajardo-Pinzon[18] made 1-bromo, 1-phenoxy ethene in this way, with yields in excess of 18%.

The only product isolated from this reaction, (65%) was identified as 1-bromo-2,2-diethoxy ethane, the major product recorded by McElvain et al. when the reactants were added in the reverse order. No 1-bromo ether was isolated.

d) This synthetic route was used by Arens et al..[19] The ethoxy acetylene was synthesised according to Nazarov et al..[17] The yields obtained were similar to those of previous workers, (ca. 17% referred to the ethoxy ethene starting material). It should be noted that the first stage of dehydrobromination can be extremely dangerous.[20] The temperature of the diethyl aniline mixture must not rise above 378 K. If no product has distilled over before this temperature is reached, the mixture should be allowed to cool and should be discarded. It has been known for such mixtures to explode, although this did not happen during the work described here.

It is advantageous to grind the KOH for the second stage of the dehydrobromination to a fine powder under nitrogen. Best results were obtained when a fresh bottle of KOH was used.

e) Klementschitz and Gischthaler[21] used this route to prepare 1-chloro, 1-phenoxy ethene in very low yield, (0.05%) from the phenyl ester. Since the product was known to hydrolyse, the work-up suggested in the reference was not used. The reactants, (39.0 g of $CH_3CO_2C_2H_5$ and 102.0 g of PCl_5) were refluxed in carefully dried apparatus flushed with dry nitrogen. Small samples of the distillate were taken at hourly intervals for 5 h and analysed by G.L.C. and NMR. No sign of even small amounts of product were seen.

The product from route c) was used in the polymerisation reactions. The major impurity was the hydrolysis product of the ether, ethyl acetate.[19] Careful distillation even under rigorously dry conditions did not yield spectroscopically pure material. The best results were obtained by first distilling the material carefully under dry nitrogen and then transferring it, quickly, to a flask containing PCl_5. The latter was then attached to a vacuum line. After degassing the liquid by the freeze-pump-thaw technique, the liquid was distilled onto activated charcoal where it was stored and warmed for 24 h before being redistilled ready for use. It was found that distillation straight from charcoal into the reaction vessel resulted, even with great care, in some of the charcoal being taken over into the reaction vessel. This purification technique was found to reduce the amount of ethyl acetate remaining in the sample to ca. 2%.

1-chloro, 1-ethoxy ethene: b.p. 362-3 K / 760 mm Hg.
(Lit.[19] 363.5-366.5 K.)
n_D^{25} 1.4202 (Lit.[19] 1.4128)

1-Chloro, 2-phenoxy ethene (II).

For this compound a preparation in a patent[22] was reproduced and modified. (Scheme 5.3.2) The attempts to reproduce the patent using an autoclave, both with water and with toluene as solvents were unsuccessful. With water as the solvent, a catalytic amount of copper filings was added at the second attempt.[23] It should be noted that the pressures produced during these reactions in aqueous medium were as high as 147.5 atmos. at 468 K which indicates that at these temperatures the mixture is not homogeneous. Attempts to reproduce the patent using aqueous medium resulted in the formation of very viscous black tar from which no products were isolated despite extraction with hexane, acetone and CH_2Cl_2. With toluene as solvent the phenoxide was made from metallic K and C_6H_5OH before being transferred to the autoclave. A very small amount of (II) was isolated from this reaction.

Scheme 5.3.2.

$$CH_2CCl_2 + KOC_6H_5 \xrightarrow[\substack{420\text{-}440\ K \\ \text{high p.}}]{} CH_2CClOC_6H_5 + KCl$$

The conditions of reaction were modified to improve the yield. To this end several cyclic ethers were tried as solvents. The addition of TMEDA to a solution of $NaOC_6H_5$ was also tried. This last attempt gave no high boiling products at all. An example of the method used is given below.

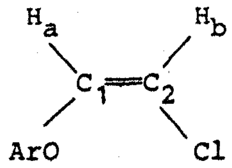
0.5 mol of KOC_6H_5 in 600 ml of 1,4-dioxan, freshly distilled from CaH_2, was prepared in the usual way. The slurry, while still warm, was transferred to a 1 l autoclave which was then

Table 5.3.1.

NMR Data for Compounds II and III*.

Compound	Vinylic H ppm (J Hz)	Aromatic and aliphatic H ppm (J Hz)	^{13}C Chem. Shift/ppm C_1	 C_2
II	H_a 6.6 (1H,d)	6.8-7.3 (5H,m)	99.1	142.0
	H_b 5.45 (1H,d)			
	(J_{ab} = 5)			
III	H_a 6.55 (1H,d)	6.75(4H,d)	98.6	142.7
	H_b 5.3 (1H,d)	(J = 3)		
	(J_{ab} = 5)	3.55 (3H,s)		

* The structure and numbering used in the table refer to:



^1H NMR spectra were recorded on a Perkin-Elmer 60MHz machine with 10% samples in CCl_4. ppm relative to TMS = 0.

^{13}C NMR spectra were recorded on a Jeol 100MHz machine with 10% samples in $CDCl_3$, ppm relative to TMS = 0.

flushed with nitrogen while it was cooled in an ice bath to ca. 298 K. Then 1.0 mol of vinylidene chloride was added and the vessel was sealed quickly. The autoclave was then heated to 448 K (p = 140 p.s.i.) for 4 h. After allowing the reactor to cool it was opened and the liquid contents were then extracted with a filter stick connected via a 1 l flask to a water pump. The dioxan was then removed on a "Rotavapor" and 200 ml of hexane were added. The resulting slurry was then filtered and the filtrate returned to the "Rotavapor" to remove the bulk of the hexane. The residue, (ca. 100 ml) was then placed over CaH_2 and fractionally distilled on a spinning band column. 25.0 ml of 99.9% pure material was collected. This was a colourless liquid. b.p. 361 K /12 mm Hg.
(Lit.[6] 347-50 K /4 mm Hg.) (Yield; 40%)

Washing the product in hexane with 10% NaOH aq. did not lower the phenolic impurities in the final product significantly. This procedure was not repeated.

1-Chloro, 2-(4-methoxy)phenoxy ethene (III) and 1-chloro, 2-(4-chloro)phenoxy ethene (IV).

A similar method was used to prepare (III). For this preparation the best yields were obtained with a temperature of 403 K (p = 65 p.s.i.). No significant improvement in yield was obtained by longer reaction times or higher temperatures. After fractionally distilling the product on a spinning band column 10.0 ml of 99.5% pure material was obtained. This was a colourless liquid. b.p. 397-9 K /1 mm Hg. n_D^{25}: 1.5463.

A small scale Carius tube experiment was used to examine the posibility of making IV, but only trace amounts of product were produced after 5 h at 425 K. No higher temperature could be used for the small scale experiments with safety because of the pressures involved.

Final purification of the materials for the polymerisation tests was accomplished in vacuo. The unsubstituted phenyl ether II was distilled from Na ribbon. This procedure led to the formation of tar when tried with III; subsequently this compound was distilled from CaH_2.

Although the patent[22] reports that the 1-chloro ethers can be prepared in this way, the products from the above preparations were shown to be the cis-2-chloro derivatives by comparison of their NMR spectra and their physical data with the literature.[6,24] The NMR data are tabulated in Table 5.3.1.

5.4: Polymerisatons.

The report that follows is in two sections. The first concerns the efforts to polymerise I and includes information on the basic techniques which were used in the subsequent trials on II and III which are described in Section 5.4.2.

5.4.1.1: Solvents.

CH_2Cl_2 was purified as described in Chapter 1.

Propylene dichloride (PDC) was used as supplied by Aldrich Chem. Co.. It was analysed by G.L.C. before use and stored in vacuo over CaH_2. It was freshly distilled in vacuo before each experiment.

5.4.1.2: Initiators.

BF_3Et_2O: As supplied by B.D.H..

$HgCl_2$ and $CdCl_2$: These were washed with CH_2Cl_2 and dried in vacuo before use.

$AlCl_3$: The anhydrous coumpound (B.D.H.) was placed in a boiling tube and covered with ca. 10 ml of CH_2Cl_2. This was then boiled for a few minutes. The CH_2Cl_2 was decanted and the process repeated until the liquid remained clear on cooling. The clear solution was then decanted and used immediately.

CF_3CO_2H: Used as supplied. (Koch Light.)

I_2: This was sublimed in vacuo before use.

$AgClO_4$: Used as supplied. (Hopkins and Williams.)

$TiCl_4$: Used as a 1% solution in CH_2Cl_2 made from freshly broken phials of $TiCl_4$.

5.4.1.3: Killing agents.

MeOH: Used as supplied.

H_2O: Deionised and distilled water was used.

Et_3N: Used as supplied. (Hopkins and Williams.)

$(C_6H_5)_3N$: Used as supplied. (B.D.H.)

1,1-diphenyl ethene: Used as supplied. (Koch Light.)

In the experiments with II and III the aim was to isolate the unhydrolysed polymer. Et_3N, $(C_6H_5)_3N$ and 1,1-diphenyl ethene were used as the killing agent. Et_3N allowed the analysis of end-groups by NMR. Where this was done it indicated that almost all of the oligomer chains were terminated by $-N^+Et_3$.

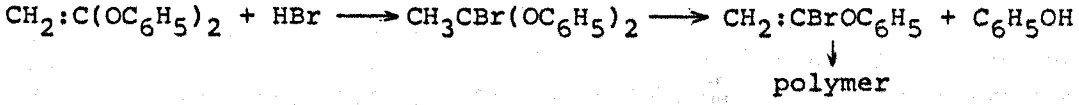
The $(C_6H_5)_3N$ and 1,1-diphenyl ethene permitted end-group analysis by U.V.. The latter had the advantage that there was no possibility of attack along the chain. The analysis of end-groups in this way was not studied in depth and no conclusive evidence was obtained.

5.4.1.4: 1-Chloro, 1-ethoxy ethene.

1-Halo-vinyl ethers have not been polymerised before. The information on this group of compounds is confined to their use as organic intermediates in the synthesis of ketene acetals.

McElvain et al.[18] reported that 1-bromo-1,1-diphenoxy ethane decomposed into phenol and a brown viscous polymer when an attempt was made to distil it. Their explanation of this is given by Scheme 5.4.1.

Scheme 5.4.1.

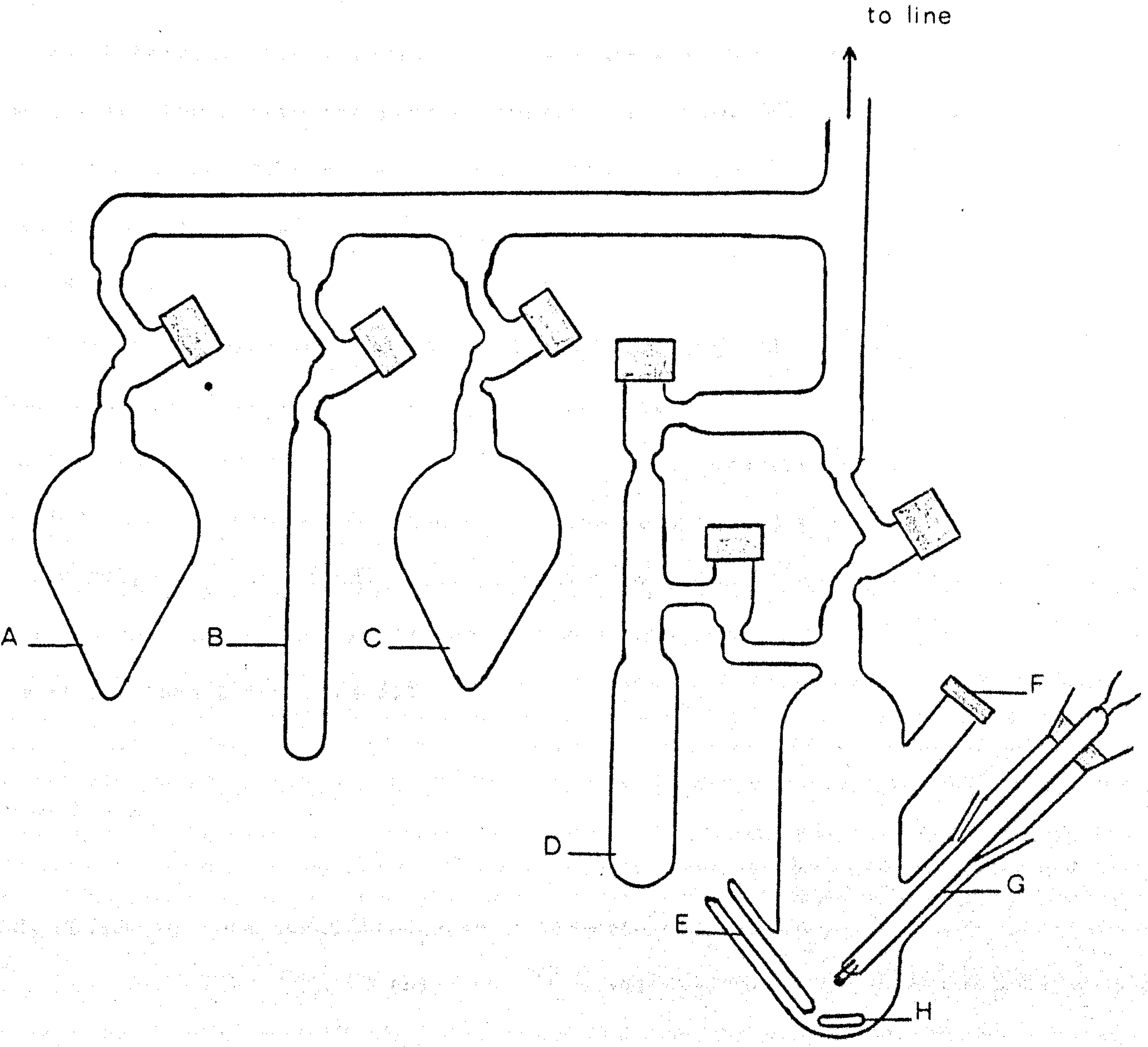


$$CH_2{:}C(OC_6H_5)_2 + HBr \longrightarrow CH_3CBr(OC_6H_5)_2 \longrightarrow \underset{\substack{\downarrow \\ \text{polymer}}}{CH_2{:}CBrOC_6H_5} + C_6H_5OH$$

The initial tests on I suggested that it might polymerise with both BF_3Et_2O and metal halide initiators. Protonic acid initiators reacted with I to form acid chlorides and ethyl acetate. Bz_2O_2 in boiling benzene under dry nitrogen gave no polymeric products. The solution was not analysed further. Hydrolysis of I was a major problem and further attempts at polymerisation were carried out in vacuo. Fig 5.4.1 shows the apparatus used. Temperature changes were measured with a thermistor connected via a Rikadenki (Model A10) micro voltmeter to a Rikadenki two pen recorder. Conductivity was measured by a Wayne Kerr Bridge and Auto Balance and was recorded in the same manner. All glassware was thoroughly cleaned before being pumped out on the vacuum line. An example of the method is given below.

Fig.5.4.1: Apparatus for vacuum polymerisation tests on II and III.

Key: A= monomer reservoir.
B= hanging burette.
C= hexane reservoir.
D= freshly distilled hexane.
E= thermocouple pocket.
F= silicone rubber seal.
G= "Plade C" electrode.
H= magnetic stirrer.


to line
A
B
C
D
E
F
G
H

5.4.1.5: Experimental method for test polymerisations.

All joints were greased with Edwards high vacuum grease. The system was pumped out, after checking for leaks, for two hours or until no Tesla coil disharge was seen. The solvent was then run into the apparatus from a burette. The monomer was then distilled from its reservoir into the hanging burette (See Fig.5.4.1.) and from there into the reaction vessel. The initiator was then added via a silicone rubber seal with a syringe. The killing agent was added in the same way.

Experiments were carried out with the following initiators: $AlCl_3$, BF_3Et_2O, $CdCl_2$. $HgCl_2$ and I_2. The monomer to initiator ratio was varied from 10 to 100. Temperature was varied from 190 to 298 K and monomer concentrations were varied from 1.0 M to bulk polymerisation conditions. No polymeric products were isolated either as the simple polymer (A) or as the hydrolysis product (B),(See Scheme 5.4.2.).

Scheme 5.4.2.

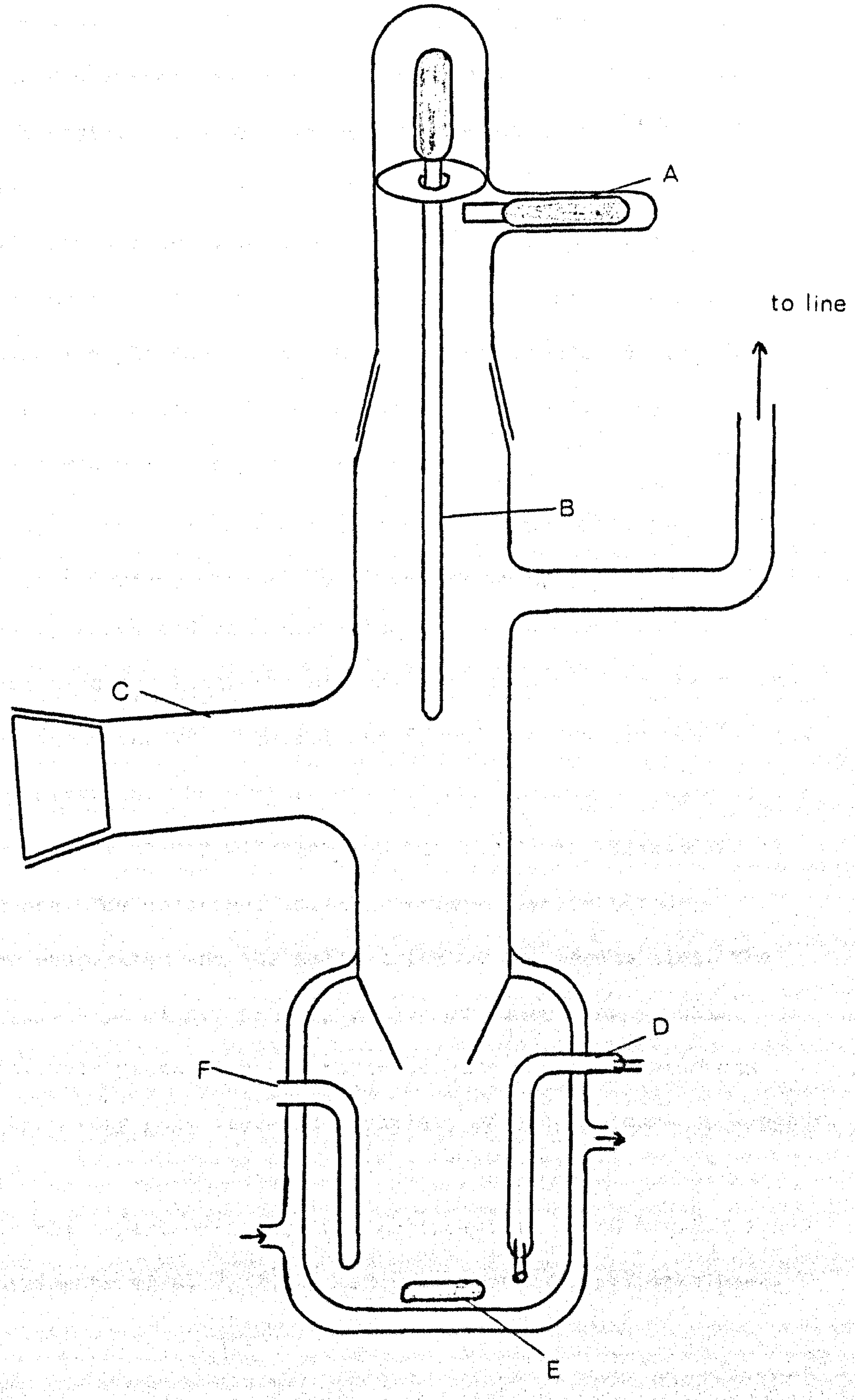
$$CH_2{:}CCl(OC_2H_5 \xrightarrow{I^+} +CH_2CCl(OC_2H_5)+_n \xrightarrow{H_2O} +CH_2CO+_n$$

(A) (B)

The products from the reactions included salts formed from the initiators and killing agents and the hydrolysis product of the monomer, ethyl acetate.

Fig.5.4.2: The modified Krummenacher reaction vessel.

Key: A= magnetically controlled glass breaker.
B= glass breaker.
C= phial magazine.
D= conductivity electrodes.
E= magnetic "demon".
F= thermocouple pocket.


A
to line
B
C
D
F
E

5.4.2: Polymerisation of II and III.

The monomers, II and III were made to react under vacuum conditions as is shown in Table 5.4.1. Where the apparatus differs from that shown in Fig.5.4.1 the experiment is marked with a star. For these experiments the apparatus was that shown in Fig.5.4.2. This is a modification of that used by Krummenacher.[24]

Test reactions under nitrogen with Bz_2O_2 in boiling C_6H_6 and with sodium naphthalene in THF gave no polymeric products and the solutions were not analysed further. A solution of II in C_6H_6 was placed in a quartz tube and irradiated with U.V. light for three weeks and apart from a slight yellowing of the solution there was no apparent reaction.

The isolation of polymers from reaction mixtures was carried out in the following manner: The reaction mixture was poured into dry hexane, which had been distilled from CaH_2 under vacuum. If no precipitate resulted, the mixture was released from the vacuum line and analysed. If a precipitate formed, the vacuum was let down with dry nitrogen. The mixture was filtered through a glass sinter under a blanket of dry nitrogen and the solid was redissolved in butan-2-one. The solution, usually orange-brown in colour, was then evaporated and the solid dried on the vacuum line. The solids were kept either under nitrogen or under vacuum until analysis. This precaution was taken because the solid products turned from very pale cream to a variety of deep colours on exposure to air.

For the experiments with the equipment shown in Fig.5.4.2 and for experiments v2/6, 7, 21 and 22 phials of reagents were used.

Phials were prepared in the manner described in Chapter 7 of this thesis and the contents determined by the mid-point method.

Table 5.4.1.

A Summary of Polymerisations of II and III.

Exp.	Solvent	T/°C	Mon.,conc.	Initiator	m_o/c_o	time[a]	D.P.[b]	% Prod. Mon.	Olig.
v1/7	CH_2Cl_2	-30	II, 2.0M	BF_3Et_2O	20	0.17h	8.4		80
v1/8	"	20	", "	"	10	8.0h	4.1		80
v1/9	"	30	", "	"	10	1.5h	2.3		60
v1/10	"	16	", "	"	20	8.0h	3.1		65
v2/1	PDC	35	", 1.0M	"	10	10.0h	3.8		95
v2/2	"	60	", "	"	10	4.0h	5.0		75
v2/3	"	75	", "	"	10	0.6h	-	95	
v2/4*	"	17	", "	$EtAlCl_2$[g]	100	0.5h	-	95	
v2/5*	"	20&40	", "	BF_3Et_2O[h]	100	24&24h	-	95	
v2/6[c]	None	85	", bulk	$EtAlCl_2$[g]	1000	0.75h	7.6[j]		95
v2/7[c]	"	20	", "	"	"	504h	-	85	
v2/8	PDC	60	", 1.5M	"	"	24h	-	90	
v2/9	"	60	", "	$CdCl_2$	10	24h	-	95	
v2/10	"	75	", "	BF_3Et_2O	10	4.0h	3.4		80
v2/11	"	60	", 1.0M	I_2	100	8.0h	-	80	
v2/12	CH_2Cl_2	-85	III, 1.0M	$TiCl_4$	100	96h[i]	3.2		75
v2/14	PDC	60	", "	BF_3Et_2O	20	20h	3.0	75	10
v2/15	"	60	", "	"	20	4.0h	-	90	5
v2/16	"	40	", "	$TiCl_4$	20	24h	-	80	
v2/17[d]	"	60	", 2.0M	BF_3(gas)	10	96h	-	80	
v2/18[d]	"	60	", "	PF_5(gas)	10	24h	-	80	
v2/19	CH_2Cl_2	24	II, 1.0M	$AgClO_4$ + CH_3OCl	500	24h		[e] not recovered	
v2/20	"	65	", "		500	24h			
v2/21[f]	None	82.5	", bulk	BF_3Et_2O[h]	20	0.5h	4.3		95
v2/22[f]	"	82.5	", "	"	20	0.5h	3.8[k]		95

Notes from Table 5.4.1.

a) The time shown is that from the time of addition of initiator to the time of addition of killing agent.

b) Molecular weights, except for experiment v1/7, were determined by vapour pressure osmometry in butan-2-one with a Mechrolab osmometer, Model 301. For the product of v1/7 the molecular weight was determined ebullioscopically in 1,4-dioxan.

c) For experiments v2/6 and 7 the apparatus is shown in Fig.5.4.3. The aim was to attempt polymerisation in bulk on freshly distilled monomer. The monomer was placed in tube A, with a few pieces of clean Na. The apparatus was then pumped for 2 h while the monomer was warmed on a water bath to maintain reflux. The monomer was then allowed to cool and the apparatus was sealed off at E. The monomer was then distilled into B until at least 1.0 ml had been collected. The tube B was then sealed off at C and a further 1.0 ml of monomer distilled into the reaction vessel D. The initator was then added by breaking the phial with the magnetic breaker. The killing agent was added in a similar manner.

d) For experiments v2/17 and 18 the apparatus used is shown in Figs.5.4.4 and 5 These reactions were done under dry nitrogen. The monomer solution was heated to 333 K before bubbling in the N_2 and BF_3, then the mixture was cooled in ice for the remainder of the reaction time.

e) The initiator for these reactions was made up in acetonitrile immediately before the reaction. The $AgClO_4$ was added first and then the CH_3COCl. A faint white precipitate was noted after the addition of the $AgClO_4$, a much heavier precipitate was noted after the addition of the CH_3COCl. After about 12 h a pink colour, attributed to colloidal silver, was observed. The reaction products were analysed by G.L.C. and NMR but were not worked up.

f) Experiments v2/21 and 22 were designed for studying the polymerisation with a dilatometer. A sketch graph for the second of these two experiments is shown in Fig.5.4.6, Fig.5.4.7 shows the temperature and conductivity changes during a typical polymerisation.

The apparatus for experiments v2/21 and 22 is shown in Fig.5.4.8. The apparatus was evacuated to a "black" vacuum and then sealed off at A. It was then immersed in a water bath for five minutes to allow temperature equilibration before initiation. For experiment v2/21 the experiment was started at 350 K, there was no apparent reaction after 30 min and the temperature was raised to 360 K, at which temperature the reaction seemed to start after about 5 min.

g) Phials of BF_3Et_2O in C_6H_5Cl were those made by Hamid.[27]

i) The mixture was allowed to come slowly to room temperature when no apparent reaction was observed after 2 h.

j) Only ca. 50% of the solid would dissolve in butan-2-one. Several other solvents were tried without success. The remaining solid was a glassy material which softened at 363-373 K and turned black above this temperature. The material also turned brown wth age even under a cover of N_2 in sealed storage vessels.

k) The unkilled reaction products were mixed with the, still liquid, fraction from the phial breaking tube, (Fig.5.4.8b.) and left over night at room temperature before being killed.

Fig.5.4.3: Apparatus for experiments v2/6 & v2/7.

Key: For A to E see text.

F= initiator phial.

G= killing reagent phial.

Fig.5.4.4: Apparatus for experiment v2/17

Key: A= H_2SO_4

B= B_2O_3 + NH_4BF_4

C= empty trap.

D= c.H_2SO_4 + H_3BO_3.

E= syringe needle.

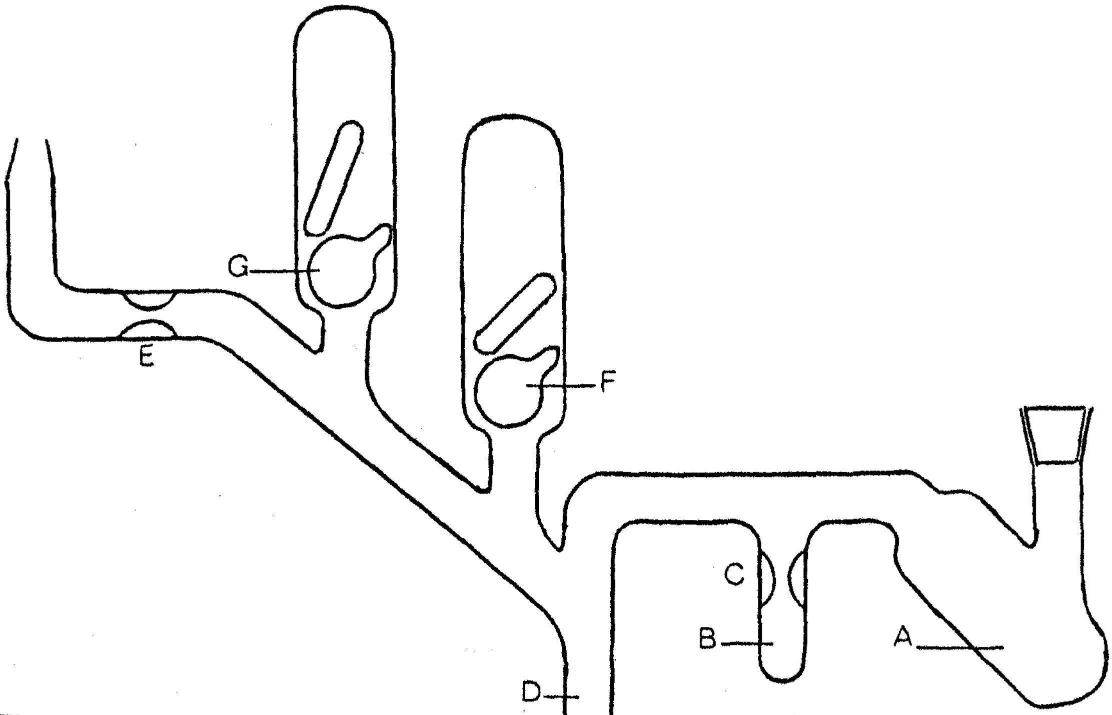
F= monomer solution.

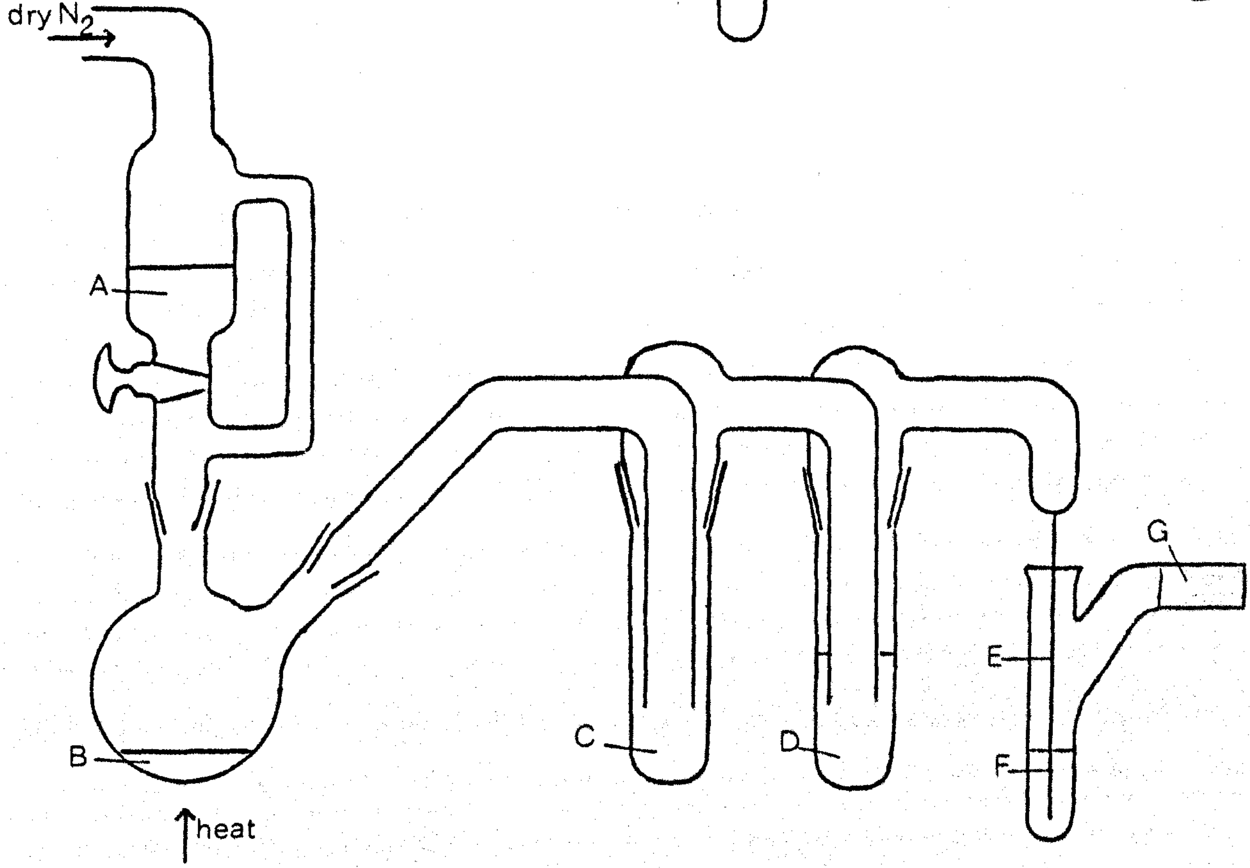
G= Si gel drying tube.

Fig.5.4.5: Apparatus to produce PF_5 for experiment v2/18.

Key: A= phosfluogen.

B= empty trap.


G
E
F
C
B
A
D


dry N2
A
B
heat
C
D
G
E
F

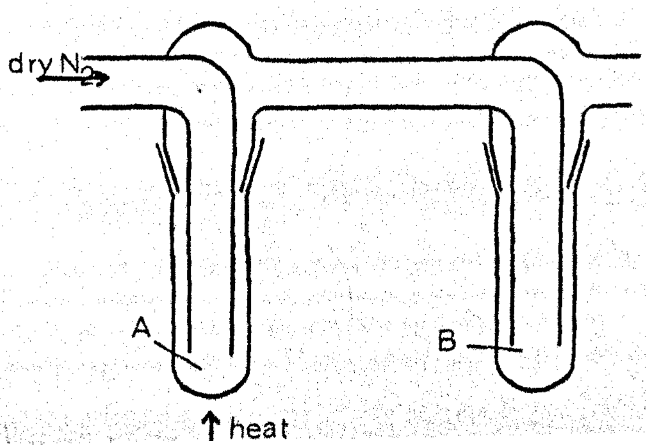
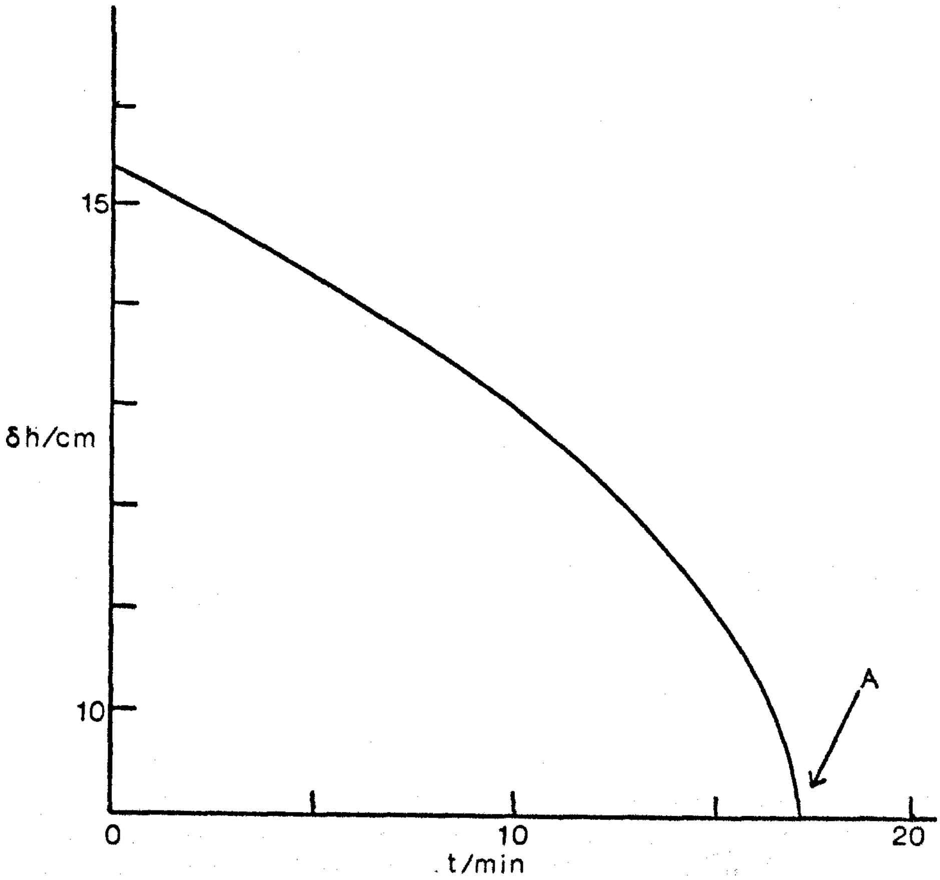

dry N2
A
B
heat

Fig.5.4.6: Graph of dilatometer readings vs.time for experiment v2/22.

n.b. After the rapid contraction of the mixture, A, the contents of the dilatometer expanded as a foam.

Fig.5.4.7: Sketch graph of the changes in temperature and conductivity vs. time for polymerisations v1/7 to v2/16.


15
δh/cm
10
A
0
10
20
t/min

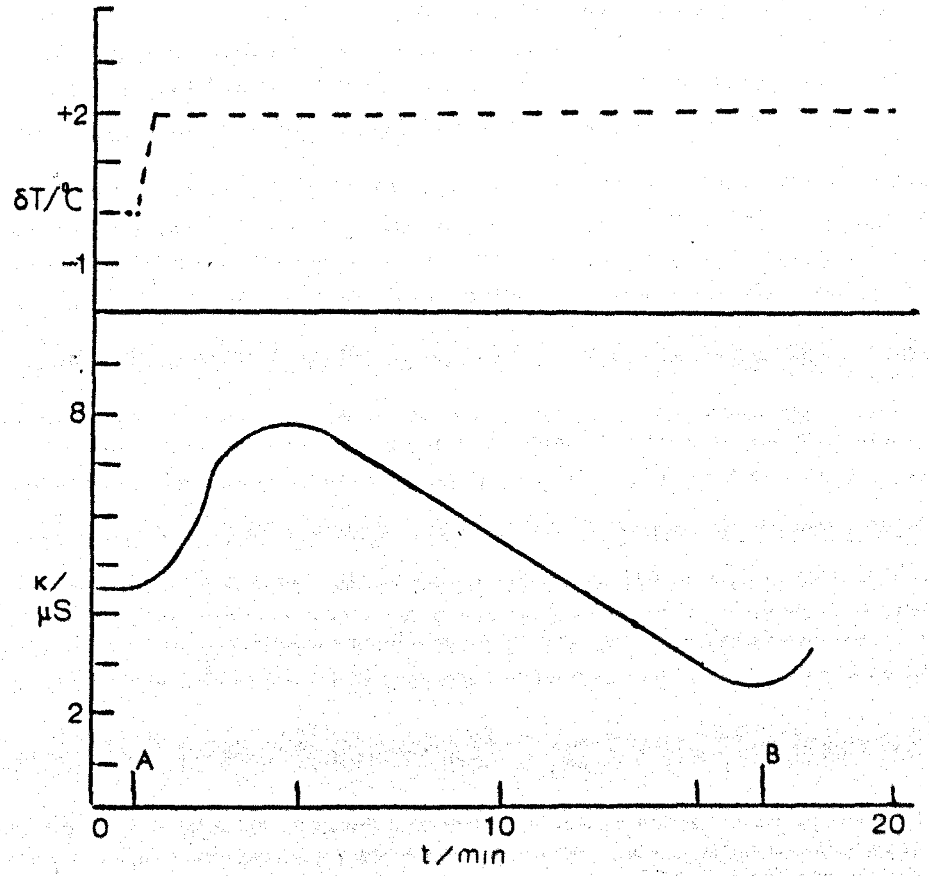

+2
δT/°C
-1
8
κ/
μS
2
A
B
0
10
20
t/min

Fig.5.4.8: Dilatometer for experiments v2/21 and 22.

Key: For A & B see text.

C= 1.2mm capillary.

D= monomer & initiator phials.

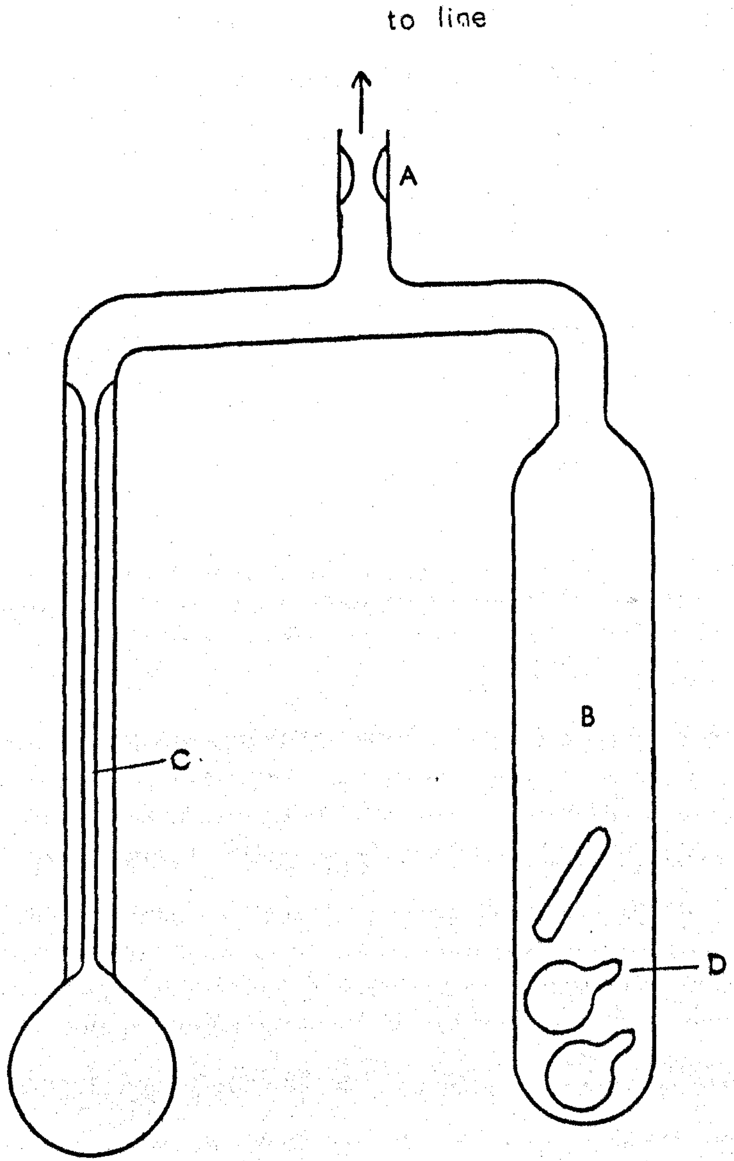

to line
A
B
C
D

Table 5.5.1: Results of the chlorine analysis of hydrolysis solutions compared with the chlorine analysis of oligomers.

Product from; Exp.No.	% of total chlorine released from oligomer into soln.		wt.% Cl in oligomer
	Acid hyd.	Alk. hyd.	(Vol. anal.)
v1/8	2%[a]	68%[b]	26.6%
v1/10	2%[a]	81%[b]	25.6%

a) No chlorine could be detected. This figure represents the error limit of the experimental method. Solutions left for one week gave similar results.

b) Analysis was after 12h of hydrolysis. Repeat experiments after a week of hydrolysis gave results close to 100%.

5.5: Hydrolysis of oligomers.

One of the suggested uses of the poly (1-halo-vinyl-aryl) ethers was as controlled release agents for biologically active materials. The substituted phenols, which are hydrolysis products, are well known as insecticides, molluscicides and antiseptics.[28]

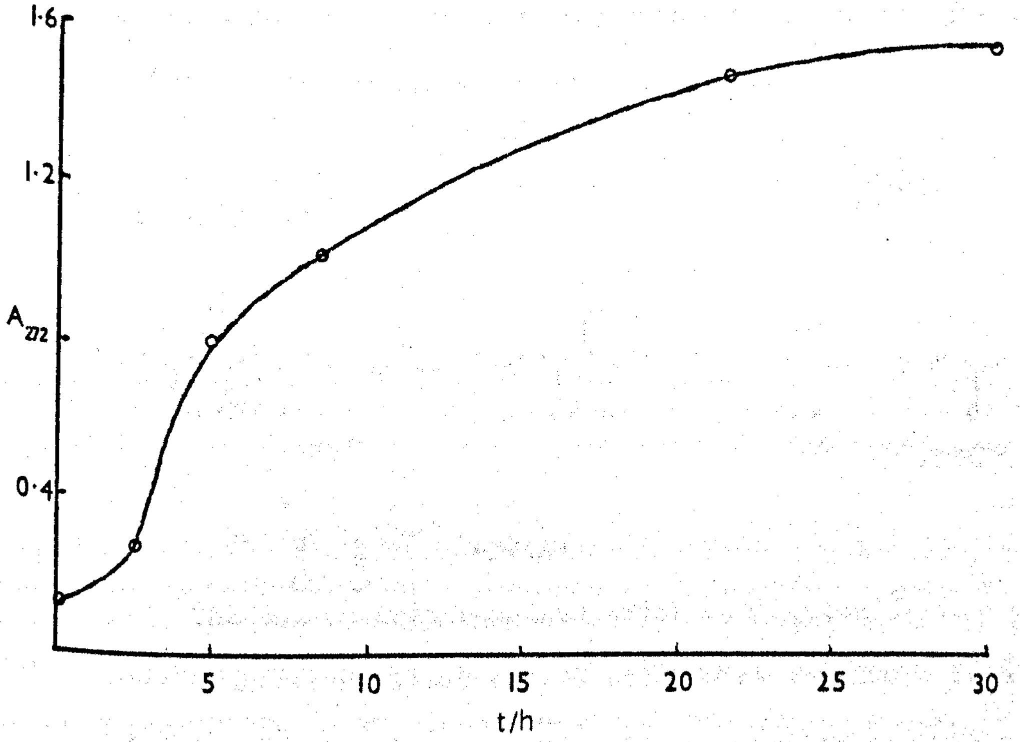
It was decided, despite the lack of high polymer formation, to examine, qualitatively, the rate of hydrolysis of the polymerisation products. In addition, a quantitative analysis of the chloride releasd from the oligomers by more vigorous acid and alkaline hydrolysis was carried out and the results were compared with a quantitative, standard chlorine analysis on the same material.

The experiments to test the rate of hydrolysis were effected by U.V. analysis of the phenol content in a water solution over the solid oligomer. The oligomers were insoluble in deionised water. ($pH = 6.75$) The experiment was carried out at ambient temperature. Fig.5.5.1 shows a graph of absorbance against time for one of these experiments. The hydrolysis of both the oligomers tested in these experiments followed a roughly first-order pattern.This result is not of great significance since the rate of hydrolysis could be governed by physical diffusion processes as well as by the purely chemical process of hydrolysis in these experiments.

The hydrolysis solutions were analysed for Cl^- by conductimetric titration with $AgNO_3$. The chlorine analysis of the oligomers was done by the standard Carius volumetric technique. The results are shown in Table 5.5.1.

For the acid hydrolysis 10% (vol/vol) H_2SO_4 was used, a few drops of HNO_3 being added before the conductimetric titrations

Fig.5.5.1: Graph of Abs_{272} vs. time for aqueous solutions above solid oligomeric II.

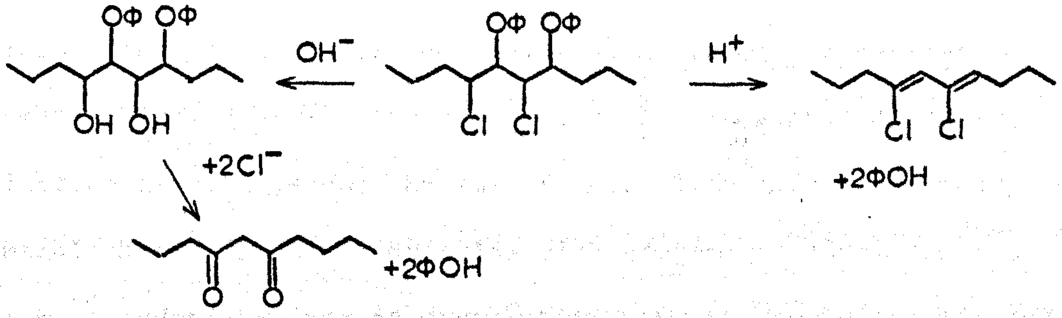

1·6
1·2
A
272
0·4
5
10
15
20
25
30
t/h

were done. The oligomers were insoluble in these solutions.

For the alkaline hydrolysis 10% (wt/wt) NaOH was used, the solutions being acidified with dil. HNO_3 before titration. On acidifying the alkaline solutions a feathery white precipitate formed which was filtered off before doing the titrations.

It is clear that the oligomers hydrolyse under alkaline (and mildly acidic) conditions to give off both chlorine and phenol. Under acid conditions the only product is phenol. The explanation of this fact is attempted in Scheme 5.5.1.

Scheme 5.5.1.



The solids that remained after completion of the hydrolysis were orange-red glassy solids which were insoluble in a wide variety of solvents. The I.R. analysis of these materials was attempted using KBr discs; no useful results were obtained.

5.6: Discussion.

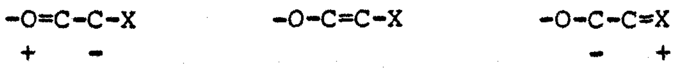
It is clear from the experimental sections that no polymers were produced from any of the compounds I,II or III. The fact that compound I did not even form oligomers was probably due to the presence of ethyl acetate which, being a base, would neutralise the initiator and trap any carbenium ions. The lack of polymer formation from II and III requires more explanation. The explanations offered here are based on considerations concerning stereochemistry, kinetics and ceiling temperature.

^{13}C chemical shifts have been reported to reflect the π-electron density of the atom under consideration;[31a,b.] this has been used[29,30,34] in attempts to correlate the ^{13}C shifts for various monomers and their reactivity with respect to cationic polymerisation. However, the correlation is not simple since the π-electron density is not the sole factor which controls either the chemical shift[33] or the reactivity with respect to electrophilic attack.[29] Indeed, a lack of correlation between chemical shift and reactivity has been used to derive information about the mechanism of polymerisation.[30]

However, the relatively high values of the ^{13}C chemical shifts for both the vinylic carbons in I and II compared with 1-ethoxy ethene[29] and styrene[34] suggest that the π-electron density on the vinylic double bond in I and II is relatively low so that one expects the cationic polymerisation of these monomers to be slow.

The double electron-pulling effect of the ether oxygen and the halogen leads to a decrease in the electron density on the double bond.[33] This can be seen from the canonical forms shown in Scheme 5.6.1.

Scheme 5.6.1.



$\underset{+}{-O}=C-\underset{-}{C}-X$ $\quad$ $-O-C=C-X$ $\quad$ $-O-\underset{-}{C}-C=\underset{+}{X}$

(a) (b) (c)

In the compounds studied by us the importance of form (a) is accentuated by resonance with the benzene ring, and the addition of a p-methoxy group to the benzene ring would lead to a further increase in this effect, which in turn leads to a relative stabilisation of the monomer with respect to cation attack. This argument is corroborated by the experimental results that III is less easily polymerised than the unsubstituted compound, II.

There are two main types of chain breaking reactions, those that involve adventitious impurities and those which are inherent to the particular system being studied. The chain breaking reactions caused by adventitious impurities can be minimised by careful purification. Low temperatures and the judicious choice of initiator and solvent can minimise the inherent chain breaking reactions.

It is possible that there were residual impurities in compounds II and III. This seems, however, unlikely since various purification techniques were tried and different solvents were used without significant change in the D.P. of the products. The figures in Table 5.4.1 suggest an increase in D.P. with an increase in temperature of polymerisation. This too suggests that adventitious impurities are not the cause of the lack of high polymer formation. Higher temperatures would also increase the rates of inherent chain breaking reactions; thus, the relationship between D.P. and temperature suggests that these are not the major causes of the lack of high polymer formation. The possibility that the polymerisation involves a stage with a large activation energy seems to give the most plausible answer to the problem of the lack of polymer formation at low temperatures. This is corroborated by the increase in D.P. with the time that the polymerisations were left before adding the killing agent. No experimental evidence can be offered to suggest the nature of the controlling stage of the reaction.

In addition, although the experimental evidence is weak, it is thought that the experimental temperatures which prevailed when rapid polymerisation took place were close to the ceiling temperature, so that high polymer formation was not possible on thermodynamic grounds.

5.7: Suggestions for further work.

As with a great deal of scientific research, the number of questions posed by the foregoing study exceeds the number of those answered.

It is clear that the polymers from phenyl substituted 2-halo-vinyl aryl ethers might prove commercially interesting materials as controlled release agents for biologically active substances. Copolymerisation with other monomers such as styrene could be interesting both as a means of raising the molecular weights of the products and possibly as a means of lowering the rate of hydrolysis. It should be noted that the method of preparing compounds II and III is almost certainly not the most efficient. Scheme 5.7.1 suggests a possible route to a variety of substituted 2-halo-vinyl-aryl ethers.

Scheme 5.7.1.

$$\mathrm{ArOCH_2CHBr} \xrightarrow{\mathrm{KOH}} \mathrm{ArOCH{:}CH_2} \xrightarrow{\mathrm{Br_2}} \mathrm{ArOCHBrCH_2Br} \xrightarrow{\mathrm{C_6H_5NEt_2}} \mathrm{ArOCH{:}CHBr}$$

The question of whether or not 1-halo-vinyl ethers do polymerise remains open. For further work on this subject it is suggested that the study should concentrate on the aryl derivatives to avoid the problems of the rapid hydrolysis of the monomers. It is suggested that a possible route to these compounds might be that reported by McElvain and Fajardo-Pinzon[8] which is shown in Scheme 5.7.2. It would also be worthwhile to examine the reaction of PCl_5 with phenyl acetate since the low yields reported in the literature[21] may result from the method of isolating the product.

Scheme 5.7.2.

$$\mathrm{ArOCH_2BrCH_2Br} \xrightarrow{\mathrm{NaOAr}} \mathrm{ArOCBr{:}CH_2}$$

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Chapter 6: Polymerisation of Oxacyclic Compounds. (Work Done at Łodz, Poland.)

6.1.: Introduction.

In September 1979, after the work described elsewhere in this thesis was completed, the author spent ten weeks in Europe, mainly in Łodz, Poland, as the guest of Prof.S.Penczek and the Polish Academy of Science (P.A.N.). Coming at the end of the author's Ph.D. work the trip provided an oportunity to put this work into perspective within a much wider context.

Table 6.1. outlines the scientific highlights of the journey from which it is apparent that the time spent in Łodz, and available for research, was less than six weeks. Thus, although it had been planned to do a short research project on the copolymerisation of tetrahydrofuran (THF) and 1,3-dioxolan (DXL), little progress was achieved.

The polymerisations of THF and DXL have been studied in great detail at Łodz but the coploymerisation of these two monomers has not been attempted before, neither, to the author's knowledge is the work being carried on by anyone in Łodz. Despite the lack of time available, a start was made on the project, but the work done will be described with an emphasis on the techniques and where applicable comparison of the techniques with those at Keele.

Although the experimental work was carried out under the guidance of Dr. Kubisa and Dr. Matyjaszewski, many useful hours of discusion were spent with the many other people in Prof. Penczek's research group which, as well as studying the cationic

Table 6.1.1.

The Scientific Highlights of the Journey.

Aug. 31st.- Sept. 1st.	Travel to Łodz, Poland.
Sept. 11th.- 13th.	Visit to Wrocław. Polish Chem. Soc. Jubilee Meeting.
Sept. 27th.	Lecture in Łodz: Vacuum Calorimetry.
Oct. 12th.- 15th.	Visit to Warsaw as a guest of Prof. Kuran, Technical University, Warsaw. Lecture: The Cationic Polymerisation of Olefins.
Oct. 23rd.	Short Lecture in Łodz: A Systematic Approach to Cationic Olefin Polymerisation.
Oct. 26th- 29th.	Stayed in Pokshivna as a guest of Prof. Nowakowska, Technical High School, Opole. Lecture: Cationic Polymerisation and its Industrial Significance.
Oct. 29th.- 30th.	Stayed in Krakow as guest of Dr. Bortel, Jagellonian University, Krakow. Lecture: Cationic Polymerisation at Keele.
Nov. 1st.	Visited Dr. Marek at the Czechoslovakian Academy of Science, Prague.
Nov. 2nd.- 7th.	Stayed in Munich, W. Germany as a guest of Dr. Nuyken, Technical University, Munich.

polymerisation of oxacyclic monomers, works on the copolymerisation of atomic sulphur with organic sulphides, the polymerisation of phosphorus-containing monomers and the polymerisation of optically active monomers initiated by optically active initiators.

6.2: Techniques and materials.

6.2.1: Glassblowing.

A great deal more glassblowing is done by the research workers in Łodz: thus, in addition to the glassblowing normally done at Keele, the author found it necessary to become adept at making break-seals and small internal seals from Pyrex tubing. Furthermore, since preformed glassware items (e.g. taps, joints, and flasks) are in short supply, it was necessary to repair items that would have been discarded at Keele.

6.2.2: Vacuum Systems.

The vacuum systems of the Łodz polymer group contain significantly more joints and taps than the Keele systems and the length of time for which apparatuses are evacuated ("pumped out") is generally about ten minutes to half an hour which is considerably shorter than the time normally allowed at Keele.

Two reasons were give for the less rigorous experimental conditions in Łodz: firstly, it was considered quicker and simpler to use taps and joints rather than an all-glass system. (Also a nearby oxygen torch is not always available.) Secondly, since the concentrations of initiators used are generally greater than 10^{-3} M and the oxacyclic polymerisations are inherently less sensitive to water than olefin polymerisations, because of the relative basicities of the monomers and water, a higher residual water concentration can be tolerated without affecting experimental reproducibility. Thus, the philosophy in Łodz is: make the system clean enough to yield reproducible, consistent, results .

6.2.3: Calibrated break-seals and phials.

Because of the short pumping time allowed, it is found to be quicker and simpler to make and fill individual phials or break-seals attached to a joint, (See Fig.6.2.1) rather than to use the tipping device traditionally used at Keele.

Phials are generally used in Łodz only for solid reagents, and liquids or solutions are more often handled in calibrated break-seals. The preparation of a calibrated breakseal is best demonstrated by the sequence of diagrams in Fig.6.2.2. The breakseal is constructed, a, calibrated with a known volume[*], b, and then filled, c. It can then be sealed off from the vacuum line by freezing a plug of liquid in the narrow tube. Since the internal diameter of the narrow tube is known (ca. 2.0 mm), the volume in a given length of tube is also known and therefore the actual volume of liquid in the breakseal can be calculated. (Eq.6.2.2.) The method is very useful and is applicable when volumes greater than ca. 0.5 ml are being handled. The lower limit is due to the difficulties in constructing smaller break-seals rather than the errors involved which are $< 10^{-3}$ ml.

[*] Volumes were calibrated with a dial syringe. Vib. Glasswerke. Ilmenau.

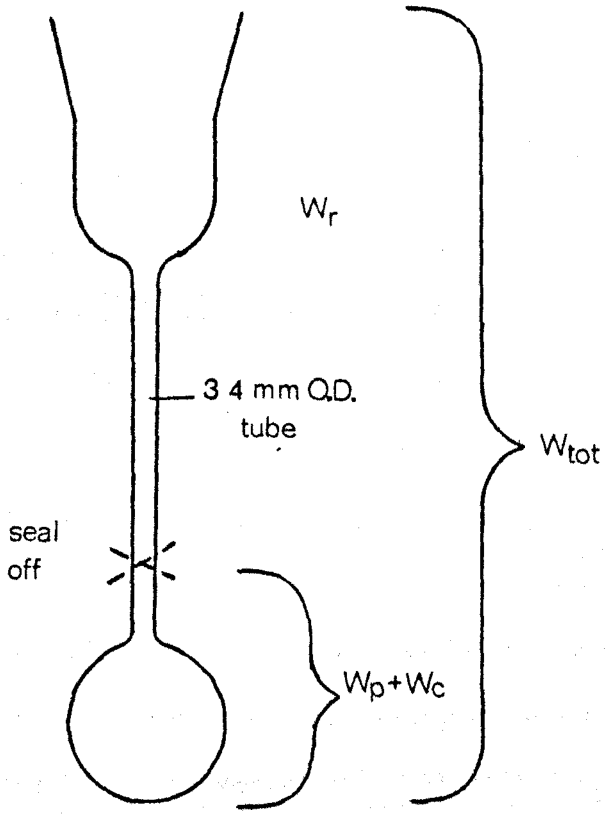
Fig.6.2.1: A vacuum phial attached to a joint.

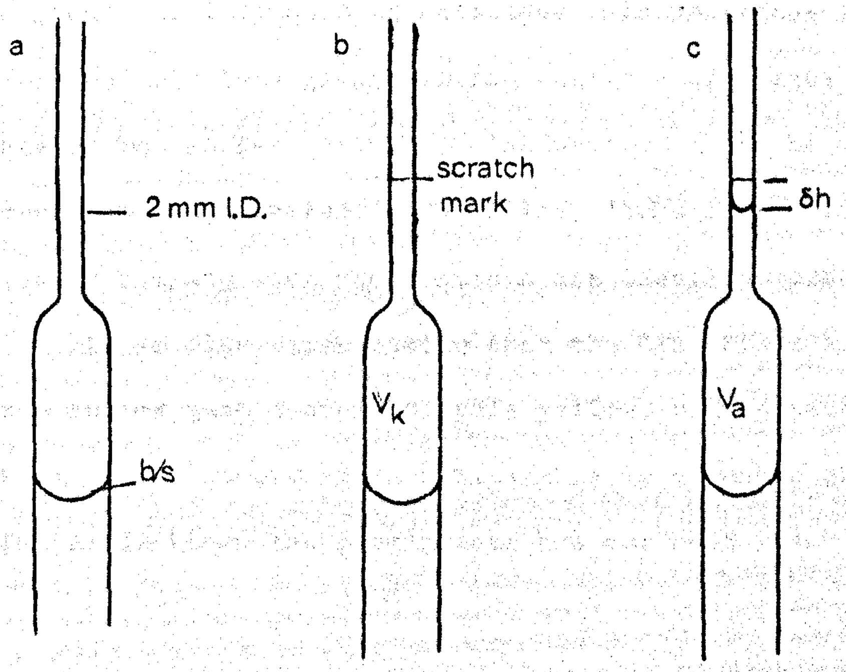
$$(W_r + W_p + W_c) - W_{tot} = W_c \qquad \text{Eq.6.2.1}$$

where W_c = the weight of the contents.

Fig.6.2.2: Calibrated breakseals.

$$V_k - (d/2)^2\ h = V_a \qquad \text{Eq.6.2.2}$$


W_r
3 4 mm O.D. tube
W_{tot}
seal off
W_p+W_c


a
2 mm I.D.
b/s
b
scratch mark
V_k
c
δh
V_a

6.2.4: Preparation of benzoyl hexafluoroantimonate.

The preparation of this salt has already been described in Section 1.3.2 and the treatment of the chemicals used in the preparation is discussed in Section 1.3.1. It should be noted that the use of a jointed apparatus, even for this air and moisture sensitive compound was found to be practical.

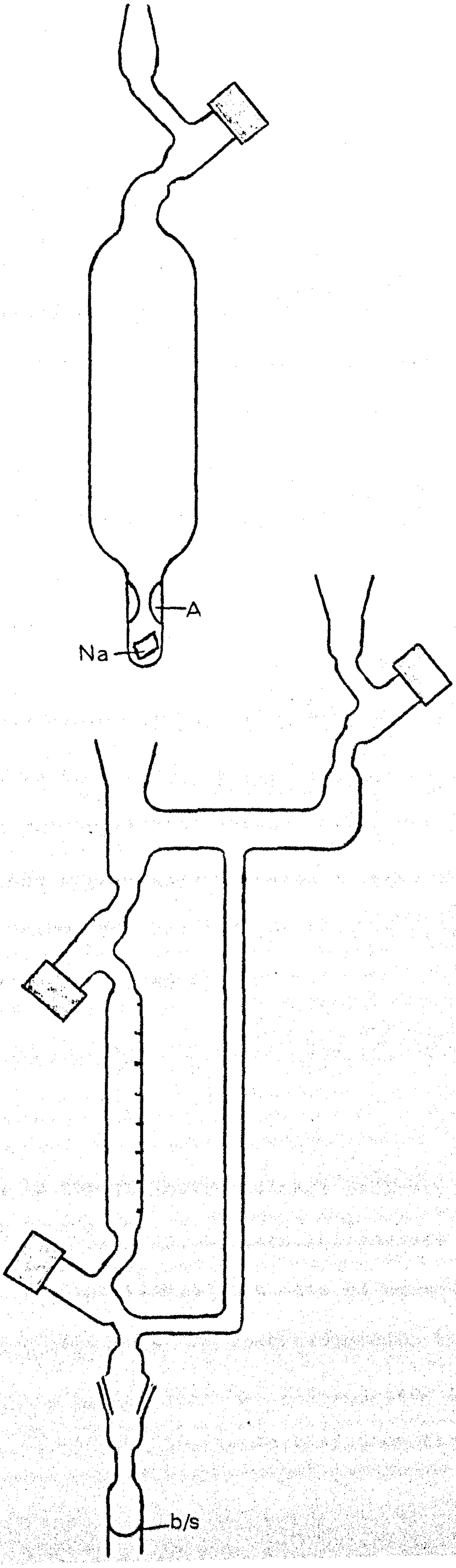
6.2.5: THF, DXL and CH_2Cl_2.

The purification of these chemicals has been described.[1,2] It is interesting to compare the reservoir designs used for these materials. The general storage vessel used, partly because of the shortage of preformed glassware, is an ampoule with a teflon tap. A sodium mirror is made by the simple arrangement shown in Fig.6.2.3; the Na is heated until the mirror is formed and the residue is then sealed of at the restriction, A. Much to the surprise of the author, ends sealed in this way were frequently frozen in liq. N_2 without any incidence of breakage. This apparatus involves considerably less glass-blowing than the apparatus generally used at Keele[4] but suffers from the disadvantage that the sodium mirror cannot be regenerated. In addition, "tube reservoirs" can lead to severe bumping when the contents are distilled out.

It is also worth noting that the DXL (Fluka A.G.) purified by the author gave a copious, pale yellow, precipitate when stored over Na/K alloy. According to Kubisa this is a common phenomenon but as far as is known the precipitate has not been identified.

Fig.6.2.3: "Tube reservoir" and sodium mirror.

Fig.6.2.4: Apparatus for distribution of liquids into phials or breakseals (b/s).


A
Na
b/s

6.2.6: Sodium ethoxide.

A solution of ca. 1.0 mol l^{-1} $NaOC_2H_5$ in C_2H_5OH was made by letting Na, twice distilled in vacuo, react with abs. C_2H_5OH which had been distilled from Na in vacuo. The resulting solution, which remained colourless for six weeks, was distributed into break-seals in the apparatus shown in Fig. 6.2.4. This apparatus is similar to that devised by Holdcroft[5] but the arrangement of taps shown here allows the contents of the burette to be isolated while the breakseal is sealed off and replaced.

6.2.7: Triphenyl phosphine.

This compound was recrystallised from abs. C_2H_5OH and immediately transferred to a vacuum phial. A solution in CH_2Cl_2 was then prepared in vacuo and distributed into calibrated break-seals. One of the break-seals prepared in this way was attached to an NMR tube (See below) and the ^{31}P spectrum recorded to ensure that no phosphine oxide was present.

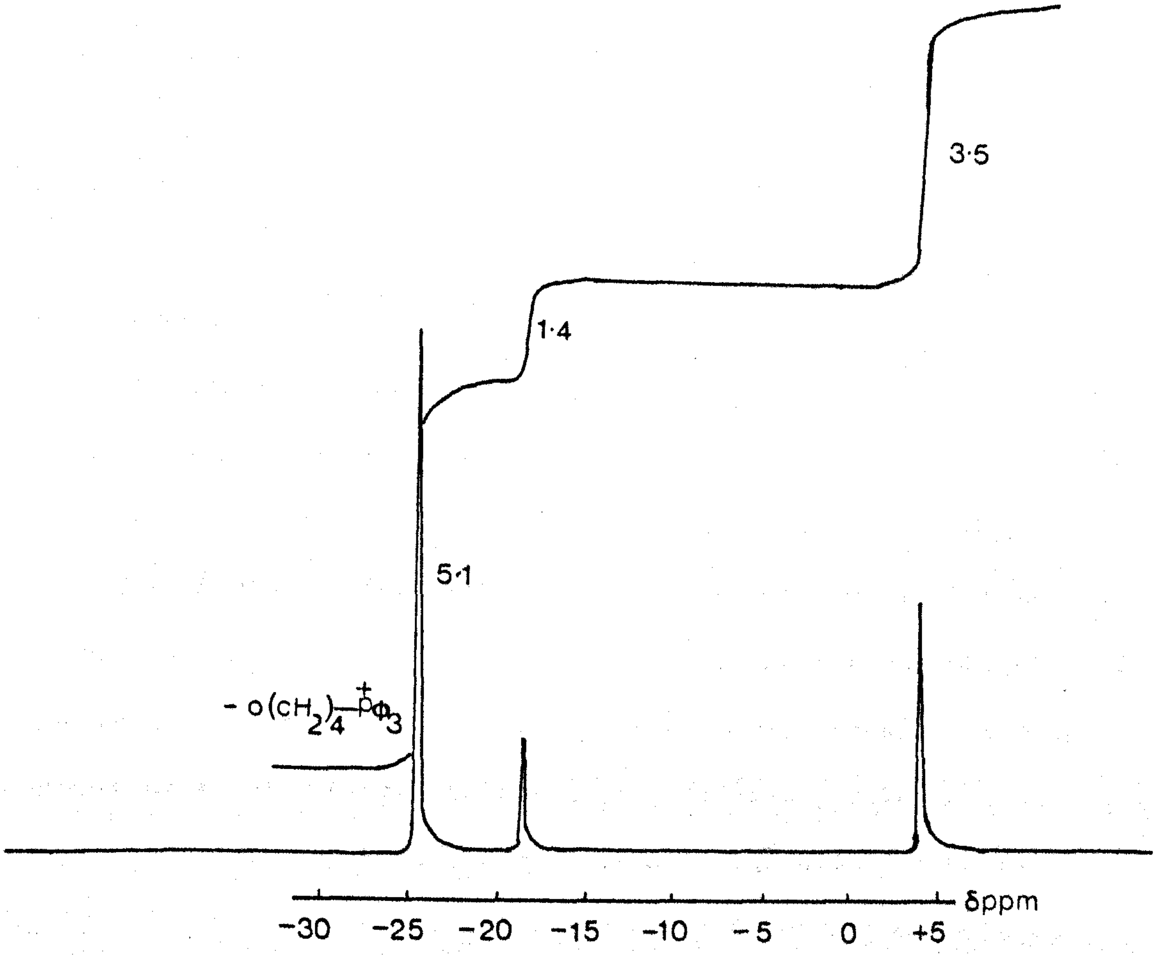
6.2.8: NMR tubes.

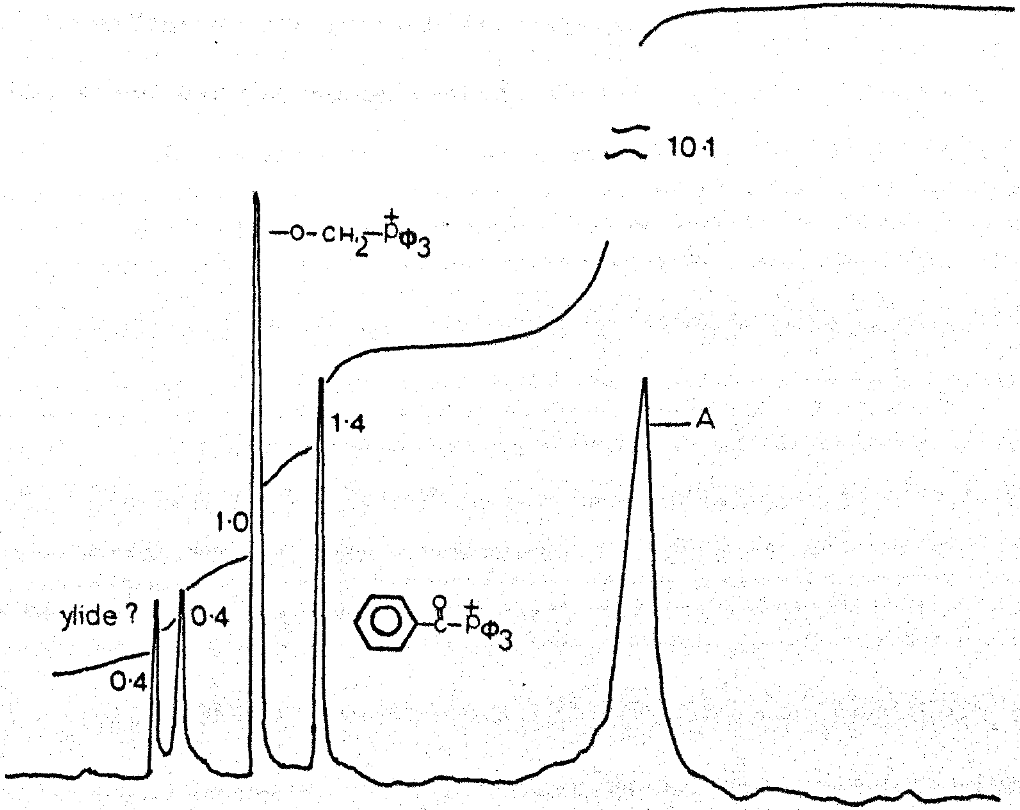
These were made in the following manner: ordinary thin-walled Pyrex tubing (ca. 10 mm O.D.) was cut into appropriate lengths, neatly sealed at one end and placed in a bath of aqueous HF until the outside diameter of the tube had been reduced to the correct size. (ca. 9.5 mm O.D.) After a thorough rinsing, the tubes were then checked in the NMR machine to ensure that they fitted the spinner mechanism.

Fig.6.2.5a: FPT ^{31}P NMR of living polymer terminated with $[\Phi_3P] = 5.8 \times 10^{-2}$ mol l^{-1}. Initiator; $[C_6H_5COSbF_6]_o = 3.8 \times 10^{-2}$ mol l^{-1}. $[THF]_o = 8.0$ mol l^{-1}, $[DXL]_o = 3.0$ mol l^{-1}. T = 303 K. T_{polym} = 273 K for 1 h.

Fig.6.2.5b: FPT ^{31}P NMR spectrum of living polydioxolan terminated by $[\Phi_3P] = 0.14$ mol l^{-1} $[DXL]_o = 4.0$ mol l^{-1}. $[C_6H_5COSbF_6]_o = 2.9 \times 10^{-2}$ mol l^{-1}. T = 303 K, T_{polym} = 273 K for 1 h.

Both Spectra were measured on a Jeol 60 MHz FPT NMR. Chemical shifts in ppm from 85% H_3PO_4.


3·5
1·4
5·1
- o(cH2)4-P+Φ3
-30
-25
-20
-15
-10
-5
0
+5
δppm


10·1
-o-CH2-P+Φ3
1·4
A
1·0
ylide ?
0·4
0·4
C(O)-P+Φ3

The spectrum in Fig.6.2.5.(a) was also recorded from the same sample at 273,253,203 and 190 K without any alteration in the integral ratios being observed. Neither was any alteration in the spectrum noticed when it was recorded after the sample had been stored for a week in the refrigerator, although, once prepared, samples were normally kept in liq.N_2 until their spectra could be recorded.

It should be noted that polymers terminated with a phosphonium salt are not suitable for polymer isolation and analysis since the polymeric salts are not stable and the polymers tend to degrade.

The phosphorus ion trapping technique works extremely well for polymerisations of oxacyclic monomers where concentrations of active centre are greater than 10^{-3} mol l^{-1}; at lower concentration the number of scans required to obtain a good spectrum becomes impractical. It may well prove to be a useful tool for olefin polymerisation studies although whether the technique would be sensitve enough to differentiate between the nuances of terminal structure in this field has yet to be tested.

6.3: Attempts at copolymerising THF and DXL.

Yamashita et al.[8] suggested that THF and DXL do not copolymerise in CH_2Cl_2 and this finding is corroborated by the evidence of Leonard et al.[9] However the later work of Enikolopyan[10] suggested that these monomers do copolymerise and that the rates of polymersation of each monomer are considerably lower in the copolymerisation reaction medium than in the respective homopolymersations.

Thus, the copolymerisation of THF and DXL is not clearly established. It is an interesting reaction since it could well provide information with respect to the nature of the growing species in the homopolymerisaton of DXL.[11]

The aim of the short reseach project was to study this reaction by making living THF with $C_6H_5CO^+SbF_6^-$ as the initiator, to add this solution to a solution of DXL in CH_2Cl_2 and then to kill the reaction, partly with a phosphine so that the growing ends could be identified and partly with $NaOC_2H_5$ so that the molecular weights and structures of the polymers could be analysed.

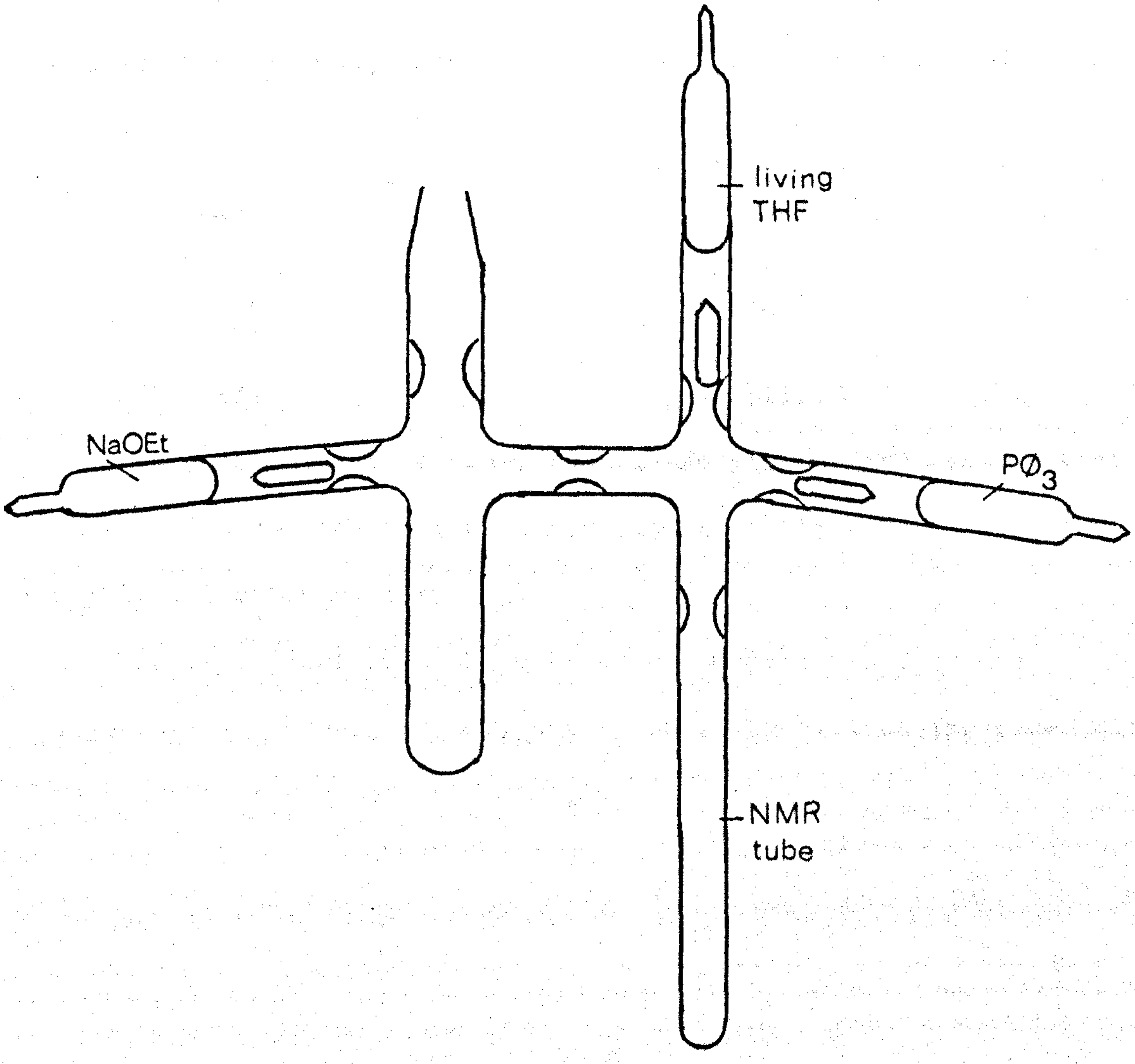
Unfortunately, in the first test experiments it was apparent that the polymerisation of DXL was not as slow in the copolymerisation system as Enikolopyan has suggested[9] and considerable difficulties were experienced in manipulating, and killing the very viscous polymer solutions.

The apparatus for the copolymerisation experiments is shown in Fig.6.3.1. It demonstrates the use of calibrated breakseals in a situation where the use of phials of reagents would have made the apparatus very much more complicated.

The final experiments which were done were carried out with

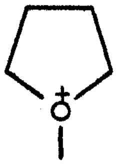
10^{-3} mol l^{-1} initiator but it was clear, from the ^{31}P spectra, that some impurity in the system, probably in the DXL, had killed off most of the growing species.

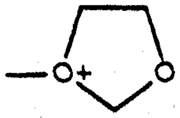
Fig.6.3.1: Apparatus for copolymerisation of THF and DXL.


living
THF
NaOEt
PØ3
NMR
tube

6.4: Conclusions.

Although three successful copolymerisation experiments were made no time was available for analysis of the polymers obtained and little useful information was obtained with respect to the copolymerisation of THF and DXL in CH_2Cl_2. However, the spectrum shown in Fig.6.2.5a does show that the growing ends derived from THF and DXL do coexist in solution and this evidence, although not necessarily implying that the two monomers do copolymerise, does suggest that ion I will attack DXL to form ion II.


(I)


(II)

In addition, it is clear from these preliminary results that the rate of DXL polymerisation is not significantly reduced in the copolymerisation medium.

Lastly, tackling a short research project provided the opportunity not only to see, but to use, the various experimental techniques of the Łodz polymer group.

6.5: Suggestions for further work.

The work described here provides the basis for a full study of the copolymerisation of THF and DXL. The next experiments should examine the nature of the growing ends and the relative monomer concentrations with respect to time. In addition a close examination of the polymers produced by G.P.C., NMR and possibly polymer degradation could then provide a demonstration of whether or not true random copolymers are produced.

6.6: Postscript.

In the nine weeks spent in Poland, and indeed in the shorter period spent, on the return jouney, in Munich, I was fortunate in gaining the experience of working in environments very different from those at Keele.

In addition to seeing at first hand a variety of different techniques and new chemistry, only a small part of which it is relevant to record here, I was able to meet chemists of different nationalities, in their very different working environments.

This chapter would not be complete without a note of extreme gratitude to Prof. Penczek and the Polish Academy of Science for providing both the financial assistance which made this journey possible and the congenial atmosphere which made the visit such a success. I am equally grateful to Prof. Kerber and Dr. Nuyken for providing financial support and hospitality during my week in Munich and to Dr. Sestakova and Dr. Marek for their hospitality during my short visit to Prague.

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135,

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Chapter 7: Improvements and an Appraisal of the "Mid-Point Method."

7.1: Technical Improvements.

7.1.1: The tube cutter.

Everyone who has practised vacuum technique is familiar with the problem of knowing what quantity of reagent is in a phial filled under vacuum.

There is a variety of answers to this problem: one can use calibrated break-seals (See Chapter 6), but for solid reagents these are inconvenient; or one can attach individual phials to the vacuum line by ground glass joint so that simply the weight difference before and after filling gives the weight of the contents, but this method becomes excessively time-consuming if long pumping times are necessary before the phial is filled.

For many years, at Keele as elsewhere, spheroidal vacuum phials (Fig.7.1.1) have been used. Initially, the pieces of the spent phial were collected from the reaction mixture in which the contents had acted, for example as an initiator, and the weight of the contents was determined by difference; the difficulties and inaccuracy of this method are obvious.

In 1962 Rutherford[1] devised and described the mid-point method; the principle of which is demonstrated in Fig.7.1.1 and equation 7.1.1. In the original work the phial was blown and weighed separately and then fused to a tube of known weight whose mid-point had been marked. It was probably in the late 1960's that the practice of blowing the phial from a single, marked, piece of glass tube was introduced. This practise became common usage without ever being recorded in detail.

Originally, the pieces of tube for the phials were cut and marked simply by using a steel scale. In the early 1970's an accurate and versatile tube cutter was designed, probably based on an Italian model. This too has been in constant use since then without being described.

The only contribution to the development of the method made by the present author has been to modify the weighted scribe of the tube cutting device.

In the earlier model the cutting edge was an industrial diamond set in the weight, which was both expensive and awkward to replace. The novel design involves a weight, with a centrally drilled hole into which is soldered the pen tip from a Jencons diamond scribe. This makes replacement of the cutting edge both simple and cheap.

With this advance in the cutting machine, which meant that the marks on the tubing were more consistently perfect, and with improvements in the general accuracy of experimental methods, it seemed timely to examine the nature of the errors involved in the mid-point method and at the same time to record the method in detail.

7.1.2: Preparation of "mid-point" phials.

For most purposes 3-4 mm O.D. Pyrex glass tubing gives satisfactory results. Usually the initial lengths of tubing for making phials are 12 cm long and the method will be described for this length. However, if a metal stop (A.Fig.7.2.1a) of a different length is used and the position of the cutting weight is altered, correspondingly different lengths can be prepared.

When the cutter is being used for the first time the position of the mid-point must be verified. This is done by cutting lengths of tube in the manner described below and measuring the weights of the two halves until, for three consecutive lengths, the two halves weigh the same, ±1 mg. The position of the cutting weight is set by the scale along the side of the apparatus and fine adjustments can be made with the terminal screw. (B. Fig.7.2.1a)

To cut a length of tube marked at the mid point, first place the metal stop (6 cm long) in the groove of the cutter, as shown schematically in Fig.7.2.1a. The tubing is then wiped with a rag soaked in hexane (to remove any grease and dust) and inserted into the cutter so that the end touches the metal stop. The cutter weight is then lowered, gently, so that the diamond tip rests on the glass tube which is then rotated between the thumb and forefinger until the diamond marks the glass in a neat circular line. Generally, only one or two complete rotations are necessary to obtain a clean sharp line. It is important that this line is clearly visible since this is the mid-point mark and must be obvious after the tube has been cleaned and fused onto the vacuum line. The metal stop is then removed, the cutting edge lifted and the tubing pushed along to the far end of the groove. (Fig.7.2.1b) The cutting weight is then lowered and the tube rotated to produce the terminal mark on the glass. Lastly, the cutting edge is lifted, the tubing removed from the cutter and the required length of tube snapped off from the full length at the terminal mark. It is important that a perfect break is achieved if the mid-point method is to be resonably accurate.

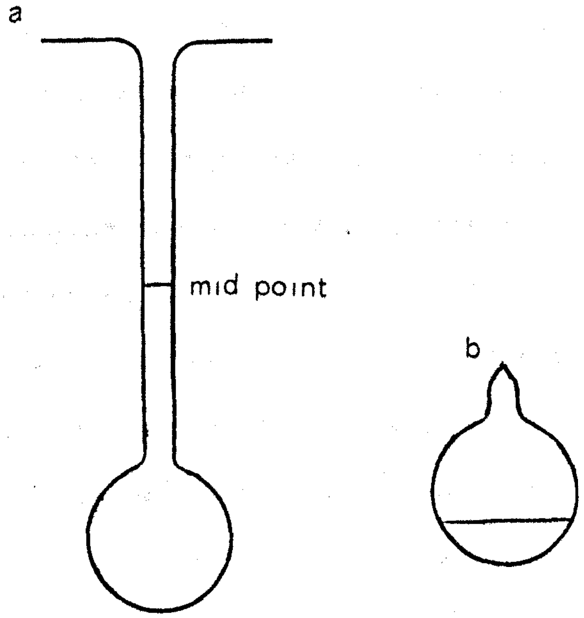
It is most convenient to cut a large number of tube lengths (say 100) at the same time as this reduces the relative amount of time spent in setting up the cutter and in cleaning the lengths ready for use. A batch of lengths is cleaned by placing them in a beaker of boiling chromic acid for about 30 min and then rinsing with distilled water, sodium hydroxide (10% w/v) and finally distilled water before drying them in an oven. Immediately before blowing the phial the end of the tube from which the phial is to be blown is rinsed with hexane and wiped dry with a clean tissue.

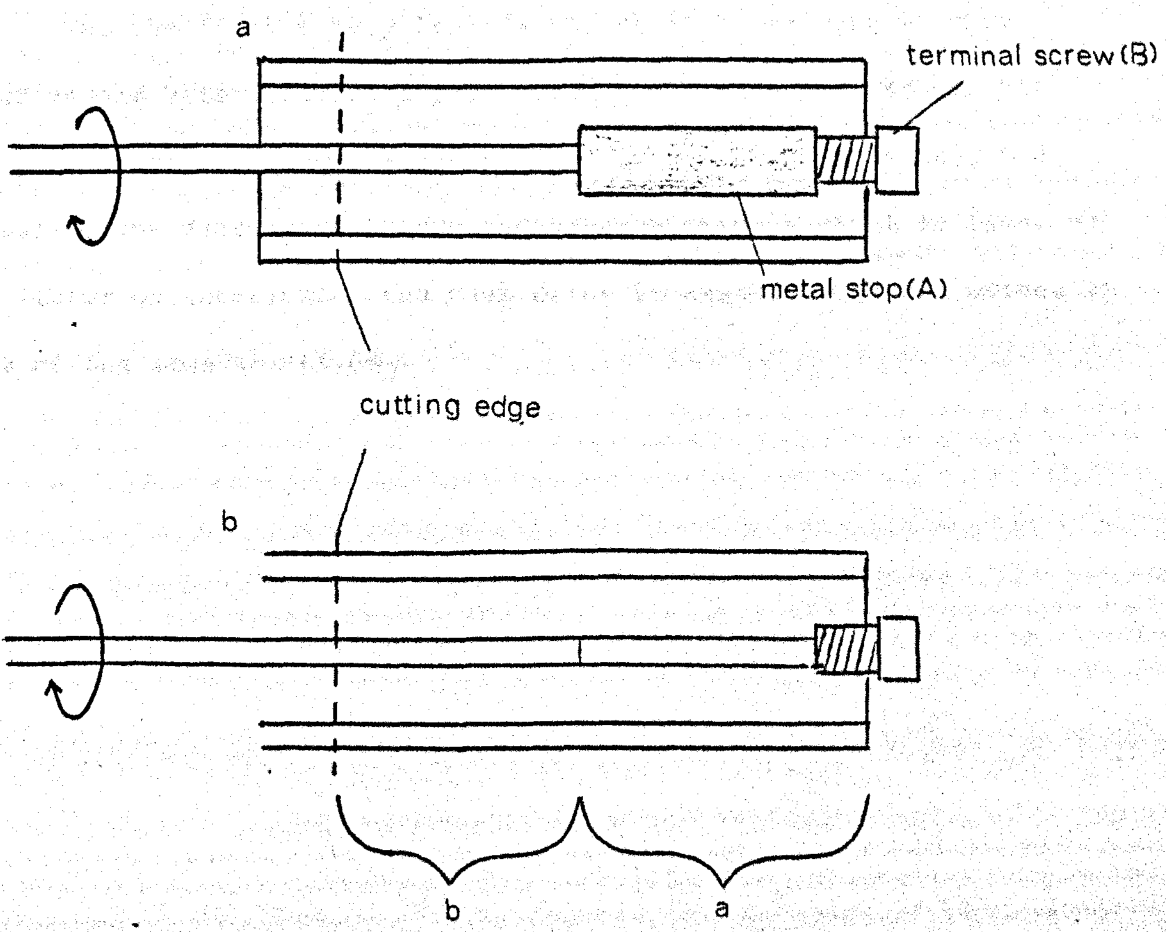
For most purposes phials of 8-16 mm diameter, which give a useful volume (ca. half full) of ca. 0.15 to 1.0 cm^3, are suitable. With practise the correct volume and thickness can be assessed intuitively, but it is worth noting that a phial which is adequately robust and yet easily broken in use produces a distinctive sound immediately after blowing and usually shows striations.

The phials, made in this way, are then weighed and fused onto the vacuum apparatus ready for use.

Fig.7.1.1: A spheroid phial as prepared by the mid-point method; a, before and b, after filling with reagent.

Fig.7.2.1: Schematic diagrams of the phial cutter set to mark the mid-point, a, and the terminal mark, b.


a
mid point
b


a
terminal screw(B)
metal stop(A)
cutting edge
b
b
a

7.2: A statistical study of the accuracy of the mid-point method.

For the statistical study 100 tubes were cut as described in the previous section. No tubes with imperfect breaks were included since in normal use such tubes would be discarded. It should be noted that with the improved cutting edge only two imperfect breaks were made when cutting the 100 lengths for this study.

The cutter was adjusted as if it were being used for the first time, as described in the previous section.

Throughout the study the two halves of the individual lengths were kept in the same order, i.e. the first marked halves were always weighed as w_a and the second marked halves were always weighed as w_b.(See Fig.7.2.1b) In this way any errors due to the setting of the tube cutter should have been emphasised rather than randomised.

For the first thirty lengths the glass tubes were weighed before and after blowing a phial from them. This process was not done for the other 70 specimens since it was noted that ΔW_1, the mean weight difference before and after blowing a phial is less, by a factor of three, than the mean error in assuming the two halves to be of the same weight,ΔW_2.

7.2.2: Results.

From the full data, given in Section 7.4., the following statistical results were obtained:

Let weight of tube before blowing a phial be: w_1
" " " " after " " " ": w_2
" " " first half of the tube be: w_a
" " " second " " " " " : w_b

$$\Delta W_1 = [\Sigma(w_1 - w_2)]/n = +5.3 \times 10^{-4} \text{ g.}$$

$$\Delta W_2 = [\Sigma(w_a - w_b)/2]/n = -(1.7 \pm 0.25) \times 10^{-3} \text{ g.}$$

$\sigma W_2 =$ The standard deviation of $(w_a - w_b)/2$

$= 2.52 \times 10^{-3}$ g.

For ΔW_1: $n = 30$, for ΔW_2: $n = 100$.

7.3: Conclusion.

As has already been pointed out, the difference between the weight of the tubes before and after blowing the phial is not significant, but even this small error may be eliminated by blowing the phial before weighing the tubes.

It is important to note that absolute values are given for the statistical quantities in the results. This has been done for two important reasons. Firstly, the tubing used is not precision tubing and therefore the individual tubes vary in total weight from ca. 1.5 to 2.5 g so that a relative error would have to be referred to an average weight. Secondly, the importance of the uncertainties quoted is in relation to the contents of the phial. The mean difference, W_2, suggests that in order to maintain the errors in the weight of the contents below 5%, the minimum content that should be put in the phial is ca. 3.5×10^{-2} g.

Occasionally it may be advantageous to produce phials from larger diameter tubing, for example when using fine powders of low density; in that case a separate determination of the errors must be made.

Reference to Chapter 7.

1. P.P.Rutherford, Chem. & Ind., 1962, 1614.

Reference to Chapter 7.

1. P.P.Rutherford, Chem. & Ind., 1962, 1614.

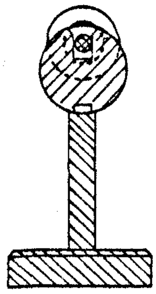
Table 7.4.1.

w_a/g	w_b/g	w_2/g	w_a/g	w_b/g	w_2/g
1.0860	1.0815	1.0818	1.1396	1.1385	1.1383
1.0716	1.0746	1.0746	1.0650	1.0617	1.0614
1.0419	1.0395	1.0393	1.1663	1.1696	1.1684
1.0570	1.0502	1.0499	1.1495	1.1523	1.1516
1.1575	1.1431	1.1422	1.1657	1.1737	1.1728
1.0716	1.0690	1.0685	1.0998	1.0953	1.0944
1.1797	1.1776	1.1774	1.1183	1.1158	1.1150
1.0451	1.0407	1.0404	1.1200	1.1132	1.1122
1.0592	1.0558	1.0556	1.1182	1.1196	1.1187
1.1664	1.1743	1.1740	1.0793	1.0877	1.0873
1.1697	1.1482	1.1477	1.1335	1.1323	1.1316
1.1168	1.1180	1.1176	1.1124	1.1144	1.1142
1.1883	1.1892	1.1886	1.0721	1.0828	1.0818
1.1707	1.1614	1.1606	1.0528	1.0470	1.0470
1.1891	1.1903	1.1899	1.0432	1.0432	1.0428
1.0954	1.0963		1.0927	1.0822	
1.0544	1.0563		1.0845	1.0916	
1.0787	1.0745		1.1133	1.1136	
1.0901	1.0818		1.1252	1.1205	
1.0873	1.0882		1.1091	1.1009	
1.0525	1.0543		1.0496	1.0489	
1.0504	1.0528		1.1166	1.1176	
1.0394	1.0476		1.1105	1.1186	
1.0873	1.0867		1.0362	1.0409	
1.0400	1.0328		0.9966	1.0035	
1.0469	1.0528		1.0101	1.0168	

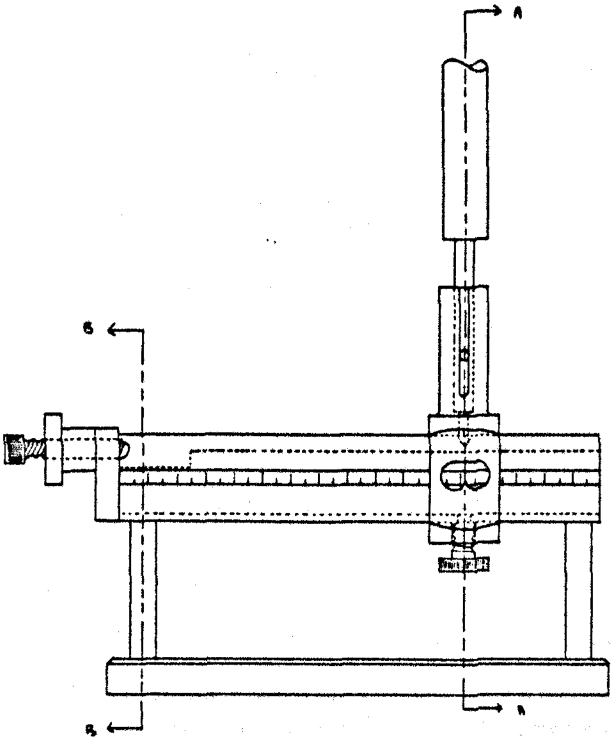
w_a/g	w_b/g	w_a/g	w_b/g
1.1621	1.1652	1.1048	1.1004
1.1113	1.1152	1.0010	0.9992
1.0444	1.0461	1.0699	1.0736
1.0590	1.0578	1.1364	1.1420
1.0808	1.0763	1.0621	1.0640
1.1232	1.1190	1.0688	1.0678
1.1156	1.1164	1.1145	1.1134
1.1292	1.1373	1.1050	1.1039
1.1486	1.1548	1.0960	1.0920
1.0903	1.0910	1.0427	1.0372
0.9966	0.9984	1.0510	1.0470
1.0373	1.0380	1.0210	1.0183
1.0446	1.0394	0.9996	0.9996
1.0705	1.0768	1.1508	1.1587
1.0455	1.0456	1.0564	1.0587
1.0310	1.0325	1.1070	1.1042
1.0396	1.0446	1.0494	1.0555
1.0714	1.0683	1.0173	1.0253
1.0830	1.0878	1.0650	1.0628
1.0380	1.0340	1.0212	1.0241
1.0111	1.0072	1.0678	1.0641
1.0242	1.0291	1.0683	1.0694
1.0701	1.0728	1.1112	1.1203
1.1468	1.1550	1.0073	1.0082

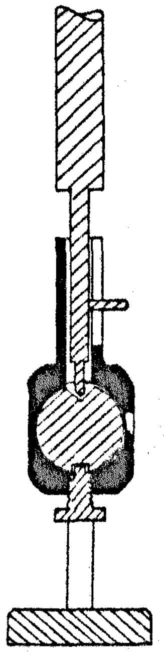
Fig.7.4.1: Tecnical drawing of the phial cutter.

(Drawing by T.Bolam.)

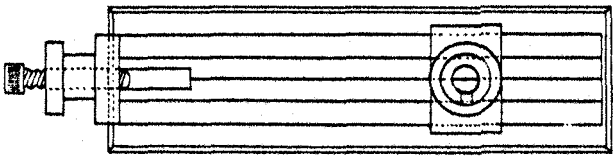


Section B-B

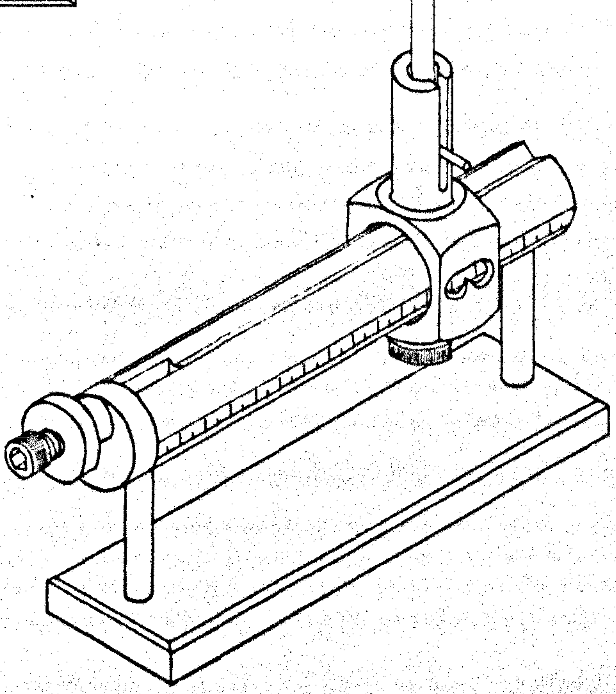




Section A-A



Plan without cutter



Scale 4mm = 1cm