"ADDITION AND POLYMERISATION REACTIONS"

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Abbreviations used in the Text.

J. Chem. Soc. - Journal of the Chemical Society.

J. Amer. Chem. Soc. - Journal of the American Chemical Society.

Trans. Faraday Soc. - Transactions of the Faraday Society.

J. Franklin Inst. - Journal of the Franklin Institute.

Bull. Soc. chim. - Bullétin de la Société chimique de France.

Z. phys. Chem. - Zeitschrift für physikalische Chemie.

Z. Elektrochem. - Zeitschrift für Elektrochemie.

Atti. Accad. Lincei - Atti della Reale Accademia Nazionale dei Lincei. Classe de Scienze fisiche, matematiche e naturali.

Ber. - Berichte der deutschen chemischen Gesellschaft.

J. Chem. Education - Journal of Chemical Education.

Can. J. Research - Canadian Journal of Research.

Rec. Trav. Chim. - Receuil des Travaux Chimiques des Pays-Bas.

J. Org. Chem. - Journal of Organic Chemistry.

J. Polymer Sci. - Journal of Polymer Science.

Proc. Roy. Soc. - Proceedings of the Royal Society.

J. Physical Chem. Russia - Shurnal Fizitscheskoi Chimii.

Annals N.Y. Acad. Sci. - Annals of the New York Academy of Sciences.

Industr. Engng. Chem. - Industrial and Engineering Chemistry.

Sci. Proc. Roy. Dublin Soc. - Scientific Proceedings of the Royal Dublin Society.

J. prakt. Chem. - Journal für praktische Chemie.

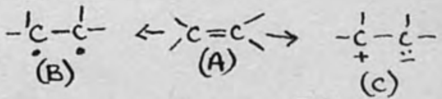
Compt. rend. - Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.

Zeitsch. Anorg. Chem. - Zeitschrift für anorganische und allgemeine Chemie.

INTRODUCTION

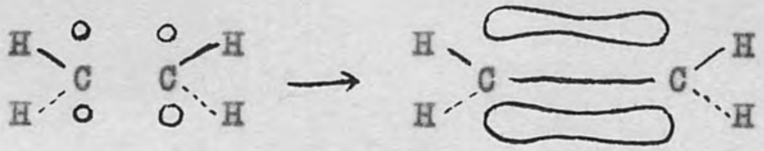
The carbon-to-carbon double bond.

Reactions of olefines (A) can be represented as proceeding by two distinct mechanisms, the one involving a free radical intermediate of the type (B), and the other proceeding by a polarisation of the electrons of the carbon-to-carbon double bond to give in the extreme case an intermediate of the type (C). Reactions of the latter type are termed ionic reactions. The ease with which either type of reaction can occur can be predicted from a knowledge of the nature of the double bond.

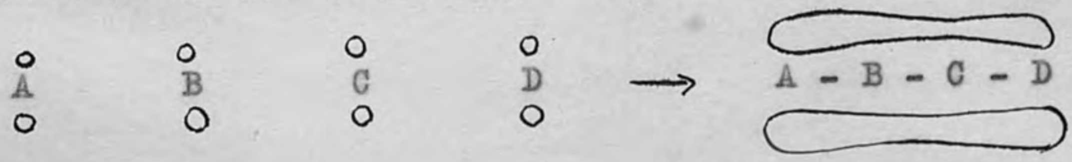


By methods involving wave mechanics it can be shown [1] that in addition to the tetrahedral tetravalent compounds carbon can form planar trivalent compounds in which the bonding orbitals are formed by hybridizing one s and two p orbitals, i.e. the 2s, $2p_x$ and $2p_y$ are compounded to give three coplanar orbitals or trigonal orbitals, pointing at angles of 120° in the xy plane. The remaining orbital is the undisturbed $2p_z$ generally referred to in this connection as the π orbital. If there are two such carbon atoms, each having two localised C-H bonds separately formed by combination of a H(1s.) atomic orbital and one of the trigonal orbitals, a C-C orbital (σ orbital) can arise from combination of the two remaining trigonal orbitals. All angles will then be 120°. The remaining $2p_z$ atomic orbitals of each carbon atom join to form a π bond, and to conform with the principle of maximum overlapping they must point in parallel directions, i.e. the two $-CH_2^{=}$ groups must be coplanar. Thus, the π bond can be represented as streamers of electron density above and below the plane containing the C-H orbitals (σ orbitals)

viz.



The normal double bond is thus seen to consist of a σ bond and a π bond superimposed. Internal rotation is restricted since there will be decreased overlap of the p_z orbitals when one end group is rotated out of coplanarity with the other. Since the π bond is strong (heat of formation, 64 Cals [9]) though not quite as strong as the σ bond (heat of formation C-C, 81.1 Cals [9]), the central part of the molecule will be rigid. Further, if there are four, six, eight etc. trigonally hybridised carbon atoms adjacent in a molecule, the molecular orbital method predicts that a series of separate π bonds are not formed but instead the p_z electrons are not localised but occupy molecular orbitals having wave functions extending over the whole system. This can be represented e.g. for butadiene as:



This delocalisation of the electrons results from the fact that with delocalisation the electrons have greater space in which to move, and that their total energy is lower, i.e. the binding energy is greater, than when they are paired in localised bonds. From this delocalisation it follows that any electrical influence in one part of the system is easily propagated to any other. The increase in binding energy corresponds to the resonance or delocalisation energy of the molecule. p Orbitals can also overlap with π orbitals to form extended molecular orbitals, e.g. in vinylamine with the nitrogen in the planar sp_2 configuration the unshared electrons in the third p orbital can overlap with the carbon π electrons. In this type of bonding, the electron affinities of the two atoms taking part, C and N, must also be taken into account. The delocalisation energy is even greater if the trigonally hybridised carbon atoms are linked in a ring system (e.g. in benzene) than in an open-chain. In styrene, the molecular orbital will include the 8 π electrons, and the delocalisation energy will be particularly high.

It seems that σ bonds can also form extended orbitals to some extent. For example in ethane the C-H bonds are formed from H(1s) orbitals and hybrid sp_3 orbitals of carbon, the p components of which overlap to some extent forming weak π bonds between the carbon atoms, leading to increased strength of the C-C bond. This effect is known as hyperconjugation, and is believed to be mainly confined to C-H bonds [cf. 1 and 4]. The effect is greater when σ orbitals overlap with π orbitals (first-order hyperconjugation) than when they overlap with other σ orbitals (second-order hyperconjugation). Hyperconjugation explains the observed high value for the resonance energy of alkyl substituted olefines [9, p.35] .

We are now in a position to consider the general features of the two types of reactions exhibited by olefines. In the first type are included all reactions of olefines which will occur in a non-polar environment in the presence of reactive atoms or free-radicals. Halogens do not react appreciably with olefines in light petroleum by the normal ionic mechanism (see p. 6) since the solvent is non-polar but in light or in the presence of peroxides addition readily occurs. The mechanism is believed to be -

$$Cl_2 \xrightarrow{h\nu} 2Cl.$$

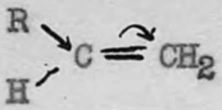
$$Cl. + CR_2 = CR_2 \rightarrow ClCR_2 - CR_2.$$

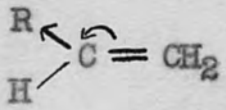
$$ClCR_2 - CR_2. + Cl_2 \rightarrow ClCR_2 - CR_2Cl + Cl. \quad ,$$

involving an attack on the nucleophilic olefine by the electrophilic halogen atom. Reactions of this type will not be dealt with further.

Substances have been defined [15] as nucleophilic (i.e. electron-donating) or electrophilic (i.e. electron-seeking) according to their tendency, respectively, to expel or to attract electrons.

The availability of the electrons in the double bond of an olefin for coordination of an electron seeking substance will be determined by the substituents at either end of the double bond. Substituents which are electron donating, i.e. which according to the classical definitions [15] have a positive inductive (+I) and negative tautomeric (-T) effect, will increase the electron availability, particularly on the unsubstituted carbon atom. Those which are electron seeking, with -I and +T effects, will decrease the electron availability. It is assumed that the substituents cause a permanent shift, or a drift of the electrons as shown below by the arrows. (A) represents the first example and (B) the second.


(A)


(B)

Polanyi and his collaborators have calculated proton affinities for ethylene, propylene and butylene [57], and found that they increase in this order, and are greatest for the unsubstituted carbon atom, showing clearly the +I and -T effect of methyl groups.

Availability of the electrons will also be lowered by the phenomenon of delocalisation for a conjugated system, and for an isolated double bond when hyperconjugation with adjacent alkyl groups can occur. However, lowering due to delocalisation by such groups as alkyl and phenyl must be more than compensated by the inductive effect of these groups, since in general they have electron-donating properties.

Reactions of the second type, involving ionic intermediates are believed to occur through the attack of a cation on the nucleophilic olefin. An example is found in the addition of bromine vapour to ethylene gas. This has been shown [5] to take place entirely on the glass walls of the reaction vessel, and to be greatly retarded if the walls are coated with non-polar paraffin wax. A coating of stearic acid, which is polar, leads to a rate which is higher even than that observed in a non-coated vessel. It is believed [cf. 15] that the polar environment induces a partial charge separation in the halogen, which is followed by a cationoid attack on the olefin by the halogen, inducing charge separation in the carbon-to-carbon double bond and the consequent formation of a carbonium ion. Further reaction occurs between this carbonium ion and the halogen anion:-

$$CH_2 \overset{\curvearrowright}{=} CH_2 + X \overset{\curvearrowright}{-} X \rightarrow \overset{+}{C}H_2 - CH_2 - X + \overset{-}{X} \rightarrow X-CH_2 - CH_2 - X$$

Amongst the evidence in favour of this mechanism is the fact that in the reaction of ethylene with bromine or iodine in aqueous solution, the addition of sodium chloride leads to the formation of chlorobromo- or chloroiodoethanes, and that $Br - CH_2 - CH_2 - NO_3$ is formed in the presence of a high concentration of nitrate ion [8].

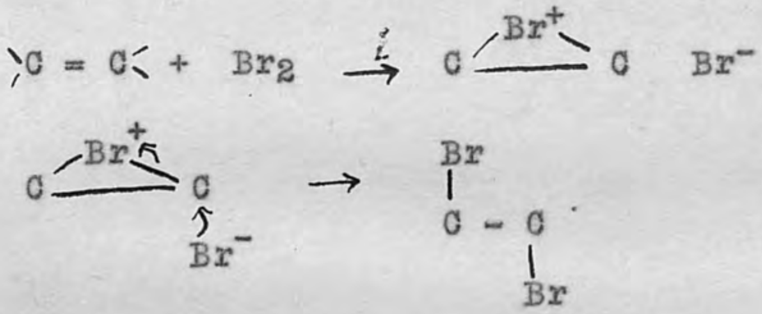
Hence it is to be expected that the addition reaction will be favoured by any factor which increases the electron density on the carbon-to-carbon double bond, i.e. the presence of an electron-donating substituent (e.g. alkyl), and that it will be retarded by the presence of an electron-seeking substituent (e.g. halogen). Good evidence for this was obtained from a study of the competitive rates of bromine addition to various olefines in methylene dichloride solution at -78°C. [7]. The ratio of the rate of addition for each substance was calculated relative to that of ethylene and was termed the reduced rate for that substance. Four examples are given below:-

Reduced rates of bromine addition to ethylene in CH_2Cl_2 solution at -78°C. [7].

$(CH_3)_2C = C(CH_3)_2$	4.0	$(CH_2 = CH_2$	$1.0)$
$(CH_3)_2C = CH_2$	5.53	$CH_2 = CH\ Br$	Small.
$C_6H_5C = CH_2$	3.35		

It is interesting to note that in this connection the phenyl group exhibits an electron-donating effect.

An additional feature of halogen addition is that trans-addition usually occurs, e.g. maleic acid with bromine gives almost exclusively racemic dibromosuccinic acid. Roberts and Kimball [8] pointed out that this effect could be explained if the intermediate carbonium ion had a cyclic structure, subsequent interaction with the anion being a bimolecular replacement in which the ring opens and a trans-adduct is formed:



However, Dewar [9 , p.143] has explained the phenomenon in terms of a π complex in which the bromous cation is linked to the π-electrons of the >C = C< bond. This interpretation of the reaction is the only one which explains satisfactorily the addition of iodine monochloride to unsymmetrical olefines. In the additions the carbonium ion is believed to be formed by the addition of I^+ to the olefin, iodine being less electronegative than chlorine. Then according to Roberts and Kimball the $\overset{-}{Cl}$ should add onto the end of the double bond with fewest electron donating substituents. The orientation observed is actually the reverse of this. For the π complex theory, however, the I^+ will be unsymmetrically attached being closer to the end of the double bond carrying most electron-donating substituents, so that the $\overset{-}{Cl}$ will add onto the other end of the double bond, as is indeed observed.

It has already been mentioned that the ionic addition of halogens to olefines is favoured by a polar environment. This is a characteristic feature of ionic reactions in general, and an explanation can be found in the lowering of the potential energy of the ionic intermediates by solution by a polar solvent. This effect was clearly described by A.G. Evans for the ionisation of alkyl halides in aqueous solution [10]. Fig. 1 gives the potential energy curves for a homopolar molecule, RI, where R is an organic radical of sufficiently low ionisation potential. Curve 'a' is the potential energy curve calculated for the RI bond in the homopolar state, curve 'b' is the potential energy curve calculated for ionic gaseous $R^+ I^-$, and 'c' the potential energy curve calculated for solvated $R^+aq.I^-aq.$

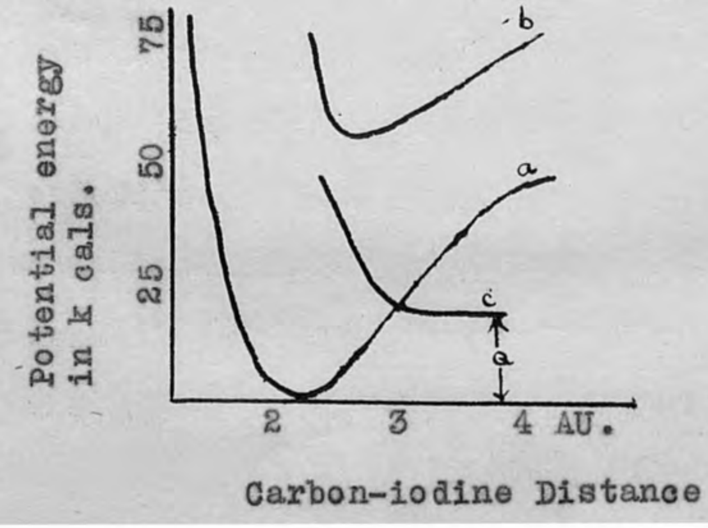


Fig. 1.

The heat absorbed, Q, in the ionisation $R - I_{aq} \rightarrow R^{+}_{aq} + I^{-}_{aq}$ is determined by the following equation:-

$$Q = D + I - E - S^{+} - S^{-}$$

Solvation of RI was assumed to be negligible. D is the heat of dissociation of the carbon iodine bond in the gaseous RI molecule.

I is the ionisation potential of the R radical.

E is the electron affinity of the iodine atom.

S^{+} is the heat of hydration of the R^{+} ion.

S^{-} " " " " " " I^{-} ion.

Curve c was derived from b by superposition of the solvation energies for the two ions. Clearly, therefore, the solvent medium will have an important effect in all reactions of olefines involving ionic intermediates.

Friedel Crafts Catalysts.

Many of the addition and polymerisation reactions of olefines are catalysed by metal halides, the so-called Friedel Crafts Catalysts, e.g. BF_3, BCl_3, $SbCl_5$, $AlCl_3$, $TiCl_4$, $SnCl_4$, $FeCl_3$, $ZnCl_2$ etc., and it would therefore be of interest to consider the structure and properties of these catalysts.

One outstanding property is that they can all function as electron acceptors. Lewis [11] carried out titrations in dioxane and acetone as solvents using as bases pyridine and triethyl amine, and as "acids" (i.e. "acceptors") SO_2, BCl_3, $SnCl_4$ and $AgClO_4$. In all cases neutralisation, as shown by indicators, was rapid and the acids and bases could be titrated back and forth, showing complete reversibility. In the covalent compounds boron trichloride and BF_3 only three of the four available orbitals (2s, and three 2p) are filled, and the fourth can be filled by the two paired electrons from one atom in a basic molecule or ion. In the case of tin ($1s^2$, $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^6$ $4d^{10}$ $5s^1$ $5p^3$) there are the 5d and 4f orbitals empty, and it is evident from the formation of complex halides of the type R_2SnCl_6 that the tin atom can use six of its orbitals for bonding purposes. It is known from X-ray investigation of crystals of these complex halides containing the $SnCl_6^{--}$ ion that the six halogen atoms are all united equivalently to the central atom which they surround octohedrally [16 p.72]. Similar treatment can be applied in the cases of the other catalysts ($AlCl_3$, $FeCl_3$, $TiCl_4$, $ZnCl_2$ etc.) which can expand their valence shells beyond an octet. Certain acids exhibit catalytic effects resembling those of the metal halides (e.g. HF, H_2SO_4, H_3PO_4, but not usually HCl). Their catalytic power is no doubt due to the acceptor powers of their protons.

Such is the acceptor tendency of aluminium chloride that it vaporises to a dimeric molecule Al_2Cl_6, and only breaks down to $AlCl_3$ above 400°C. In the dimer each Al is surrounded tetrahedrally by four halogen atoms. In the solid form it is believed to exist [17] as an ionic lattice in which each Al atom is octohedrally coordinated by six halogen atoms, as for $FeCl_3$ [17, p.284]. There is evidence that it may exist as a monomer in some solvents [17a] and as a dimer in others. Stannic chloride is a normal covalent compound with the metal forming four normal tetrahedral Sp^3 bonds [17].

Reactions of these Catalysts with other substances.

(a) Hydrogen halides.

It is well known that H.BF_4 is a very strong acid [18, p.87]. Evidence for the interaction of stannic chloride with hydrogen chloride with the formation of an acid (presumably H_2SnCl_6) was obtained by Meerwein [19]. He observed that dilute ethereal solutions of hydrogen chloride and of stannic chloride are, separately, yellow after addition of the indicator p-dimethylaminozobenzene, but that an immediate red (acid) colour is formed when the solutions are mixed.

Besson [86] showed that the slow action of dry hydrogen bromide on stannic chloride at 0°C. led to the formation of stannic chlorobromides with the elimination of hydrogen chloride. Ultimately the reaction led to complete conversion to $SnBr_4$. The products were separated by two fractionations at low pressures, and purification of the fractions was achieved by fractional crystallisation. Further fractional distillation was not possible since it resulted in decomposition of the desired products into $SnCl_4$ or $SnBr_4$. Three products were isolated, $SnCl_3Br$, $SnCl_2Br_2$, $SnClBr_3$. All were low boiling liquids which fumed on exposure to moist air giving crystalline hydrates, and which were soluble in water with decomposition.

(b) Water.

Many of the Friedel-Crafts catalysts are easily hydrolysed by water, with the formation of the corresponding hydrogen halide and the metal oxide, or hydroxy-halide, but in certain cases stable hydrates are also known. For example, treatment of stannic chloride with a limited amount of water produces the crystalline hydrate $SnCl_4.5H_2O$ which is stable up to 56°C. In the presence of excess water hydrolysis proceeds with the ultimate formation of $Sn(OH)_4$. Other hydrates are known [13] containing 3,4 and 8 molecules of water for every molecule of stannic chloride. The limits of stability for these hydrates are 83°, 63° and 19° respectively, each decomposing above the limiting temperature into the next lower hydrate. It has been shown [14] that the hydrates of stannic chloride are quite easily dissociated into their components by warming with xylene, only the free stannic chloride being soluble in xylene.

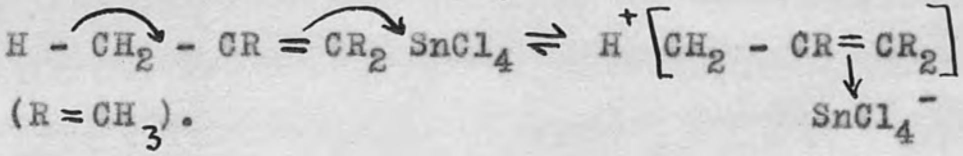
The dihydrate $BF_3.2H_2O$ and the monohydrate $BF_3.H_2O$ are well-known [18, p.58] and both are acidic [cf. 90]. Klinkenberg and Ketelaar [90] consider that the solid $BF_3.2H_2O$ is the hydroxonium salt of monohydroxyfluoboric acid $H_3\overset{+}{O}(B\overset{-}{F_3}OH)$, which indicates that the transfer of a proton can take place from $BF_3.H_2O$ to H_2O.

(c) Organic Compounds.

Many instances are quoted in the literature of the isolation of crystalline complex compounds form from Friedel-Crafts catalysts and organic compounds, e.g. aldehydes, ketones, acids, esters or amides and stannic chloride or stannic bromide in ether, benzene or chloroform form compounds of the type $SnX_4.2RCOA$ (A=-H,-Me, -OH, -OEt, -NH) [20]. These compounds often exhibit halochroism, which can be explained if it is assumed that only the partial valency of oxygen in the $>C=O$ group is used, leaving the C more unsaturated and hence increasing its chromophoric properties. Tin halides also add two moles of pyridinium or quinolinium halides.

In addition there is much physical evidence for the interaction of Friedel-Crafts catalysts with aromatic compounds. By vapour pressure and freezing point measurements for solutions of aluminium bromide in benzene, Ross E. Van Dyke gave evidence for the existence of a compound $(C_6H_6)_2Al_2Br_6$ [21]. A summary of the other evidence for aluminium halides is given by Dilke, Eley and Perry [22] who succeeded in isolating a red viscous oil of the composition $(CH_3)_2C_6H_4.AlCl_3$ from interaction of aluminium chloride and xylene in chlorobenzene. The reaction is slow, but there is a considerable heat of mixing, 30 k cal., as obtained from hydrolysis of the oil. They suggest that the complex may be a π complex, or a polarisation complex, and mention that there is also some evidence for ionisation, e.g. $2XyAlCl_3 \rightleftharpoons Xy_2AlCl_2^+ + AlCl_4^-$. The positive ion would account for the colour observed. A suggestion has been made [23] from vapour-pressure/concentration measurements that stannic chloride exists chiefly as a dimer in benzene solution, and does not form a compound with the solvent. However, compound formation between nitrobenzene and stannic chloride is indicated by thermal analysis (1:1) and viscosity measurements (2:1) [24]. For stannic bromide the proportions are believed to be 2:1. This is in agreement with the observation that use of nitrobenzene as solvent lowers the rate of Friedel-Crafts reactions [cf. 31b]. Presumably the oxygen atoms of the solvent can coordinate with the metal halides hence lowering the concentration of free catalyst available for the reaction. The fall with time of the rate of Friedel-Crafts reactions using aluminium chloride has been taken as evidence for complex formation between the catalyst and the products, i.e. alkylated or acylated aromatic compounds [25].

Since olefines form stable coordination compounds with platinous salts e.g. ($C_2H_4,PtCl_2$) [26] it is to be expected that they might form complexes with Friedel-Crafts catalysts. One theory advanced to account for the formation of the platinous compounds [12a] was that a π complex was formed involving the π electrons of the olefin and empty orbitals in the metal atom. This theory led to a prediction that compounds such as $BF_3.C_2H_4$ should be expected [12b]. More recently [26] Chatt has suggested that the formation of the platinous compounds is due to the ability of the metal to form bonds with the olefin, possibly by using d-orbitals, e.g. one carbon would be linked by a strong Pt(dsp^2)-C/sp^3) bond and the other by a weaker Pt(d)-C(sp^3) bond. Clearly, this type of bonding would not be possible for boron compounds, and indeed, Evans, Meadows and Polanyi [56] showed that there is no observable reaction between pure BF_3 and isobutene. There is, however, some evidence for a type of interaction between stannic chloride and olefines. Skraup and Freundlich [27] found that a colour was produced on mixing solutions of aryl-substituted ethylenes and of stannic chloride or stannic bromide in benzene. The colour decreased in intensity on dilution of the solutions indicating ready dissociation of the coloured complexes, none of which were isolated. There is also spectral evidence [55] for interaction between diphenyl-ethylene and Friedel-Crafts catalysts. Furthermore, J.W. Baker [28] observed a green colouration on mixing trimethyl-ethylene and stannic chloride, and was able to carry out a reaction requiring proton catalysis in the presence of these reagents. He suggested that the proton was supplied from the olefin-stannic chloride acid complex:-

ie.


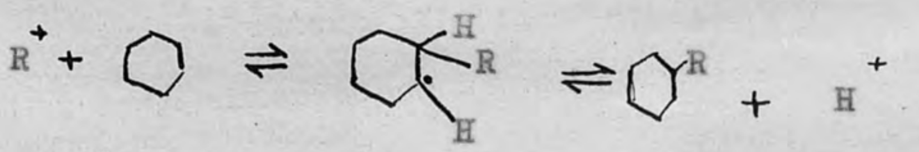
$$H - CH_2 - CR = CR_2\,SnCl_4 \rightleftharpoons H^+\left[CH_2 - \underset{\downarrow\atop SnCl_4^-}{CR} = CR_2\right]$$

$(R = CH_3)$.

The phenomenon was also observed for several other olefines in the presence of stannic chloride.

Interaction of Friedel-Crafts catalysts with alkyl or acyl halides is believed to account for the alkylation and acylation of aromatic compounds by means of these reagents. The subject has been reviewed by Price [29], and the initial stage in the reaction is assumed to be the formation of an ionised complex between the organic halide and the metal halide, generating a carbonium ion which then can coordinate with a pair of electrons in the aromatic nucleus, the final stage being the elimination of a proton, viz:

$$R - X + MX_m \rightleftharpoons R^+ + MX^-_{m+1} \qquad ①$$



②

$$H^+ + MX^-_{m+1} \rightleftharpoons HX + MX_m \qquad ③$$

The metal halide is regenerated at the end of the reaction, and less than a molecular proportion is required for the catalysis. As pointed out by Boeseken [48] the ionised complex need only be present in small amount. An exception is found in boron trifluoride which will not catalyse the alkylation of benzene by alkyl chlorides [30a] unless water, alcohol, or some other polar entity is also present [30], although vigorous alkylation occurs with cyclohexyl fluoride, BF_3 and benzene even in the absence of another polar substance [30b]. Burnell and Archer [30b] attributed this to the relative sizes of the fluoride and chloride ions, and to the much greater stability expected for BF_4^- than for BF_3^-Cl. The co-catalyst effect of water and alcohol can be explained by postulating a mechanism such as:-

$$BF_3 + H_2O \rightleftharpoons BF_3^-OH + H^+$$

$$H^+ + RCl \rightleftharpoons HCl + R^+$$

$$R^+ + ArH \rightarrow ArR + H^+$$

$BF_3\,OH^-$ is a stable ion [cf. 18, p. 53 et seq] since the OH^- ion is of approximately the same size as the F^-.

On the other hand, Thomas [6] has suggested that for aluminium chloride also the effective catalyst is not $AlCl_3$, but $HAlCl_4$, the HCl being present in small amounts as an impurity in the $AlCl_3$. Presumably, then the catalyst dissociates into $H^+AlCl_4^-$, and a proton attack on the alkyl halide occurs as shown above.

The work of Fairbrother has afforded some evidence for the interaction of acetyl chloride and aluminium chloride [36] since he showed that radioactive hydrogen chloride is evolved when acetylation of benzene is catalysed by $AlCl_3$ containing Cl^{36}. But he pointed out that the results might also be explained if the HCl liberated in the acylation reacted subsequently with the $AlCl_3$ as shown in ③ on p. 17

Evidence for the interaction of alkyl halides and Friedel-Crafts catalysts has been sought by chemical and physical means. Wertyporoch and others [31a] found that the conductivity of ethyl bromide was increased by the addition of aluminium bromide. On measuring transport numbers for the solutions, the concentration of aluminium at the anode was found to be greater than at the cathode, which Wertyporoch took as an indication of the formation of an autocomplex of $AlBr_3$, viz. $Al[AlBr_4]_3$, with solvation of the complex by ethyl bromide. On the addition of benzene, tetramethyl-ethylene or naphthalene there was a marked increase in conductivity which he ascribed to conversion of the autocomplex to something akin to a true salt. The conductivity increased to a maximum at 5-6 hr. after the addition of the benzene, ethyl benzenes and hydrogen bromide being formed. The latter was shown not to be responsible for the increase in conductivity. Migration experiments for $AlBr_3$ in ethyl bromide and

benzene showed that aluminium atoms wander to the anode and cathode approximately in the ratio of 3:1, and that formed or added hexaethyl benzene becomes five times as highly concentrated at the cathode as at the anode, thus indicating a complex $[Al(EtBr)_n\ (C_6Et_6)_4][AlBr_4]_3$. Wertyporoch suggested that the Friedel-Crafts reaction occurs through the loosening of the C-Br and C-H bonds, respectively, of the ethyl halide and the aromatic hydrocarbon in this type of tertiary complex. Analogous results were obtained for $AlCl_3$ and for $FeCl_3$ using a variety of alkyl halides. Complex formation was less pronounced for the $FeCl_3$ [31a, 31b]. More recently Van Dyke carried out the electrolysis of solutions of $AlBr_3$ in methyl bromide at -78 °C. and obtained deposition of aluminium at the cathode and evolution of bromine at the anode, which was the typical behaviour of a 1:3 electrolyte. Dissociation was believed to be:-
$AlBr_3 \rightarrow Br^- + AlBr_2^+$. There was no evidence for compound formation.

Evidence for the existence for alkyl halides of equilibrium (1) (p. 17) was obtained by Fairbrother. On treatment of various organic halides with metal halides containing radioactive halogen, and isolation and analysis of the products after a given time, it was found [32a] that halogen exchange was rapid and complete, except in the case of aryl halides or of weak catalysts ($SnBr_4$). Some of the results are shown in Table A.

Table A [32a].

Metal Bromide	Organic bromide	Time (min.)	Ratio of Organic $Br^*/M\ Br^*$
$Al_2Br_6^*$	EtBr	5	0.9
"	BuBr	5	1.0
"	CBr_4	20	0.89
"	C_6H_5Br	90	0.03
$SnBr_4^*$	EtBr	120	<0.01
"	$Bu^{\gamma}Br$	150	0.92
"	$C_6H_5CH_2Br$	150	1.05

These results were in striking contrast to his previous experiments [32b] on the measurement of the dielectric polarisation of solutions of alkyl halides and metal halides in cyclohexane solution. In these experiments, the increase in polarisation for $AlBr_3$ and ethyl bromide corresponded to only 3-4% ionisation of the ethyl bromide. No increase was observed in experiments with stannic bromide, even with very reactive organic bromides (e.g. $Bu^{\gamma}Br$). He therefore concluded that there was a dynamic equilibrium ① obtaining in which the concentration of the ion-pair was very small. He suggested that if the carbonium ion concentration were high there would be elimination of HBr with the formation of an olefin. This was observed for $Bu^{\gamma}Br$. He considered that the formation of the ion-pair might often be an endothermic process, and that the ease with which it could occur would depend on (i) the energy of formation of the metal complex ion, which would be determined by the electron affinity of the metal and the size of the halide ion, and (ii) the ionisation potential of the organic radical which should increase in the order benzyl < 3ry alkyl < 2ry alkyl < 1ry alkyl < aryl.

The existence of an equilibrium such as ① was used to explain the racemisation in organic solvents of optically active organic halides, under the influence of Friedel-Crafts catalysts [33,34]. From the labile planar carbonium ion either antipode could be reformed as the halide, resulting in a gradual loss in optical activity, i.e.

$$\begin{array}{c} Ph - CHClCH_3 + MCl_{(x)} \\ \rightleftharpoons \\ Ph - \underset{+}{CH} - CH_3 + MCl_{(x+1)} \end{array} \qquad \text{(1a)}$$

The phenomenon was first studied by Bodendorf and Böhme [33] who treated (-)-1-phenylethyl chloride with various metal halides ($HgCl_2$, $ZnCl_2$, BCl_3, $TiCl_4$, $SnCl_4$, $SbCl_5$, $SbCl_3$, $SiCl_4$, $AsCl_3$) in a variety of organic solvents (acetone, benzene, nitromethane, nitrobenzene, ethyl acetate and formic acid). In formic acid solution as in sulphur dioxide 91 racemisation occurred even in the absence of added catalyst and was presumably due to the self-ionisation of the alkyl halide, i.e. $R - Cl_{(Solv)} \rightleftharpoons \overset{+}{R}_{(Solv)} + \overset{-}{Cl}_{(Solv)}$.

In the other solvents, all the metal halides effected the racemisation with the exception of $SiCl_4$, $AsCl_3$. The effect

was very slow with $SbCl_3$ as a catalyst. Similar differences in the degree of the catalytic effect for the metal halides has been observed in polymerisation reactions [cf. 60, 62]. The rate of racemisation was of the first order with respect to the phenylethyl chloride, and was approximately proportional to the dielectric constant ϵ of the medium, except for solutions in nitrobenzene as solvent, when the rate was lower than would have been predicted from ϵ [cf. 31b and 32a]. Further experiments with (-)-1-phenylethyl chloride and stannic chloride in benzene [34] showed that the rate of racemisation could be lowered by the addition of small amounts of hydrogen chloride, but could not be completely inhibited by addition of larger amounts. This agreed with the concept of a dynamic equilibrium 1a accompanied by another equilibrium -
$HCl + SnCl_4 \rightleftharpoons \overset{+}{H}\overset{-}{SnCl_5}$ (3a). The inhibiting effect of the HCl would then be due to its interaction with stannic chloride with a consequent lowering in concentration of the metal halide responsible for the racemisation. These authors also considered the possibility of another equilibrium which would also account for the racemisation and for its inhibition by HCl, namely:-

$$Ph - CHCl - CH_3 \rightleftharpoons Ph - CH = CH_2 + HCl \qquad ④$$

They assumed that stannic chloride would facilitate the establishment of the equilibrium ④. However, no styrene could be detected after treatment of inactive phenylethyl chloride with stannic chloride [cf. also Williams , 60], and furthermore styrene was recovered unchanged after treatment with quantities of hydrogen chloride and stannic chloride similar to those used in the racemisations. Hence it was evident that equilibrium ④ could not explain the racemisation observed by them. It appeared also that an activating group (phenyl or olefinic) adjacent to the centre of asymmetry was essential for racemisation, since active 2-chloro-Δ^3- butene and 2-chloro-Δ^3-pentene were racemised under the conditions described above, but not 2-chlorobutane nor 1-phenyl-2-chloropropane [34]. Presumably an unsaturated grouping adjacent to the incipient positive centre would stabilise the carbonium ion.

It appears that even carbon tetrachloride and carbon tetrabromide interact quite readily with aluminium halides [35, 32a]. Dilke, Eley and Perry [22] were unable to study the interaction of xylene and $AlBr_3$ in carbon tetrachloride solution because of the vigorous evolution of hydrogen chloride. More recently still, Wallace and Willard [35] have used $AlCl_3^{36}$ to show that the chlorine in solid $AlCl_3$ exchanges rapidly with carbon tetrachloride and with chloroform. On energetic grounds it was considered unlikely that this reaction proceeded by the normal Friedel-Crafts mechanism -

i.e. $CCl_4 + AlCl_3 \rightleftharpoons CCl_3^+ + AlCl_4^-$

and a suggestion was made that the carbon tetrachloride was adsorbed onto the surface of the aluminium chloride by electrostatic attraction between a positive centre on the lattice and polarisation induced in the carbon tetrachloride. The halogen exchange could occur in the desorption process. It is further suggested that a surface mechanism may explain the Friedel-Crafts reaction of carbon tetrachloride, and other similar reactions involving solid ionic inorganic halides.

Summarising, the evidence available favours the existence of the equilibrium between alkyl halides and Friedel-Crafts catalysts in organic solvents. The position of the equilibrium for any system will be governed not only by the nature of the alkyl halide and catalyst, but also by the solvent, so that the proportion of ion-pairs formed will increase with the dielectric constant of the solvent. The extent of dissociation of the ion-pairs into free ions is probably very small, except in highly polar media [cf. 55].

It is of interest that recent work has shown that under certain conditions bromine [37] and hydrogen bromide [38] are capable of producing ionisation of 1-phenylethyl bromide. It was observed [37] that (+)-1-phenylethyl bromide racemised rapidly in solution in carbon tetrachloride at 73°C. in the presence of bromine and silver bromide, although racemisation was slow in the presence of bromine alone, and only slight with silver bromide. It was further found [38] that (+)-1-phenylethyl bromide underwent racemisation in carbon tetrachloride saturated with hydrogen bromide at 73°C., by a surface mechanism. Various solid catalysts were employed, and their effectiveness was found to be: silver bromide > charcoal > powdered glass >> potassium bromide. No definite mechanism is suggested for the experiments using bromine alone, but the other results are explained [38] on the basis of a mechanism involving adsorption of the 1-phenylethyl bromide onto the catalyst surface, with a consequent weakening of the alkyl-bromine bond by interaction of the halogen either with positive centres on the catalyst surface, or with adsorbed protons from the adsorbed hydrogen bromide. Racemisation then proceeds either by a bimolecular substitution process (by Br^- or HBr), or by the formation of a planar carbonium ion which subsequently combines with Br^- or HBr to yield the (±) bromide. The idea of a surface reaction agrees with the predictions of Wallace and Willard [35] for reactions involving solid inorganic halides.

Addition Reactions of Olefines.

(a) Addition of Halogens to olefines.

The kinetics of the addition of bromine to olefines in non-polar solvents in the absence of peroxides are often difficult to interpret with certainty [cf. 39]. It is possible to have a homogeneous reaction of a high order, and a heterogeneous reaction occurring on a polar surface which is of first order with respect to bromine. In dissociating solvents an ionic mechanism is likely, or a two stage molecular mechanism in dissociating solvents such as acetic acid [42].

(b) Addition of hydrogen halides to olefines.

In addition to a symmetrical olefin there can only be one product - e.g. $CH_2=CH_2 + HCl \rightarrow CH_3 - CH_2Cl$.
But for an unsymmetrical olefin there are two possibilities -

$$\text{e.g. } CH_3 - CH = CH_2 + HI \begin{array}{l} \nearrow CH_3 - CHI - CH_3 \\ \searrow CH_3 - CH_2 - CH_2I. \end{array}$$

The orientation rule of Marownikoff [43] states that in the addition of a halogen acid to an olefin the halogen adds onto that end of the double bond which carries fewest hydrogen atoms. However, the orientation as well as the ease of the reaction will be affected by neighbouring groups by virtue of their influence upon the electrons of the double bond. Thus acrylic acid gives β-brom-propionic acid although this is contrary to the Markownikoff rule, by virtue of the electron attraction of the carboxyl group. The data on orientation in these reactions were reviewed by Kharasch [44a], much of which he found to be contradictory and requiring reinvestigation. In the course of further investigation he himself discovered the "peroxide effect" [44b,c]. It was discovered during an investigation of the addition of HBr to alkyl bromide. This could take either of two courses -

$$CH_2=CH - CH_2Br + HBr \begin{array}{ll} \nearrow CH_3CHBr - CH_2Br & ① \\ \searrow CH_2Br - CH_2 - CH_2Br & ② \end{array}$$

If the reagents were pure and freshly prepared, and if oxygen were excluded from the reaction vessel, ① was formed exclusively. But in the presence of small amounts of oxygen, or of added peroxide, or when old alkyl bromide was used, the second reaction took place almost quantitatively. This reversal was called the peroxide effect, and was observed in additions of hydrogen bromide to many ethylene derivatives [45]. It was known that oxygen or peroxides could liberate bromine atoms from HBr, and these were presumed to add onto the end of the double bond with the highest electron density. Subsequent addition of a hydrogen atom from another molecule of HBr completed the addition, and led to a chain reaction. Dilution by solvents and addition of inhibitors are regarded as effecting the chain reactions. No peroxide effect was observed in addition reactions with hydrogen chloride or hydrogen iodide, which always gave the "normal addition", yielding only the product predicted by Markownikoff's rule [45].

Addition of hydrogen halides to olefines is very slow in dilute aqueous solution because of the high free energy of solution of the hydrogen halide. In aprotic solvents [cf. 40 p.442], however, the overall free-energy change differs little from that of the gaseous reaction [cf. 40, p.272]. In the gaseous phase, however, alkenes either do not react with HCl or HBr, or they react very slowly [cf. 41]. The activation energies for the non-ionic addition of HCl and HBr to isobutylene are high (29 and 23 k.cals. respectively).

But a dry liquid mixture of isobutylene and hydrogen chloride react instantaneously at 0°, and within one minute at -78°C., hence in the liquid state it is unlikely that the addition proceeds by a non-ionic process. Mayo and Katz [41] studied the addition of hydrogen chloride to butylene in heptane at 0°C by a dilatometric technique. The sole product of the addition was tertiary butyl chloride, and the reaction was catalysed by traces of water, mercury, and phosphorus pentoxide. The rate of the uncatalysed reaction was proportional to the third power of the hydrogen chloride concentration, and directly proportional to the concentration of isobutylene. For the catalysed reaction the rate was directly proportional to the concentration of each reactant. An unusual temperature effect was observed in that a reaction proceeding at 0° was greatly accelerated by cooling to -80° and warming to 0°.

Maas and his associates [46] studied the liquid phase reactions of several olefines with hydrogen chloride in the absence of solvents. They measured the melting point curves of mixtures of the components, and found that some olefines (e.g. propylene and allylene) gave 1:1 complexes with hydrogen chloride, whereas others gave none (e.g. ethylene and acetylene). In the cases where complexes were not formed, rate of addition was very slow, whereas olefines which gave complexes reacted readily with HCl, and the rate of addition increased rapidly with increase in concentration of HCl when the proportion of HCl to olefin exceeded 1:1. It was therefore suggested that reaction occurs between HCl and an HCl-olefin complex. A positive temperature coefficient was observed for the addition of HCl to propylene except for a 25^{o} temperature range just below the critical temperature region of the mixture [47]. In this region there is a rapid decrease in the density of the medium, and a negative temperature coefficient is observed. Maas attributed this to a breaking up of the liquid "structure" of the reaction medium in this region.

In view of these results, Mayo suggested that the high order and unusual temperature effect observed in their experiments might be accounted for if HCl-isobutylene complexes were involved in these reactions also [41]. Addition of hydrogen bromide to propylene in the presence of an inhibitor for the abnormal addition showed similar properties [49]. Some hexyl bromide is produced in addition to the isopropyl bromide.

It is well-known that metal halides will catalyse the gas-phase reaction of olefines and hydrogen halides [e.g. 50]. There seems to be some doubt as to whether the catalysts can affect the direction as well as the rate of the addition [50,51], but it is evident that the reaction proceeds by a surface mechanism.

Williams and Thomas [52] have studied the addition of hydrogen chloride to styrene in carbon tetrachloride solution in the presence of stannic chloride at 20-25°C. They found that the chief product was 1-phenylethyl chloride together with small amounts of low molecular weight polystyrene, up to the pentomer, and a saturated isomer of distyrene which was believed to be 1-phenyl-3-methyl-indane. They suggested possible mechanisms to explain the formation of these products. Since the uncatalysed addition of hydrogen chloride to styrene does not take place in carbon tetrachloride, the stannic chloride must catalyse the reaction by activating either the hydrogen chloride or the olefin, or both. Their kinetic measurements [53] failed to distinguish between these effects, but they show that under certain limiting conditions of concentration (i.e. styrene $\sim$ 0.1 M, and low catalyst concentration) the rate of disappearance of styrene is proportional to the concentration of catalyst and of each reagent. This is in agreement with the results of Mayo and Katz [41].

Thus it seems that the catalysed and uncatalysed addition of hydrogen halides to olefines in non-polar media are still not fully understood, and further investigation, particularly of the role of the catalyst, is required before the mechanisms of the reactions can be properly elucidated.

Polymerisation Reactions of Olefines.

It is now generally recognised [cf. e.g. 54] that the polymerisation of olefines induced thermally or by organic peroxides proceeds by free-radical chain reactions. The kinetics of such polymerisations have been explained on the radical chain theory, and measurements have been made of the activation energies of all the elementary kinetic steps [58, 59]. These polymerisation reactions are relatively slow ; the overall activation energies lie in the range 15-30 k cal., and the temperatures of 50-150° C. are needed to give conveniently measurable rates of reaction. Molecular weights of the polymers vary with temperature and with added catalyst but a large group lies in the region $6 \times 10^4 - 6 \times 10^5$.

In contrast, polymerisations induced by acids and Friedel-Crafts catalysts proceed rapidly, sometimes explosively, at room temperatures, and even below -100° C. The overall activation energy must therefore be very low, as in fact reported values of 3 k cal., and -7.5 k cal. indicate [60a, 61]. Furthermore isobutene, which is not affected by catalysts which are used for free radical polymerisation, is readily polymerised by metal halides e.g. $TiCl_4$ [62] in hydrocarbon solvents. The rate of this polymerisation has a negative temperature coefficient and is quite insensitive to the presence of oxygen. It is so rapid even at -120° C. that energetic considerations preclude the possibility of a free radical mechanism. The molecular weights of the polymers also differ from those produced by free radical polymerisations. They increase with decreasing temperatures, but for polymers produced in the region 0° – 20°C are of the order $1 \times 10^3 - 1 \times 10^4$. The theory at present accepted is that these polymerisations take place by a mechanism involving carbonium ions, but the details of the reactions are not completely known. Some general account of their most important features will therefore be given.

Investigation of these polymerisation reactions appears to present considerable experimental difficulties, and it has frequently been stated that reproducible results could not be obtained. The first indication of a possible cause of this irreproducibility came when Polanyi and his collaborators [62,63] showed that in the polymerisation of isobutene some substance, not active alone, other than the monomer and the catalyst was required for the reaction to proceed at an appreciable rate. The phenomenon was called co-catalysis, and the third component was believed in their experiments, to be water. It was found that the polymerisation of isobutene in hexane solution by $TiCl_4$ at -80°C. would not proceed with carefully dried reagents, but that the passage of moist air through the non-reacting mixture brought about rapid polymerisation. Dry air had no effect. Requirement of a co-catalyst has since been shown conclusively in several cases for Friedel-

Crafts polymerisations, viz:

Olefin	Catalyst	Solvent	Temp.	Co-Cat.	Ref.
Isobutene	BF_3	Gas-Phase	Room temp.	Water	64
				Tertiary Bu-ol	57
				Acetic Acid	66
Isobutene	BF_3	Gas-Phase	-80°	Water, tertiary butyl alcohol, acetic acid	56
Isobutene	$TiCl_4$	Hexane	$-90-0^\circ$	Water, trichloracetic acid, sulphuric acid	67,61
Isobutene	$TiCl_4$	Ethyl chloride	C.-80°	Water	68
Propene	$AlBr_3$	Butane	-72°	HBr	70

The discovery of the phenomenon of co-catalysis raises the question of whether it might not have played a part in the earlier work, e.g. that of Williams [60] on the polymerisation of styrene in the presence of stannic chloride in carbon tetrachloride at 25°C., when no special precautions were taken to exclude moisture from the reaction vessel during the polymerisations. The effect must clearly be taken into account in all experiments in which moisture is not rigidly excluded.

In other cases, although a catalyst has not been shown to be essential for a reaction to occur, an added substance has been shown to accelerate greatly the reaction rate, and this effect might also be regarded as a case of co-catalysis, e.g.

Olefin	Catalyst	Solvent	Co-Catalyst	Temp.	Ref.
Styrene	$SnCl_4$	Benzene	Water	25°C.	65
Styrene	$SnCl_4$	Ethyl chloride	HCl H_2O	25°C.	71

In the last instance [71] the added substance caused an increase in rate up to concentrations in 1:1 ratio with that of the catalyst. Above this ratio the rate became constant. On the other hand, instances of inhibition of catalysis by added substances have been observed, e.g.

Olefin	Catalyst	Solvent	Inhibitor	Temp.	Ref.
Styrene	$SnCl_4$	CCl_4	HCl	25°C.	60b
Styrene	$SnCl_4$	Ethylene dichloride Nitrobenzene	Water	25°C.	65, 69
Styrene	$SnCl_4$	Nitrobenzene CCl_4	Amines	25°C.	72
Methyl-cyclohexyl-Vinyl ether	$SnCl_4$, I_2	Petrol ether	n-butyl alcohol	25°C.	73
Isobutene	$TiCl_4$	Hexane	Acetic acid, tertiary butanol	-80°C.	62

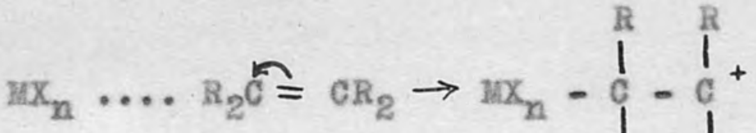
The inhibition by amines is probably explained by the formation of the very stable ammonium ion by interaction of the amine and an active carbonium ion [72]. A similar explanation may hold for the effect of the alcohol. The other instances of inhibition are difficult to explain, especially since substances which are believed to function in one instance as co-catalysts act in another as inhibitors.

This calls to mind the fact that oxygen can sometimes inhibit free radical polymerisations by formation of a stable radical on combination with an active one [52]. p.57,58. A full explanation can only be put forward after a consideration of the possible mechanism of these polymerisation reactions.

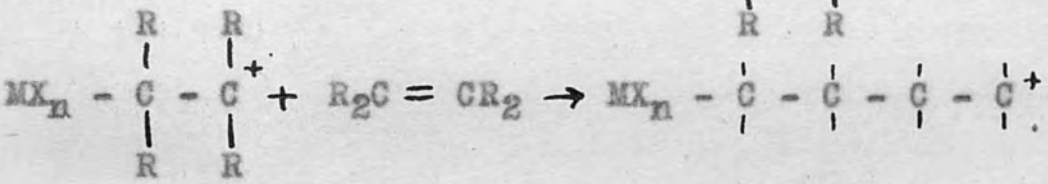
Mechanism of Friedel-Crafts Polymerisations.

Polymerisations of vinyl compounds are regarded as chain reactions in which the distinct phases of chain initiation, chain growth and termination lead to the formation of the long polymers. The rate determining step is usually supposed to be chain initiation, whilst the average chain length of the polymer produced is determined by the relative speeds of chain growth and chain termination. It has not yet been decided [cf. 73], whether it is permissible to apply the stationary state method to all ionic polymerisations, but as a first approximation it is assumed that the overall rate will be related to $k_i k_p/k_t$ and that the molecular weight will be proportional to k_p/k_t where k_i, k_p and k_t are the rate constants of the initiation, propagation and termination reactions. If this is so, then the overall activation energy E will be given by $E = E_i + E_p - E_t$ where E_i, E_p, E_t are the activation energies respectively of the initiation, propagation and termination reactions. There will thus be a negative temperature coefficient if $E_t > E_i + E_p$, and the molecular weight will increase as the reaction temperature is lowered if $E_t > E_p$.

Before the discovery of the co-catalyst effect Price, and Hunter and Yohe [74,75] put forward a mechanism for the initiation step which assumed that the metal halide alone associated with the double bond and polarised it sufficiently to initiate a carbonium ion chain -



$$MX_n \ldots\ldots R_2C=CR_2 \rightarrow MX_n-\overset{R}{\underset{R}{C}}-\overset{R}{\underset{R}{C}}^{+}$$ ①



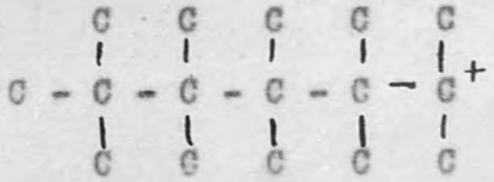
$$MX_n-\overset{R}{\underset{R}{C}}-\overset{R}{\underset{R}{C}}^{+}+R_2C=CR_2 \rightarrow MX_n-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}^{+}\ \text{etc.}$$ ②

As a result of their work with isobutene Polanyi and his associates proposed a new carbonium ion theory [62,57] which resembles that of Whitmore [76] in that a proton is believed to add onto the double bond, generating a carbonium ion. The proton [62,57] is supplied from a complex acid formed by the interaction of catalyst and co-catalyst -

$$TiCl_4 + RH \longrightarrow TiCl_4R^{-}H^{+}$$ ③

$$H^{+} + (CH_3)_2C=CH_2 \longrightarrow (CH_3)_3C^{+}$$ ④

The carbonium ion then reacts with further monomer molecules by head-to-tail addition, regenerating the carbonium ion at the end of the chain at each step. The skeleton of the growing chain would be —



There is evidence for such a regular structure for polyisobutene [77], and according to Evans and Polanyi, it is the only energetically possible structure for a carbonium ion mechanism [57]. In a non-polar medium, the anion (TiCl$_4^-$R) would be held in close proximity to the positive centre in the growing chain [cf. 55], and the propagation step should not require an activation energy as it involves the approach of a positive ion to a neutral molecule [57]. This mechanism overcomes the difficulty of separation of charges implicit in the polarisation mechanism (①and②).

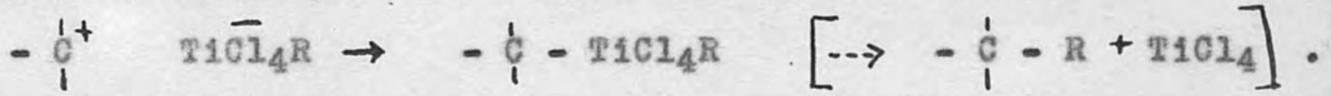
In the experiments of Eley and Pepper [73] and Richards and Pepper [78] on the polymerisation of n-butyl-vinyl-ether and ofoctyl vinyl ether by $SnCl_4$ and I_2 in petrol ether, the monomer might function as a co-catalyst, since ethers are known to react readily with Friedel-Crafts catalysts. These authors found [73] that the rate of polymerisation increased as the reaction proceeded, but this may have been due to the unintentional introduction of small amounts of moisture into the reaction vessel. Presumably water would be a more effective co-catalyst than the ether. It is at first sight surprising that a co-catalyst (water) is required for polymerisations in ethyl chloride [68] since $C_2H_5^+$ ions should exist in the solution, but they are probably present in very minute amounts [cf. Fairbrother, 32].

Chain transfer might occur in several ways. For instance, there might be elimination of a proton from a terminal carbonium ion with the formation of a terminal double bond and a regeneration of the catalyst:

$$-\overset{|}{\underset{|}{C}}-\overset{|+}{\underset{|}{C}}\quad \overline{TiCl_4R} \rightarrow -\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} + \overset{+}{H}\,\overline{TiCl_4R}.$$

That this does occur in the low-temperature polymerisation of isobutylene with BF_3-water [56] is shown (a) by the fact that the activity of the catalyst does not decrease as the polymerisation reaction proceeds, and (b) since 0·01 m.m. pressure of water vapour is sufficient to cause the complete, though very slow, polymerisation of 100 m.m. pressure of isobutene, i.e. one water molecule is effective in the polymerisation of 10,000 molecules of isobutene. This represents the production of 2,000 polyisobutene molecules. Also, Dainton and Sutherland [79] have shown by infra-red spectroscopy that in the polymerisation of isobutylene with BF_3 in the presence of D_2O, the end groups are chiefly $(CH_3)_3C$ - and - CH_2 - $C(CH_3)=CH_2$, and that the co-catalyst is gradually converted from D_2O to H_2O as the reaction proceeds. This is good evidence for reactions of the type ③ and ⑤. Similar evidence has been presented by Fletter and Plesch [80] for the polymerisation of isobutylene by $TiCl_4$ in the presence of water, sulphuric acid and trichloracetic acids. As pointed out by Evans and Meadows [56], proton transfer to another monomer molecule would also explain their observation.

The method of termination which appears to operate for isobutylene in hexane solution with $TiCl_4$ and trichloracetic acid at low temperatures [61] is one in which the catalyst anion and active carbonium ion combine to give a neutral molecule, which may remain as such, or decompose with liberation of the catalyst, since chlorine is found to be present in the polymer isolated from these reactions.



$$-\overset{|}{\underset{|}{C}}{}^{+}\quad \overline{TiCl_4R} \rightarrow -\overset{|}{\underset{|}{C}}-TiCl_4R \quad \left[\dashrightarrow -\overset{|}{\underset{|}{C}}-R + TiCl_4 \right].$$

This is in agreement with the earlier observation of Staudinger [81] and also of Lander [82], and seems to be the most reasonable mechanism for chain termination.

Thus, although there may be two types of initiation reaction, and various chain-transfer reactions for these polymerisations, their general character has been established.

Pepper [83] has presented good evidence for the general ionic mechanism in that for α-methyl styrene in the presence of stannic chloride at room temperature both the rate and degree of polymerisation increase with increasing dielectric constant of the solvent medium.

Unfortunately, reliable kinetic data for these reactions are few. The first results were those of Williams [60] who showed that the overall rate equation for the polymerisation of styrene in the presence of stannic chloride in carbon tetrachloride at $25^{\circ}C$. was:

$$\frac{-d(a-x)}{dt} = k.c.a\ (a-x)^3$$

where a,c are the initial concentrations of monomer and of catalyst, and (a-x) is the styrene concentration at time t, k is a constant. He also found that the molecular weight of the product was proportional to $\sqrt{a}$, and was independent of c. The kinetic data published since then are as follows:-

(Table B overleaf)

Table B.

M = initial monomer concentration; c = initial catalyst concentration

Ref. No.	Olefin	Catalyst	Solvent	Temp.	Rate	Dependence of M.wt. on M,c, and temp.
78a	Octylvinyl ether	I_2	Petrol ether (Diethyl ether Ethylene dichloride	25°	$\propto kMc^2$ (Increase with ϵ of solvent)	No systematic effect for M and c. Small decrease with increasing temp.
78b	"	$SnCl_4$	Petrol ether	25°	$= kMc^2$	$\propto$ M, independent of c. Decrease with increase in temp.
		$AgClO_4$	Ether	25°	$= kMc^2$	$\propto$ M, independent of c.
	"	$(C_6H_5)_3COH$	m-Cresol	25°	$= kMc^2$	-
71	Styrene	$SnCl_4$ (HCl or H_2O in some cases)	Ethyl chloride	25°	$= \frac{k5c.M^2}{k3 + k5M}$ ($\propto$ to conc. HCl or H O up to ratio of 1:1 with c)	$\propto$ M, independent of c.
70	Propylene	$AlBr_3/HBr$	Butane	-78°-c.5°c	$\frac{kKcM^2}{1 + KM}$	-
61	Isobutene	$\left\{\begin{array}{l}TiCl_4\\CCl_3CO_2H\end{array}\right.$	Hexane	$-90^\circ \to 0^\circ$	$\propto$ to co-cat. concentration	Increases with decreasing temperature.
69	Styrene	$SnCl_4$	Ethylene dichloride	25°	$= kM^2c$	$\propto$ M, independent of c.

In order to explain the high order for the reaction in carbon tetrachloride and the independence of molecular weight on catalyst concentration, Williams [60] proposed an activating collision (3-stage) of stannic chloride with three styrene molecules for the rate determining chain-initiation step, and a termination step involving stabilising rearrangement of the growing polymer chain. Thus, if M_n and P_n denote stable and activated monomer or polymer molecules, then we have -

Chain initiation $\quad M_1 + c \rightarrow M_1c$

$\qquad\qquad\qquad\quad M_1c + 2M_1 \rightarrow P_3c$ (or $P_3 + c$)

Chain termination $\quad P_nc \rightarrow M_nc.$

The other kinetic data show in the main a direct dependence of rate on catalyst concentration; and a dependence of rate on either the square of the monomer concentration or a fractional power of it. These two effects can be explained in the following way. Firstly, for $\frac{-d(M)}{dt} = k.cM^2$, there is a very simple scheme to explain the kinetic relations [78,73] viz:

Initiation $\quad M + c \xrightarrow{ki} Mc \quad (P_1^+)$ ion or polarised molecule

Propagation $\quad P_1^+ + M \xrightarrow{kp} P_2^+$

$\qquad\qquad\quad P_x^+ + M \xrightarrow{kp} P_{x+1}^+$

Termination $\quad P_n^+ c \xrightarrow{kt} P_n + c.$

Assuming a stationary state, we derive:

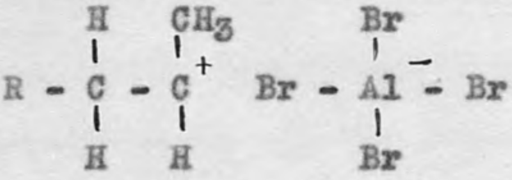
$$\text{Rate} = \frac{ki \times kp}{kt} \times M^2c.$$

$$\text{M.wt.} = \frac{kp}{kt} \times M .$$

The fractional relationships are obtained by making certain other assumptions [70]. Fontana and Kidder observed in the polymerisation of propylene at low temperature in butane solution in the presence of aluminium bromide that the rate appeared to depend only on the concentration of an active complex containing one molecule of hydrogen bromide, and probably one molecule of aluminium bromide until towards the end of the reaction there was a marked decrease in rate which they showed to be conditioned by the low concentration of olefin. They therefore proposed a stepwise process for the polymerisation in which at any stage of the reaction chain there was an associative equilibrium of the type -

$$m_nc + m \overset{K}{\rightleftharpoons} m_ncm$$

where m_nc is a polymer-catalyst/co-catalyst complex, and m is olefin monomer. The complex m_nc may be regarded as a carbonium ion coupled with an anion such as -



$$R-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C^+}}\quad Br-\overset{Br}{\underset{Br}{Al^-}}-Br$$

They then assumed that the rate controlling step in the polymerisation was the rearrangement of the associated monomer to form a new complex with one more unit on the polymer -

i.e. $m_ncm \xrightarrow{k} m_{n+1}c$

Putting $c = \sum_n [m_nc] + \sum_n [m_ncm]$ the resulting rate equation was found to be -

$$\frac{-d[m]}{dt} = \frac{kKe[m]}{1 + K[m]} \quad .$$

This is the only example in the literature in which a stepwise process has been suggested for ionic polymerisations, rather than a slow initiation reaction followed by rapid propagation. The fact that Fontana and Kidder found that the molecular weight of the polymers increased during the polymerisation is in contrast to the work of Williams [60] and Pepper [73] who obtained polymers of high molecular weight even in the initial stages of their reactions. The increase in molecular weight is suggestive of a stepwise process in this particular system, but it seems very unlikely that this mechanism is of general application as suggested by Mayo and Walling [87].

Thus, divers mechanisms appear to hold for Friedel-Crafts polymerisations under different conditions. It remains to be seen whether a general explanation can be found which will account for and correlate all the results.

Determinations of activation energies for the various steps involved in the polymerisations have only been made in one or two instances. Williams [60] found that the overall activation energy for polymerisation of styrene in the presence of stannic chloride in carbon tetrachloride was low, namely 3 kcal/mole. One would expect that the initiation process which probably involves the formation of ion-pairs in a non-polar environment would be fairly high. The propagation step, which consists of the reaction of a positive ion with a neutral molecule should have little or no activation energy in a solvent of low ϵ . The activation energy for the termination reaction, if it involves rearrangement of an ion-pair, may be fairly high.

Eley and Richards [78a] found that for vinyloctyl ether and iodine the velocity constant increased approximately exponentially with the dielectric constant of the solvent, but the molecular weight at 20% polymerisation was almost unaffected. Furthermore, calculation from kinetic data of overall activation energies for the polymerisations gave values of 10,000 cal (petrol ether) and 16,000 cal (ethylene dichloride). The increased polymerisation velocity in solvents of higher ϵ was thus not due to a lower overall activation energy, and it was assumed that the dielectric constant must affect mainly the entropy of activation. They also investigated the effect of temperature on the molecular weight, and found the activation energy for this effect to be -3,300 cal for each solvent investigated. As already stated the two activation energies can be expressed as:

$$E_{rate} = E_i + E_p - E_t. \quad , \text{ i.e. } \propto \frac{k_i . k_p .}{k_t}$$

$$E_{M.Wt.} = E_p - E_t. \quad , \text{ i.e. } \propto \frac{k_p .}{k_t} \quad .$$

Increasing the ϵ of the solvent should increase k_i since electric charges are developed in the initiation process, but should cause a slight decrease in kp, which represents reaction between an ion and a neutral molecule, and also should cause k_t to decrease still more if the termination occurs by interaction between a positively charged growing chain and a negative catalyst fragment. Thus one can see how an increase in ϵ of the solvent can cause an increase in rate whilst having little effect on molecular weight.

From these values, and identical values for stannic chloride catalysis in petrol ether [78b] Eley and Richards predicted that $E_i \sim 13,300$ cal/mole. It had previously been shown that vinyl ethers polymerise at -80°C., which was taken [78b] as an indication that $E_p \sim 2,000$ cal/mole (assuming an A factor of 10^5 for propagation), and hence the activation energy of spontaneous termination, E_t, $\sim$ 5,000 cal/mole.

Plesch [61] obtained a much lower value for E_i for isobutene catalysed by $TiCl_4$-CCl_3CO_2H in hexane solution. The overall activation energy was found to be -7.5 kcal/mole ± 2 kcals, and the activation energy for the effect of temperature on molecular weight was identical. Hence the upper limit for E_i was 4 kcal/mole. Then assuming that E_p was low, E_t was of the order of 6-10 kcal/mole.

The overall activation energy for the polymerisation of propylene by $AlBr_3$/HBr in butane, studied by Fontana and Kidder [70], was found to be 16.4 kcal/mole.

These are the only systems for which values of activation energies have been given, but the low values do serve to explain the rapidity with which the ionic polymerisations occur, even at low temperatures.

SECTION II. EXPERIMENTAL.

ADDITION EXPERIMENTS (NORMAL CONDITIONS).

MATERIALS.

Pure commercial styrene stabilised with quinol was redistilled under reduced pressure before use. The stannic chloride was obtained by the distillation (in vacuo) of pure commercial stannic chloride (fig.i), as described on p.95 and was kept in a ground glass stoppered bottle in a desiccator containing phosphorus pentoxide, and pipetted into the solvent medium at the commencement of a reaction. Stannic bromide was likewise obtained by distillation (in vacuo) of pure commercial stannic bromide (fig.ii) as described on p.58. The bulbs of stannic bromide were scored and cracked with a hot rod near to the surface of the solvent medium and then dropped into the solvent at the commencement of a reaction. Analar carbon tetrachloride was stored over phosphorus pentoxide and redistilled immediately before use. Chlorobenzene was dried for several days over calcium chloride and distilled under reduced pressure immediately before use. Nitrobenzene was dried in a similar manner.

Samples of 1-phenyl-ethyl bromide and 1-phenyl-ethyl chloride required for the standardisation of analytical techniques were prepared by the action of phosphorus tribromide (c.f. Rupe and Toni, Ber.(1914), 47, 3074) and thionyl chloride (c.f. McKenzie and Clough, J. Chem.Soc., (1913), 103, 694), respectively, on 1-phenyl ethyl alcohol.

The 1-phenyl ethyl alcohol was prepared by the dropwise addition of freshly distilled acetaldehyde (4.4 g.) to a solution of phenyl magnesium bromide in sodium dried ether (50 ml. ether, 20 g. dry bromobenzene, 3.2 g. dry magnesium). When the addition was complete, ice (20 g.) was added to the reaction mixture followed by 5N hydrochloric acid (150 ml.). The ethereal layer was separated, washed three times with water and dried for 4 hours over sodium sulphate. The ether was removed by distillation, and the product, a mobile liquid, was distilled under reduced pressure (18.8 g., b.p. 88.5°C./14 mm.). Some diphenyl (2.2 g., m.p. 70°C.) was left in the flask after the distillation.

Commercial phosphorus tribromide was redistilled (b.p. 68-70°C./53 mm.) and 4.8 g. were gradually added from a dropping funnel to 1-phenyl ethyl alcohol (3 g.) in a flask fitted with a reflux condenser to which a phosphorus pentoxide tube was attached. During the addition the flask was cooled in an ice-water bath, and afterwards it was warmed on a water bath for 3/4 hour. The product was then cooled and poured into a separating funnel containing water and ether, and the funnel was shaken thoroughly. The ethereal layer was separated, washed with a strong solution of sodium bicarbonate, then with water, and dried overnight over sodium sulphate. After removal of the ether by distillation, the product was distilled under reduced pressure (b.p. 95-99°C./38 mm., 3.9 g.), shaken with anhydrous potassium carbonate and redistilled (b.p. 88-91°C./30 mm.). (Found: Br_2 43.20, 43.40%. Theoretical: Br_2 43.50%).

2 ? p70

Thionyl chloride was purified by two fractional distillations off pure, dry quinoline (c.f. Ott, Ber. (1928), 61, 2140), and the fraction boiling at 75.5-76°C. was taken each time. 1-phenyl-ethyl alcohol (4 g.) was added dropwise to thionyl chloride (10 g.) in a distillation apparatus fitted with a dropping funnel, the exits having phosphorus pentoxide tubes attached. After fifteen minutes at room temperature, the excess thionyl chloride was removed under reduced pressure (at about 20°C.), and the residue was distilled in vacuo (b.p. 88-90°C./34 mm., 3.5 g.), shaken with anhydrous potassium carbonate and redistilled (b.p. 84-85°C./32 mm.). (Found: Cl_2 25.1, 25.3%. Theoretical: Cl_2 25.3%).

APPARATUS.

Reactions in which hydrogen chloride was used were carried out at room temperature (15-25°C.) in a round bottomed flask (J) fitted with inlet and exit tubes for the dry gas (fig. iii). Reactions in which hydrogen bromide was used were carried out under similar conditions (fig. iv).

In either case the apparatus beyond Z was cleaned and dried between experiments by washing with dry solvent and blowing dry with a current of air.

PROCEDURE.

The reactions were carried out by leading a stream of the dry hydrogen halide through solutions of styrene and stannic halide in carbon tetrachloride, chlorobenzene or nitrobenzene. Hydrogen chloride gas was generated by dropping concentrated hydrochloric acid from A (fig. iii) and concentrated sulphuric acid from B into flask C, and leading the gas through concentrated sulphuric acid in D. The hydrogen bromide was obtained (fig. iv) by allowing bromine to drop from E onto a mixture of red phosphorus (30 g.) and water (75 ml.), in flask F, and passing the gas evolved over towers packed with moist red phosphorus and glass wool (G) and phosphorus pentoxide and glass wool (H). The exit tube of each apparatus was closed with a phosphorus pentoxide tube.

Samples of the solutions were withdrawn at suitable intervals and run into an excess of a standard solution of bromine in acetic acid. The excess bromine was titrated with sodium thiosulphate after the addition of potassium iodide in order to determine the concentration of styrene in the reaction mixture. When the styrene concentration had fallen almost to zero the flasks J were detached from the apparatus, and the reaction products were washed three times with water, dried for 6-12 hours over sodium sulphate, and finally filtered into a distilling flask. The pieces of the phials of stannic bromide were collected from the flask, washed with carbon tetrachloride, dried in an oven at 110°C. and weighed . For reactions carried out in chlorobenzene or carbon tetrachloride as solvent, the bulk of the solvent was distilled off under reduced pressure, and the residue transferred to a small Claisen flask and separated into fractions by distillation under reduced pressure. No attempt was made to fractionate the mixtures of 1-phenylethyl bromide and 1-phenylethyl chloride but these mixtures were separated by fractional distillation from unchanged styrene, distyrene and other low molecular weight polystyrenes known to be formed in the addition reactions. When nitrobenzene was used as a solvent, special methods were used for isolating the reaction products (pp89-93).

Similar methods were employed in the halogen exchange reactions.

ADDITION EXPERIMENTS
(APPROXIMATELY ANHYDROUS CONDITIONS).

MATERIALS.

Pure commercial styrene stabilised with quinol was redistilled under reduced pressure, dried over sodium for a few hours, redistilled and finally dried over sodium and redistilled immediately before use. A large first fraction was rejected in each distillation. The flask in which the styrene was finally collected was calibrated before use by the addition of known volumes of water. The level of the water was marked on a strip of adhesive material placed around the flask. The final distillation was carried out at < 1mm. pressure (rotary pump), and the apparatus was evacuated at 10^{-3}mm. for three hours and heated with a naked flame beforehand.

Analar carbon tetrachloride, stored for several weeks over phosphorus pentoxide, was refluxed over this reagent for twelve hours and fractionally distilled in an all glass apparatus immediately before use. It was collected in the receiving flask described on p.83. This receiving flask also was calibrated before use in the way described above.

Stannic chloride was fractionally distilled at 10^{-5}mm. in the apparatus shown in fig.v. There were no rubber connections beyond Z. The principle used was in part that employed by Briscoe (J.Chem.Soc., (1914), 105, 1321), namely that of refluxing the crude stannic chloride and allowing its crystalline hydrate to settle on a cooled surface which could subsequently be sealed off from the rest of the apparatus, and also use was made of the fact observed in an earlier distillation, that the crystalline hydrate ($SnCl_4,5H_2O$) appeared to be slightly more volatile than anhydrous stannic chloride. Two large fractions were therefore sealed off and rejected (in flasks F and H).

The whole of the apparatus was evacuated at 10^{-5}mm. for 36 hours and was heated frequently with a hand blowlamp during this time, (taps L,T,S open; taps A,B,U,R closed). Tap T was then closed. Dry air was then introduced into the apparatus through R and U, which were afterwards closed again. The apparatus was connected to an air compressor by means of rubber tubing at A. Tap A was opened and the aspirator was swept out with a stream of dry air from the compressor. The sealed tube was removed from C simultaneously with the opening of tap B, and then with dry air circulating throughout the aspirator and down the central tube at C, a fresh bottle of stannic chloride was lifted up into the aspirator and the stopper removed. It was held so that the bottom of the tube at C was just below the surface of the stannic chloride. Tap B was closed and the stannic chloride was drawn up into tube C by opening tap L for a few seconds. The stannic chloride was allowed to syphon over from the bottle into flask E, and when about 300 ml. had come over, tap B was opened and the bottle lowered from the syphon tube. The sealed tube at C was then replaced and tap B was closed. A bath of carbon tetrachloride and solid carbon dioxide (temp. -22°C.) was placed round flask E which was immersed up to the sidearm. The apparatus was then evacuated (10^{-4}mm.), and the vacuum jacket around the Widmer column was sealed at capillary c. The capillaries a and b were also sealed. A small amount of the crystalline hydrate of stannic chloride separated out along the syphon tube, but there was only a trace visible in flask E. After 2 hours the cooling bath was removed from flask E, and was replaced by a bath of water at 20°C. A bath of carbon tetrachloride and carbon dioxide was placed around flask F which was immersed up to the capillary m. The stannic chloride distilled up to the column and collected in F. A deposit of the crystalline hydrate appeared on the cooled surface at the top of the column. Some stannic chloride and its hydrate passed down the tube leading to the crash seal at G, but these were subsequently driven back into F by warming the tube with a hand blowlamp. A very faint white film of non-volatile material was left on this tube, and was assumed to be stannic oxide. When about 100 ml. of liquid had been collected in F, the water bath was removed from flask E and replaced by a bath at

-22°C. Flask F was then removed from the apparatus by sealing capillary m, and the capillary e was also sealed. The seal at G was then broken by carrying the thick glass capsule x (fig.v.a) over the bend with a magnet and allowing it to drop onto the thin glass bulb of the seal. A Dewar flask containing liquid air was placed around flask H, and the capillary g was sealed. Some crystalline hydrate was still left on the walls of the apparatus above the Widmer column and on the neck of flask E, and these were warmed to carry the hydrate into flask H. The cooling bath on E was replaced by a water bath at 20°C., and another large fraction (about 50 ml.) was collected in flask H. E was then cooled once more whilst capillary f was sealed, and the seal at K was broken. Flask J was then immersed in a bath at -22°C., and E was warmed on a water bath until almost all the residual liquid in E had distilled into flask J. E was then cooled to -22°C., and h was sealed. With liquid air around Q and taps S and T open, the tubes on M,N,O and P were once again heated thoroughly. S was then closed and J was warmed on a water bath at 20°C. It was hoped to distil liquid into each tube on the racks separately, but stannic chloride distilled into all the tubes simultaneously. The temperature of the bath around J was slowly raised to 25°C., and within 3/4 hour the stannic chloride had distilled into all the tubes on M,N,O and P, and each tube contained approximately 1-1.5 ml. of stannic chloride. Each tube was then sealed off in turn by cooling to -22°C. and sealing at the upper capillary i. 83 tubes were collected and numbered in the order in which they were sealed off. After 24 hours there were traces of crystalline hydrate in about five of the tubes, and in the remainder the stannic chloride remained perfectly clear.

Stannic bromide was distilled in the apparatus shown in fig. ii. Rubber connections were eliminated beyond Z and X. The apparatus was evacuated for 12 hours at 10^{-4}mm. with liquid air on J, and was heated for 15 min. with a hand blowlamp at the beginning of the evacuation. H was then closed and F opened. The score mark at A was broken and simultaneously a stream of dry nitrogen was introduced through F. Commercial pure stannic bromide (about 80 g. of white crystals) was introduced into C through the side arm, after which B was sealed. Flask C was then warmed on an oil bath at 100-110°C. for 1 hour so as to decompose any hydrate to stannic oxide and hydrogen bromide, the former being non-volatile (c.f. Fairbrother, J. Chem.Soc., (1945), 503.) When the flask had cooled to room temperature again, F was shut and H opened. The apparatus was evacuated at 10^{-4}mm. once more, all the distillation tubes and the neck of C being well flamed during this period. Flask C was warmed gently, (60-70°C.) on an oil bath, and with liquid air around D, a large first fraction (about 20g.) was collected, which should have contained any hydrogen bromide present in C. Before sealing off D all the other tubes were heated, and d was then sealed. The other tubes were then cooled in turn in liquid air, and the upper capillaries c sealed when sufficient stannic bromide had been collected. A slight residue was left in flask C at the end of the distillation.

Dry hydrogen chloride was generated in the apparatus shown in fig. vi, which was sealed onto the reaction vessel at A before evacuation of the vessel. Concentrated sulphuric acid was dropped at a convenient rate from B onto the analar ammonium chloride (200 g.) in C, and the gas evolved was led through a column of sulphuric acid and glass beads (D), then carbon tetrachloride (E) and finally over a series of tubes containing phosphorus pentoxide (F).

The apparatus used for generation of the dry hydrogen bromide is likewise shown in fig. vi. This was likewise sealed onto the reaction vessel at A, when required, before the evacuation of the vessel. Tetralin was dried by azeotropic distillation with benzene (500 ml. benzene/

500 ml. tetralin), and finally fractionally distilled under reduced pressure immediately before use (98-101°C./24 mm.). Pure commercial bromine (180 ml.) was dropped from B onto the tetralin (500 ml.) in C, and the gas evolved was passed through a column containing tetralin and glass beads (D), then carbon tetrachloride (E), and finally through a series of tubes containing phosphorus pentoxide (F).

APPARATUS.

The source of dry nitrogen used is shown in fig. vii. The reaction vessel and vacuum line used in the addition experiments under approximately anhydrous conditions are shown in fig. viii. In the hydrogen chloride experiments when the catalyst used was stannic bromide, ordinary stoppers were used at H and J. Between experiments the reaction vessel was washed out with carbon tetrachloride, acetone, water, cleaning acid, water, acetone, pure, dry carbon tetrachloride in that order. All taps were cleaned with ether and regreased (Apiezon High-Vacuum grease). Taps G,H, J,K,L were sealed with mercury. The apparatus was reassembled and evacuated for at least 12 hours at 10^{-5}mm. (taps G,P,Q and K closed, L open), being heated with a naked flame for 15 min. at the commencement of the evacuation. Tap L was then closed. Dry air was introduced by opening tap K which was then closed again.

When stannic chloride was to be used as catalyst, a weighed phial with scored capillaries was washed down with dry carbon tetrachloride and placed in position in the reaction vessel as shown before evacuation.

METHOD.

A line from the dry nitrogen supply was attached at Q and as the stopper J was removed, tap Q was opened. Whenever J or H was removed, it was immediately placed on the holder (fig. viiia). The syphon tube of the carbon tetrachloride flask was then introduced through J into N, and by means of dry nitrogen an appropriate volume of carbon tetrachloride was blown over into N, the level in the storage flask being measured before and after the addition. Styrene was introduced in a similar manner from its storage flask. Stopper J was then replaced and Q was closed. In this way an estimate of the initial styrene concentration was obtained. In the case of stannic chloride catalysis, the catalyst was introduced by breaking the capillaries of the phial by turning stoppers H and J respectively. The phial dropped down into the solution and the stannic chloride dissolved. When stannic bromide was used, a tube from the dry nitrogen supply was connected at P, and tap P was opened as stopper H was removed. A weighed scored phial of the catalyst was cracked above H, and dropped immediately into the reaction vessel. P was replaced and H closed. Solution of the stannic bromide was always complete within 15 minutes from the time of the addition. Taps K and G were then opened, and the hydrogen halide was allowed to flow through the solution in N at the rate of about 1-2 bubbles/second. This was maintained for at least 6 hours in the case of hydrogen chloride and 3 hours for hydrogen bromide before sampling. It was found difficult to regulate the supply of hydrogen bromide, and the rate of passage fell considerably at times (1-2 bubbles/minute), hence the experiments were sometimes of rather long duration. This difficulty was also encountered to some extent in the hydrogen chloride reactions.

In removing samples for analysis from N a 2 ml. pipette was used, controlled at the top by a tap. It was rinsed three times with analar carbon tetrachloride and blown dry with dry nitrogen between samplings. When a sample was to be taken, a line from the dry nitrogen supply was connected at Q, and Q was opened. As stopper J was removed, K was closed. The pipette was introduced into N, and a sample of the solution drawn up into it after which it was removed from N. J was replaced and K and Q were closed. The level in the pipette was adjusted to the mark, and the sample was run into 10 ml. of a standard solution of bromine in acetic acid. The excess bromine was titrated with sodium thiosulphate after the addition of potassium iodide. When the styrene concentration had fallen to a low value, N was removed from the apparatus and the reaction products isolated in the usual way.

STRUCTURE AND ANALYSIS OF THE PRODUCTS.

1-Phenyl ethyl halides.

It had already been shown (c.f. Williams, J.Chem.Soc., (1938), 1046; Thomas and Williams, J.Chem.Soc., (1948),1867) that the chief product of the interaction of styrene with hydrogen chloride in carbon tetrachloride in the presence of stannic chloride was 1-phenylethyl chloride. Analysis of a product obtained with these reagents in the present series of experiments confirmed these results. A mobile liquid was obtained, b.p. 82-84 C. (Found: C,68.8; H,6.5; Cl_2,25.3%. Theoretical: C,68.3; H,6.4; Cl_2,25.3%).

It was assumed that the product from the addition of hydrogen bromide to styrene, both in the presence and the absence of stannic bromide, would be 1-phenylethyl bromide (c.f. Walling, Kharasch and Mayo, J.Amer.Chem.Soc., (1939), 61, 2693), and evidence for this was obtained by the method of Ashworth and Burkhardt (J.Chem.Soc. (1928), 1798). The bromide was hydrolysed to the corresponding alcohol, which was identified by means of its 3:5-dinitrobenzoate.

A sample of the product to be identified (2.2 ml.) was heated under reflux for ½ hour with potassium hydroxide (1.2 g.), water (20 ml.) and ethyl alcohol (30 ml.), cooled, diluted with water followed by excess of ether. The mixture was shaken, and, after separation, the ethereal layer was washed with dilute hydrochloric acid, water, and finally dried over anhydrous potassium carbonate. After filtration, the ether was removed by distillation. A sample (0.1974 g.) of the residue (1.5993 g.) was dissolved in carbon tetrachloride and 10 ml. of 0.2N bromine in acetic acid was added. The amount of styrene present in the sample was estimated by titration of the excess bromine with sodium thiosulphate:

10 ml. of the bromine solution $\equiv$ 18.36 ml. 0.0997N thiosulphate.

Back titration = 12.44 ml.

0.1974 g. of the sample contain 0.0258 g. styrene, i.e. 14.1%.

A sample of the residue (0.54 g.) was heated with 3:5-dinitrobenzoyl chloride (1.08 g.), benzene (11 ml.) and anhydrous pyridine (3 ml.) for ½ hour on a water bath. After cooling, ether (50 ml.) was added and the solution was washed with dilute hydrochloric acid, dilute sodium carbonate solution, water and finally dried over calcium chloride. The solvents were removed by distillation and a small volume of methyl alcohol was added to the residue which was cooled on solid carbon dioxide. The cream coloured crystals which formed were filtered and air dried (m.p. = 92-94°C. wt. = 1.14 g.) and recrystallised from ether (m.p. = 94-95°C. wt. = 1.08 g., mixed m.p. with the 3:5-dinitrobenzoate of synthetic 1-phenyl ethyl alcohol (p.50) = 94-95°C., mixed m.p. with the 3:5-dinitro benzoate of commercial 2-phenyl ethyl alcohol = 70°C.). Recovery of the alcohol from the sample under investigation = 80.1%, recovery as styrene = 13.7%. Similar results were obtained with samples of product from the addition of hydrogen bromide in the presence and absence of stannic bromide.

In a control experiment, using a sample of synthetic 1-phenyl ethyl bromide (c.f. p.50), recovery of the 1-phenyl ethyl alcohol was 85.2% and of styrene 12.4%.

Distyrene.

The second fraction (b.p. 174-175°C./33 mm.) in the distillations of the reaction products had previously been shown (Gwyn Williams, J.Chem.Soc., (1938), 1046) to be identical with the distyrene prepared by Erlenmeyer (Ann.(1865), 135, 122), which Stobbe and Posnjak (Ann.(1909), 371, 287) had identified as 1:3 diphenyl-but-1-ene.

Low Molecular Weight Polystyrenes.

The low molecular weight polystyrenes obtained as a non-distillable residue in some of the reactions had previously been identified (Thomas and Williams, loc.cit.). The molecular weights of those obtained in the addition reactions in nitrobenzene solution were determined by the cryoscopic method in benzene solution.

ANALYSIS OF THE MIXTURES OF 1-PHENYL ETHYL HALIDES.

(a) Total Halogen.

A sample of the mixture to be analysed was weighed accurately in a small capsule which was dropped into a long-necked 50 ml. quick-fit flask, and heated for 3 hours under reflux with a slight excess of 0.2N alcoholic sodium hydroxide. The flask was then transferred to an apparatus for the removal of the alcohol, styrene and 1-phenyl ethyl alcohol by steam distillation (about ½ hour). The residue in the flask, which consisted of an aqueous solution of the sodium halide and a slight excess of sodium hydroxide, was washed carefully into a beaker, and 5 ml. concentrated nitric acid were added followed by 20 ml. of standard approximately 0.2N silver nitrate solution. When the precipitate had been coagulated by warming the beaker gently to about 100°C. for 15-30 minutes and leaving to cool in the dark, the precipitate was filtered on a G4 sintered crucible and heated to constant weight at 120°C. The filtrate was titrated against standard approximately decinormal ammonium thiocyanate using ferric alum indicator

(0.5 ml.) (Volhard Method). The silver nitrate solution used in these estimations was standardised by the gravimetric method using weighed samples of pure sodium chloride previously dried for 2 hours at 120°C., and was used to standardise the ammonium thiocyanate. The normality of the latter solution was checked using a second standard silver nitrate solution.

Deviations from the theoretical values for total halogen for mixtures of various compositions were calculated and compared with the results actually obtained for several mixtures (Tables Ia, Ib, II).

(b) Estimation of bromide in the presence of chloride.

From a survey of the methods available for the estimation of bromide in the presence of chloride, that of B.S. Evans (Analyst (1930), 590) appeared to be the most satisfactory. This consisted in the oxidation of mixtures of sodium chloride and sodium bromide with chromium trioxide in sulphuric acid medium (7-9N). The chloride was unchanged, whilst the bromide was oxidised to bromine. This was led into excess of standard arsenious oxide, which was then back titrated with standard iodine. The accuracy claimed was 2-3% for mixtures containing as little as 2% of sodium bromide.

This method was first standardised in the apparatus shown in fig. xiv. 20 ml. of standard approximately 0.2N arsenious oxide was introduced into flask B, 5 g. analar sodium bicarbonate were added, followed by 200 ml. distilled water. Flask C contained 10 ml. standard arsenious oxide, 5 g. analar sodium bicarbonate and 200 ml. distilled water. Into flask A was introduced a known volume of a standard solution of potassium bromide, followed by 3 ml. concentrated sulphuric acid and, after cooling, 5 g. analar chromium trioxide. The neck of the flask was washed down with 3:1 sulphuric acid, and the flask was then clamped into position. A stream of air was led through the apparatus at the rate of 1-2 bubbles/second for about three hours. Flasks B and C were then detached and the delivery tubes were washed down with distilled water. The contents of B and of C were titrated with standard approximately decinormal iodine solution using starch indicator. The results are shown in Table III.

A standard bromide solution was prepared from a known weight of potassium bromide previously dried at 120°C. for 2 hours, and the normality of the solution was checked gravimetrically as silver bromide and by a Volhard Estimation:

Normality of the solution by weight of KBr taken = 0.1016 N
" " " " " Volhard Estimation = 0.1017 N
" " " " " Gravimetric Method = 0.1017 N

A standard solution of potassium chloride was prepared in a similar manner:

Normality of the solution by weight of KCl taken = 0.8318 N
" " " " " Volhard Estimation = 0.8316 N
" " " " " Gravimetric Method = 0.8317 N

As will be seen from Table III, using 1:3 sulphuric acid (8-9 N), the accuracy of bromine estimations was ±2%, but when chloride solution as well as bromide solution was present in flask A, an error of +5% was introduced. By carefully adjusting the volume of the sulphuric acid added to flask A so that the final acidity was approximately 7N (i.e. 2.7ml. sulphuric acid/10 ml. solution in A), and using 7N sulphuric acid to wash down the neck of A, an accuracy of ± 1.5-2% was obtained in the bromide estimations even in the presence of excess of sodium chloride (Table IV).

In determining the amount of bromine present in the mixtures of the 1-phenylethyl halides, a known weight of the sample to be analysed was first hydrolysed and steam distilled in flask A as previously described. Flask A was then cooled under the tap, the appropriate volume of concentrated sulphuric acid was added followed by 5 g. chromium trioxide, the neck of the flask was washed down with 7N sulphuric acid and the flask was finally clamped into position. The bromine evolved was absorbed and estimated as before. Using pure 1-phenylethyl bromide

(Found: C,52.54; H,5.11; Br_2,43.21%. Theoretical: C,51,9; H,4.9; Br_2,43.2%), the accuracy obtained for 3 hour absorption of bromine was ± 2-3%, and using mixtures of known composition of pure 1-phenylethyl bromide and 1-phenylethyl chloride (see p. 51), the accuracy of the determination of the amount of 1-phenylethyl bromide present was ±1% (Table V).

Total halogen analyses and bromine analyses for some of the products from addition experiments are shown in Table VI.

Calculations were made of deviations from the theoretical values for total halogen which would arise by analysis of mixtures of the 1-phenylethyl halides analysed by gravimetric method, by Volhard estimation, and for the direct halogen estimation of Weiler and Strauss (Tables Ia, Ib). These deviations were in quite good agreement with those observed in total halogen analyses (Table II). Similar calculations were made for carbon and hydrogen analyses.

(c) Analysis of the mixtures of 1-phenylethyl halides by Pycnometric Density Method.

Since the densities of 1-phenylethyl chloride (D^{13} = 1.0598 [Kharasch and Brown, J.Amer.Chem.Soc., (1939), 61,2142]) and 1-phenylethyl bromide (D_4^{20} = 1.3478 [Copenhamer, Roy and Marvel, J. Amer.Chem.Soc., (1935), 57, 1311]) differ considerably, it was thought that density determination might provide a speedy and accurate estimate of the composition of the mixtures. This proved to be correct.

The pycnometer used (fig. ix) was cleaned by filling with cleaning acid, leaving for 12 hours, rinsing thoroughly with distilled water, and drying by drawing through it for ½ hour a current of filtered air. It was always left suspended on the balance for 10 minutes before weighing, counterpoised with a pycnometer of approximately equal dimensions. The pycnometer was filled with the liquid to be analysed, and left in the thermostat at 25°C. for 15 min., then whilst still in the thermostat the level of the liquid in the longer of the two side-arms of the pycnometer was brought to the mark by withdrawing liquid from the tip of the shorter side-arm with filter paper. The pycnometer was then dried thoroughly and put on the balance. The mean of three values agreeing to within 0.3 mg. was taken in each density determination.

The standard used in the determinations was pure water, i.e. distilled water which had been redistilled twice off potassium permanganate. The densities of pure 1-phenylethyl chloride (p.51) and pure 1-phenylethyl bromide (p.50) were determined:

Wt. pycnometer empty = 1.7621 g.

Wt. plus pure water at 25° = 3.3508 g.

Wt. " " C_8H_9Cl " " = 3.4483 g.

Wt. " " C_8H_9Br " " = 3.9203 g.

D_{25}^{25} C_8H_9Cl = 1.0631.

D_{25}^{25} C_8H_9Br = 1.3584.

Determinations were made of the densities of mixtures of known amounts of these compounds (Table VIa). These values were plotted, and a graph was obtained from which the composition of any mixture of these 1-phenylethyl halides could be found if its density were known (fig. x).

Table VIa

Wt. C_8H_9Cl taken (g.)	Wt. C_8H_9Br taken (g.)	% C_8H_9Br present	Wt. pycnometer + mixture (25°)	Wt. pyc^r. empty (25°)	D_{25}^{25} of mixture.
1.63635	2.09045	49.2	3.6853	1.7621	1.212
0.6134	3.3388	80.7	3.8327	1.7621	1.302
1.8544	0.7796	24.2	3.5648	1.7609	1.136

The densities were determined for four mixtures previously analysed for total halogen and for bromine. The values for the percentage of 1-phenylethyl bromide in the mixtures determined by the two methods were in very good agreement, (Table VIIa).

Table VIIa

Compound	$\%C_8H_9Br$ found (bromine estimation)	Wt. pycnometer + mixture (25°)	Wt. pyc^r. empty (25°)	D^{25}_{25}	$\%C_8H_9Br$ by density method.
KM/14	9.85	3.4920	1.7616	1.0881	9.90
KM/11	87.13	3.8601	1.7618	1.3203	87.5
KM/27	54.2	3.7037	1.7618	1.2223	55.0
KM/25	6.35	3.4780	1.7616	1.080	6.7

Products of the Addition Reactions.

There was no observable reaction between styrene and hydrogen chloride alone in carbon tetrachloride solution at 25°C. After 48 hours the styrene concentration of the solution was unchanged, and 88% of the initial styrene was recovered from the reaction:-

Initial styrene concentration = 0.3331 M.

After 2 days = 0.3336 M.

Expt. No.	Initial (C_8H_8)(M.)	Time of Expt.(hrs.)	% Styrene recovered as:- C_8H_8	$(C_8H_8)_n$	C_8H_9X	Total
20	0.333	48	88	0	0	88

On the other hand, styrene and hydrogen bromide were found to react readily under these conditions.

Hydrogen bromide was passed through solutions of styrene in carbon tetrachloride at 20-25°C., and the amount of bromine present in the product was determined. The product was shown to be 1-phenylethyl bromide as described on p.63 .

Expt. No.	Name of Product	Initial C_8H_8 (M.)	Time of Expt. (hrs.)	%Styrene recovered as:-		% Brom in product	
				C_8H_9Br	Total	Found	Theort
24	-	0.333	$2\frac{1}{4}$	89.3	89.3	-	-
25	KM/16	0.333	$1\frac{3}{4}$	94	94	42.81	43.2
26	-	0.333	$3\frac{1}{2}$	95	95	-	-

When a stream of hydrogen chloride was passed through carbon tetrachloride solutions of styrene and stannic bromide, the styrene gradually reacted. The amounts of bromine and total halogen in the products were determined. In one experiment chlorobenzene was used as solvent (Table VIII).

Similar experiments were carried out by passing hydrogen bromide through solutions of styrene and stannic chloride in carbon tetrachloride, and the products were analysed in the same way. In the first series of experiments (Table IX) a constant current (2-3 bubbles/second) of hydrogen bromide was maintained for the whole of the reaction time, but in the second series the stream of hydrogen bromide was either discontinued completely after adding the reagents to the solvent, or a very slow stream of the gas was maintained (Table X).

Halogen Exchange Experiments.

The interaction of hydrogen chloride with 1-phenylethyl bromide and of hydrogen bromide with 1-phenylethyl chloride was measured by passing a stream of the required hydrogen halide through a solution of the particular 1-phenylethyl halide and analysing the products (Table XI).

The amount of halogen exchange between the stannic halides and the 1-phenylethyl halides in carbon tetrachloride solution was determined by allowing the reagents to interact for the required length of time in the solvent medium, and then analysing the products. In some of the experiments a stream of the required hydrogen halide was led through the solutions (Tables XII and XIII).

A solution in carbon tetrachloride of styrene, 1-phenylethyl bromide and stannic chloride was left for four hours, after which time the products were isolated and analysed (Table XIV).

RACEMISATION OF OPTICALLY ACTIVE 1-PHENYLETHYL CHLORIDE.

The optically active 1-phenylethyl chloride was prepared by treatment of active 1-phenylethyl alcohol with pure thionyl chloride (c.f. Houssa and Kenyon J.Chem.Soc., (1930)2260; McKenzie and Clough, J.Chem.Soc., (1913), 103, 694). Racemic 1-phenylethyl alcohol was resolved by the fractional crystallisation of the brucine salts of the hydrogen phthalate in acetone solution.

Preparation of Racemic 1-phenylethyl alcohol.

This preparation was carried out as described on p. 50 The product was a mobile liquid, b.p. 91-93°C./12mm., 88-90°C./10mm.

Preparation of the hydrogen phthalate of 1-phenylethyl alcohol.

(c.f. Houssa and Kenyon, loc. cit. and also Pickard and Kenyon ibid, (1911) 99, 45).

Commercial pyridine was dried for several days over sodium hydroxide pellets, and then fractionally distilled up a Dufton column. The fraction boiling at 114-114.5° was collected. The racemic 1-phenylethyl alcohol (11.3 g.) was heated with phthalic anhydride (13.9 g., 1 mol.) and pyridine (8.5 g.) for 2 hours on a boiling water bath. To the cooled mixture was added 2N sodium bicarbonate until the solution was alkaline to litmus, and 50 ml. excess was then added. It was left to stand until all the solid had dissolved, when it was extracted with ether to remove any neutral phthalate which might have been formed. The aqueous layer was then acidified with 5N hydrochloric acid, and extracted with chloroform. The chloroform layer was separated, washed twice with water, and dried over sodium sulphate. After removal of the chloroform by distillation, a solid was obtained which was recrystallised from benzene. Wt. = 20.2 g. (81% yield), m.p., 99-102°C.

<u>Resolution of this hydrogen phthalate.</u> (c.f. Ott, Ber. (1928), <u>61</u>, 2140).

To a solution of the hydrogen phthalate (42.3 g.) in hot acetone (310 ml.) was added gradually a molecular proportion of commercial powdered brucine (60.7 g., m.p. 172-173°C.). The solution was evaporated to about 250 ml. volume and then left to cool. The fine white needles which separated were filtered and washed with a little acetone. (Wt., 40.0 g., m.p. 146-147°C.). The needles were then refluxed with acetone (120 ml.) for 15 hours, filtered from the hot solvent and washed with hot acetone. (Wt., 33.0 g., m.p. 150-152°C.)

<u>Rotatory Power.</u>

0.4973 g. of the purified salt was dissolved in chloroform in a 25 ml. standard flask, and the rotation of the solution measured at 5890Å and 5461Å in a 2 dm. polarimeter tube: (Temp., 14.7°C.)

At λ = 5890Å, a = -1.36°, $[\alpha]^{14.7}_{5890}$ = -34.1°.

At λ = 5461Å, a = -1.86°, $[\alpha]^{14.7}_{5461}$ = -46.9°.

After refluxing twice more with 120 ml. acetone the melting point and the specific rotation of the needles was unchanged (m.p. 150-152°C., $[\alpha]^{15}_{5890}$ = -34.00°, $[\alpha]^{15}_{5461}$ = -46.75°). (c.f. Houssa and Kenyon, loc.cit., for (-)-1-phenylethyl alcohol hydrogen phthalate brucine salt, $[\alpha]^{17}_{5461}$ = -47.7°). On evaporation of the first mother liquor to about 70 ml. and allowing to cool more crystals separated. (Wt., 43 g., m.p. 83-85°C, $[\alpha]^{17}_{5461}$ = +29.5°). Evaporation of this mother liquor to about 20 ml. gave a dark coloured syrupy solution from which no more crystals could be obtained. The more soluble salt was not purified and was used for brucine recovery.

Yield of the less soluble salt (crude) = 38.8%.
Yield of the more soluble salt (crude) = 41.8%.
Total = 80.6%.

Conversion of the less soluble brucine salt to the hydrogen phthalate.

The purified less soluble brucine salt (12 g.) was dissolved in warm alcohol (200 ml.). The solution was cooled and 2N hydrochloric acid (200 ml.) was added. After shaking for 15 min. the oily suspension was extracted with two portions (300 ml.) of ether. The combined ethereal layers were washed with 2N and with 0.02N hydrochloric acid, then with water, and finally were dried over sodium sulphate. From the filtered solution the solvent was removed at 34°C., and finally at the water pump, leaving a syrupy mass which formed white crystals on standing overnight. Wt. 3.99 g. (80% yield), m.p. 81-81.5 C. (c.f. Kenyon and Phillips, loc.cit. M.p. of (-)-1-phenylethyl alcohol hydrogen phthalate 81-82°C, $[\alpha]^{20}_{5461} = +39.8$).

0.0959 g. of this solid dissolved in alcohol was equivalent to 3.46 ml. of 0.1001N sodium hydroxide (Theoretical titre = 3.54 ml.)

Rotatory Power.

0.3085 g. of this hydrogen phthalate were dissolved in 25 ml. of alcohol in a standard flask, and the rotation of the solution was measured in a 2 dm. tube at 16°C.

At λ = 5461Å, a = +1.04 , $[\alpha]^{16}_{5461} = +42.1^\circ$.

At λ = 5890Å, a = +0.88 , $[\alpha]^{16}_{5890} = +35.7^\circ$.

Hydrolysis of the active hydrogen phthalate.

Steam was passed through a heated solution of the active hydrogen phthalate (4.5 g.) and potassium hydroxide (2.4 g. Analar) in water (9 ml.) for 1½ hours. The steam distillate was collected (approximately 200 ml.) and was extracted three times with ether. The combined ethereal layers were dried for 12 hours over freshly ignited sodium carbonate. From the filtered solution the ether was removed at 34°C. and finally under reduced pressure. The residue was a clear white mobile liquid, b.p. 90-91°/16 mm.

<u>Rotatory Power</u>.

The rotatory power of the pure liquid was measured in a 0.25 dm. tube at 15.4°C.

At $\lambda = 5461\text{Å}$, $a = -12.43^{\circ}$, $[\alpha]^{15.4}_{5461} = -49.72$

($D^{15}_{4} = 1.008$, [Marshall, J.Chem.Soc.(1915)<u>107</u>, 528 for (±) C_8H_9OH])

At $\lambda = 5890\text{Å}$, $a = -10.22^{\circ}$, $[\alpha]^{15.4}_{5890} = -40.88$

($a = -13.27^{\circ}$, $l = 0.25$ for (-)-1-phenylethyl alcohol, Kenyon, loc.cit.)

<u>Conversion of active 1-phenylethyl alcohol to active 1-phenylethyl chloride</u>.

Commercial thionyl chloride (25 ml.) was fractionally distilled twice off quinoline (5 ml., dried over sodium hydroxide pellets and distilled, 113-4°/16 mm.). The fraction boiling at 75.5-76°C. was collected in each case. Thionyl chloride (5 g.) was placed in a small Claisen flask fitted with a receiving tube with a side-arm connected to a phosphorus pentoxide tube. The active carbinol (2 ml.) was added slowly from a pipette fitted with a tap and connected at the top outlet to a phosphorus pentoxide tube. The pipette passed through a closely fitting piece of rubber tubing into the neck of the Claisen flask. A vigorous reaction ensued, but the rate of addition was adjusted so that the temperature of the reaction mixture did not rise. After a further 15 minutes at room temperature, the pipette was replaced by an air leak, and the thionyl chloride was removed at 30°C. under reduced pressure and the residue distilled. The product was a clear mobile liquid, (b.p. 82.5°C./17mm., wt. 1.897 g.)

Rotatory Power.

The rotation of the pure liquid was measured in a 0.25 dm. tube at 15.1°C.

At $\lambda = 5890\text{Å}$, $a = -13.3$, $[\alpha]^{15.1}_{5890} = -50.05°$. ($D_4^{20} = 1.0631$)

(For (+)1-phenylethyl chloride, $[\alpha]^{20}_{5890} = +50.6°$, McKenzie and Clough, loc.cit.)

The rotatory power of the chloride varied somewhat for each preparation. The highest value obtained was $[\alpha]^{17}_{5890} = -51.9°$. The optical purity of the chloride used in each series of racemisation experiments was calculated for the value of $[\alpha]^{17}_{5890} = -51.9°$ for the pure compound.

Apparatus.

The polarimeter tube used in the racemisation experiments is shown in fig. xi The central tube and the three end plates were made of glass. This tube, the vessel in which the reagents were mixed and the syphon tubes (fig. xi) were cleaned between individual experiments by washing three times with analar carbon tetrachloride then with acetone, once with pure, dry carbon tetrachloride, drying for at least 30 min. in an oven at 110°C., and allowing to cool with a current of dry nitrogen flowing through. Between series of experiments they were heated in an oven for at least 12 hours. The glass end plates were covered with a thin film of dimethyl silicone which acted as a water repellent.

The pipettes were coated in the same way, and were likewise washed between experiments with acetone and carbon tetrachloride, and dried by passing a stream of dry nitrogen through them for ½ hour.

The tall ground glass stoppered bottle in which the solution of stannic chloride was prepared was cleaned between experiments by washing with carbon tetrachloride, acetone, water, then filling with cleaning acid and leaving for three hours, washing again with water, acetone, pure dry carbon tetrachloride and finally leaving in an oven for twelve hours and then allowing to cool with a stream of dry nitrogen flowing through. The measuring cylinder used for the dry carbon tetrachloride was left in an oven at 110°C. until just before it was required, and allowed to cool with a stream of dry nitrogen flowing through.

The standard flask used for the solution of 1-phenylethyl chloride was washed in the same way as the pipettes.

Materials.

Nitrogen from a cylinder was led through a long tube packed with glass beads and phosphorus pentoxide.

The (-)1-phenylethyl chloride was dried for a short while over potassium carbonate, redistilled and its rotatory power determined immediately before use. A sample was weighed into a standard flask, and dissolved in pure, dry carbon tetrachloride at 25°C. Analar carbon tetrachloride which had been stored for several weeks over phosphorus pentoxide was refluxed over this reagent for 12 hours and then fractionally distilled from an all glass apparatus into a flask whose side-arm was connected to a tube containing phosphorus pentoxide. Dry nitrogen was passed through the flask from this side-arm whilst it was being removed from the distillation apparatus until the glass stopper was inserted. The pure, dry carbon tetrachloride was stored in this flask. Samples were removed as required by inserting in place of the glass stopper a syphon tube, and removing carbon tetrachloride through this tube by means of dry nitrogen passed through the side-arm of the flask.

The phials of stannic chloride were obtained from the

XVII Expt 5

Time – from where reckoned?

$a_{t_1} - a_{\infty} = -1.86$ how calc.?

Def. of t_1?

length of tube? 2dm?

Times of reaction – what zero taken
(a) for time ?
(b) for rotation

---

p.85 $\overline{\text{XVI}}$a

$l = 0.25$ dm ?

Rotations why smaller than those of Expt. 5' ?

distillation described on p.54-58. The capillaries were scored, 50 ml. of pure, dry carbon tetrachloride at 25°C. were measured from a cylinder into the tall storage bottle, and the 2 phials of stannic chloride, washed down with pure dry solvent, were placed in the bottle. The capillaries were then broken by pressing down the stopper of the bottle.

Commercial styrene, redistilled, was twice dried over sodium and redistilled.

Method.

Water was circulated at 25°C. through the jacket of the polarimeter tube from a thermostat maintained at this temperature.

10 ml. of the solution of phenylethyl chloride, followed in some experiments by 1 ml. of styrene, were measured at 25°C. into a glass stoppered bottle in the thermostat, and 10 ml. of the stannic chloride solution were added. The stop-watch was started when half the stannic chloride solution had flowed from the pipette. The vessel was swirled, and the glass stopper replaced by a syphon tube, and approximately 12 ml. of the solution displaced into the polarimeter tube by means of dry nitrogen. The vertical neck of the polarimeter tube was then immediately closed. The rotatory power of the solution was measured at frequent

intervals using the D-line of sodium (5890Å). In some experiments a faint opalescence developed on mixing the solutions, and in three experiments there was a definite cloudiness. These experiments were abandoned owing to the difficulty in obtaining readings in the polarimeter. In the majority of cases, however, the solutions remained perfectly clear, and readings were very distinct . In some experiments the styrene concentration of the solution was determined after 1-2 hours.

The results are summarised in Table XVI

A control experiment was performed in which a solution of (-)1-phenylethyl chloride in carbon tetrachloride was left in the polarimeter tube for 2 days and its rotatory power was measured from time to time. There was no loss in rotatory power, (Table XVIa:

Table XVIa

(-)-1-phenylethyl chloride, b.p. 83.5-85°C./20mm.

$[\alpha]^{25}_{5890} = -36.5^\circ$, (l = 0.25 dm.)

Concn. of the solution = 0.1510 M. Temp. = 25°C.

Time (hrs.)	Observed Rotation (°).
0.05	0.95
0.1	0.960
4.0	0.96
33.0	0.97
48.0	0.96

In the majority of the experiments the rate of racemisation was first order with respect to the phenylethyl chloride, i.e. plots of $\log\left(\frac{a_{t_1}-a_{\alpha}}{a_{t_2}-a_{\alpha}}\right)$ gave straight lines (see Part III), and k_1 was independent of the initial concentration of the organic halide. But in those experiments where the polarimeter tube had been dried in the oven for over 12 hours before use usually either a very slow first order reaction occurred, or a reaction of higher order with respect to phenylethyl chloride. Added styrene had no perceptible effect on k_1.

Interaction of Styrene, 1-phenylethyl chloride and stannic chloride in carbon tetrachloride solution.

Using racemic 1-phenylethyl chloride instead of the optically active isomer, the reagents were purified, and the apparatus was dried, as for the racemisation experiments.

A stock solution in carbon tetrachloride of stannic chloride and one of 1-phenylethyl chloride were prepared as previously described. The reaction vessel consisted of a ground-glass stoppered bottle which had been washed and dried in the same manner as the storage bottle for the stannic chloride solution. At the commencement of an experiment 10 ml. portions of the stannic chloride and of the 1-phenylethyl chloride solutions were pipetted into the reagent bottle at 25°C. in the thermostat followed by the requisite amount of styrene. The bottle was kept in the thermostat throughout the experiment. Samples were withdrawn from time to time, for estimation of the styrene concentration by the usual method.

The results of experiments using different initial styrene concentration are shown below (Tables XXIII-XXV, figs. XXVa+b XVIII). In all experiments the styrene concentration fell quite slowly, but it was not possible to express the rate of fall in any simple kinetic form. Assuming a bimolecular reaction between styrene and 1-phenylethyl chloride values of log(a-x)/(b-x) were plotted against t for experiment 84 (fig. XXVb), where (a-x), (b-x) are the concentrations of styrene and of 1-phenylethyl chloride, respectively, at time t. A curve was obtained, indicating that the second-order rate equation -

$$t = \frac{2.303}{k(a-b)} \log \frac{b}{a} + \frac{2.303}{k(a-b)} \log \frac{(a-x)}{(b-x)} ,$$

where k is the rate constant, and a,b the initial concentrations of styrene and 1-phenylethyl chloride, is not valid for these reactions. The fact that the rate falls below that for a true bimolecular reaction indicates that the reaction is of a higher order with respect to one or both of the reactants.

Table XXIII Experiment 84 (figs. xxva&b xviii).

Initial Styrene = 0.385 M. Temperature = 25°C.

Initial 1-phenylethyl chloride = 0.176 M.

Stannic chloride = .0666 M. Solvent = Carbon tetrachloride.

hrs.	Time		(a-x)	%	(b-x)	log (a-x)/(b-x).
0.023	1.35		.3854	–	.1760	-
0.34	20.45	.008	.3770	2.1	.1676	.3520
1.19	71.30	.039	.3463	10.1	.1369	.4031
2.35	141.20	.042	.3430	10.9	.1336	.4094
3.07	184.00	.051	.3335	13.2	.1241	.4294
5.05	303.00	.061	.3242	15.8	.1148	.4509
6.57	394.40	.061	.3237	15.8	.1143	.4521
18	18 hrs.	.102	.283	26.5	-	-
22	22 hrs.	.113	.2719	29.3	-	-
42.5	42½ hrs.	.164	.2196	42.6	-	-
55	55 hrs.	.209	.1756	54.3		

Table XXIII Experiment 85 (Fig xviii).

Initial Styrene = 0.7425 M. Temperature = 25°C.

Initial 1-phenylethyl chloride = .1678 M.

Stannic chloride = .0636 M. Solvent: Carbon tetrachloride.

Time	hrs	(a-x)		%
1.10		.7425		
12.00	0.200	.7293	.0132	1.8
25.15	0.419	.7257	.0168	2.3
64.30	1.071	.7131	.0294	4.0
113.20	1.886	.6981	.0444	6.0
200.40	3.34	.6537	.0888	12.0
522.20	8.71	.5950	.1475	19.9
20 hrs.	20	.4746	.2679	36.1
44 hrs.	44	.3084	.4341	58.5
52 hrs.	52	.3009	.4416	59.5

Table XXIV. Experiment 86 (Fig. xviii).

Initial Styrene = 1.378 M. Temperature = 25°C.

Initial 1-phenylethyl chloride = .1536 M.

Stannic chloride = .0582 M. Solvent: Carbon tetrachloride.

Time	hrs	(a-x)	x	%
1.20		1.378		
18.55	0.309	1.369	.009	0.7
35.00	0.583	1.352	.026	1.9
42.25	0.704	1.339	.039	2.8
79.00	1.316	1.317	.061	4.4
98.05	1.635	1.290	.088	6.4
159.50	2.658	1.239	.139	10.1
311.40	5.19	1.106	.272	19.7
466.10	7.77	1.003	.375	27.2
20¼ hrs.	20.25	0.5876	.790	57.2
43 hrs.	43	0.2003	1.178	85.5

Interaction of Styrene and hydrogen chloride in Nitrobenzene.

Commercial styrene redistilled (10 ml., 9g., 0.34 M) was added to a saturated solution of hydrogen chloride in nitrobenzene, and the current of the gas was maintained until all the styrene had reacted, as shown by bromine estimation, (70 min.). The solution was washed with water, dried over sodium sulphate, and the nitrobenzene removed at the rotary pump, ($<$0.1 mm.). A slight viscous residue (0.3725 g.) remained, which was assumed to be short-chain polystyrene.

The nitrobenzene distillate gave a negative result when tested with nitric acid and silver nitrate for chloride ions. It was heated under reflux with 200 ml. distilled water for 3 hours and then left to cool. The two layers were separated and the aqueous layer was diluted to 1 litre with distilled water. Portions were analysed by the Volhard method for halide ions.

Volhard Estimation of the Aqueous Layers.

20 ml. of the solution was added to 20 ml. of silver nitrate (0.2056 N), and titrated with ammonium thiocyanate (0.1058 N).

Titres: 27.23, 27.10, 27.10.

Normality of the aqueous solution = 0.063 N.

Normality of the nitrobenzene solution with respect to halide ions = 0.252 N

Theoretical for complete conversion of C_8H_8 to C_8H_9Cl
= 0.34 M.

These results can be summarised as follows:-

<u>% styrene estimated as</u>:-

$(C_8H_8)n$	Halide	Total
4.14	77.2	81.34

The nitrobenzene layer was dried with sodium sulphate and then refluxed with a quantity of 3:5-dinitrobenzoyl chloride and pyridine sufficient to convert to its ester all the 1-phenylethyl alcohol which might have been present, assuming that the styrene had yielded completely 1-phenylethyl chloride, which had subsequently been converted to the corresponding alcohol. The nitrobenzene was then removed at the rotary pump, and ether was added to the residue. The ethereal solution was washed with dilute acid and alkali and twice with water, dried over sodium sulphate, and the ether removed under reduced pressure. A solid was obtained which melted at 94-95.5°C. Wt., 4.2 g. (M.p. 1-phenylethyl-3:5-dinitrobenzoate, 95°C. (Ashworth and Burkhardt, J.Chem.Soc., (1928), 1798)).

The second nitrobenzene distillate was then treated with excess of a solution of bromine in carbon tetrachloride, left for several hours, and then the solvents and excess bromine removed at the rotary pump. The crystalline residue, recrystallised from ethyl alcohol melted at 72-73°C. (M.p. of styrene dibromide, 74-75°C. (Evans and Morgan, J.Amer.Chem.Soc. (1913), 35, 56). Wt. = 4.9 g.

Hence,

% styrene recovered as:-

$(C_8H_8)_n$	C_8H_9OH (ester)	$C_8H_8Br_2$	Total
4.14	14.7	34.6	53.4

Interaction of styrene, stannic chloride and hydrogen chloride in nitrobenzene.

Commercial styrene redistilled (10 ml., 9 g., 0.34) was added to a saturated solution of hydrogen chloride in nitrobenzene (250 ml.), containing stannic chloride (1 ml., 2.28 g. 0.0034 M). Bromine titrations showed that all the styrene had disappeared within 3 minutes.

On addition of excess methyl alcohol, two fractions of sticky solid material were obtained, which were filtered on sintered crucibles, washed with methyl alcohol and weighed. Wts., 3.0g., 0.6 g. respectively. The methyl alcohol was removed from the filtrate by distillation under reduced pressure, and the nitrobenzene solution remaining was washed twice with water, dried over sodium sulphate, and the nitrobenzene removed by distillation under reduced pressure. A viscous residue remained.

The average molecular weights of these three fractions were determined by the Beckmann freezing point method using benzene as solvent. Benzene, dried for several days over sodium and redistilled, was used. Wt. = 4.9g.

The equation used in calculating the molecular weights was,

$$M = K. \frac{w}{W. \delta}$$

where M = M. Wt.

K = F.p. depression constant for benzene (5120)

W = Wt. in g. of solvent.

w = " " g. of solute.

δ = Depression of f.pt. in the experiment.

The results are summarised in Table XVIIa

Table XVIIa.

Fraction	Wt. benzene (g.)	Wt. polymer (g.)	F.p. benzene (°)	F.p. solution (°)	δ (°)	M.
1	20.0408	1.5360	4.415	5.27	0.855	459.1
2	20.5333	1.0193	4.415	4.98	0.465	434
3	20.3628	0.6508	4.36	4.83	0.47	348.1

Recovery of styrene as short-chain polystyrene = 94.5%.

Interaction of styrene and stannic chloride in nitrobenzene.

Styrene (10 ml., 0.33 M) purified by distillation at 25 mm., drying for an hour over sodium and redistillation at 25 mm., was added to nitrobenzene (250 ml.), purified as described previously, in a tall ground-glass stoppered bottle at 25°C. in a thermostat. The capillaries of two phials of purified stannic chloride (p.54) were scored and the phials were washed down with a little solvent and placed inside the bottle. The stannic chloride was introduced into the solvent by pressing down the stopper of the bottle and breaking the capillaries. The reaction vessel was kept in the thermostat for the duration of the experiment. Samples were withdrawn from the reaction mixture at convenient intervals and the styrene concentration estimated in the usual way. After 200 min., 150 ml. of the solution were added with stirring to a litre of methyl alcohol. The white flocculent precipitate which separated was filtered on a sintered crucible, dried at 40°C. for two days, and weighed. Wt. = 4.95 g. (% recovery of styrene = 89.2). The glass pieces from the reaction vessel were collected, washed, dried and weighed in the usual way.

The results are given in Table XXXIV (and fig. xix). The average value of the velocity constant was determined graphically using the first order reaction equation:-

$$k_1 = \frac{2.303}{t} \cdot \log \frac{a}{(a-x)}$$

where a and (a-x) are, respectively, the concentrations of styrene at time 0 and t.

POLYMERISATION OF STYRENE IN CARBON TETRACHLORIDE AND CHLOROFORM SOLUTIONS

Materials.

Commercial styrene, stabilised with quinol, was washed with aqueous sodium hydroxide (2N), then twice with water, dried over sodium sulphate and distilled under reduced pressure immediately before use. Polymerisation experiments indicated that this drying was not adequate, and the styrene was then dried twice with calcium chloride before distillation. In later experiments the styrene was dried over sodium before the final distillation.

The quantitative addition of bromine to the styrene double bond was used both as a means of estimating the strength of styrene solutions, and of testing the purity of the styrene. 2 ml. of a solution of styrene in carbon tetrachloride of known strength were run into 10 ml. of a solution of bromine in glacial acetic acid in an iodine flask. The excess bromine was titrated with thiosulphate after the addition of potassium iodide:-

Strength of the solution found: 1.7764 M.
" " " " theoretical: 1.7764 M.

Analar carbon tetrachloride was washed twice with water, dried twice over calcium chloride, and distilled immediately before use. One drying with calcium chloride was not adequate. In later experiments analar tetrachloride was dried for several weeks over phosphorus pentoxide, and fractionally distilled before use.

Commercial chloroform was washed five times with water, dried over calcium chloride and distilled immediately before use. It was necessary to dry the solvent twice before distilling.

Ordinary commercial methyl alcohol was used.

Stannic chloride.

The apparatus used for the distillation is shown in fig i; it was evacuated at 10^{-3}mm. and flamed before use, and dry air was then admitted through X and Y. Pure commercial stannic chloride was introduced into A through a syphon tube with Y open and X partly open to the pump. Y was then closed and X opened. A stopper was then immediately placed in the neck of A, and A and D were cooled in liquid air. The apparatus was evacuated for three hours and the whole of the distillation train heated with a naked flame, after which X was closed. The liquid air was removed from A which was subsequently warmed on a water bath at 40°C. during the distillation. E was cooled in an ice-salt bath, and the first fraction which collected in E was sealed off at capillary a and discarded, since the hydrate is reported as being more volatile than the stannic chloride itself (Briscoe, J.Chem.Soc. (1915), <u>107</u>, 63). The next fraction was similarly collected in flask F and used for the addition experiments (see p.49). When about 100 ml. had been collected, capillary b was sealed. The stannic chloride was then condensed into the bulbs by placing cotton wool, soaked in the freezing mixture, around the tube above a particular line of bulbs. The bottom bulb in the line was sealed off before the next was filled. After each bulb had been sealed off, the whole of the apparatus was warmed gently with the blow lamp and X and Y were opened. In this way it was possible to ensure that the apparatus was free of hydrate before the next bulb was collected.

Standardisation of solutions.

Analar potassium iodate, dried at 100°C. for ½ hour was used in the preparation of a solution for a primary standard. This was used to estimate the strength of the sodium thiosulphate solution, which was then checked against another standard iodate solution. Bromine solutions were standardised with the thiosulphate.

General method of procedure.

100 ml. of a solution of styrene in the required solvent was prepared in a clean, dry glass-stoppered reagent bottle (200 ml. capacity) in a thermostat maintained at the temperature of the experiment (25°C. unless otherwise stated), by measuring from a pipette the required volume of styrene, and adding from a measuring cylinder the volume of solvent required. The experiment was started by crushing beneath the solution a bulb of stannic chloride, or a phial with scored capillaries. The reagent bottle was kept in the thermostat throughout

the experiment and at convenient intervals 2 ml. samples of the solution were run into 10 ml. of standard bromine solution in an iodine flask, and the styrene concentration estimated as previously described.

The weight of the stannic chloride introduced was determined by weighing the bulb or phial before the experiment, and collecting the glass pieces from the bottle at the end of the experiment. The pieces were washed, dried and weighed as previously described.

Samples of the polymer required for molecular weight determination were obtained when polymerisation was complete by slowly running a volume of the reaction mixture into a tenfold volume of methyl alcohol, stirring the mixture constantly. The flocculent white precipitate which separated was filtered on a sintered glass crucible, washed well with methyl alcohol, and dried either in an oven at 100°C. for one hour, or at 40-50°C. for several hours. The precipitation of polymer was used to check the bromine titration method for determining the concentration of polymer in the solution, e.g. in experiment 1:-

% polymerisation by weight of polymer = 95.9.

% polymerisation by bromine titration = 92.08.

Determination of molecular weights (average) of products.

The molecular weights were determined by the viscosity method using Ostwald No.1 or No. 0 viscometers. The required weight of polymer was dissolved in a known volume of dry solvent, carbon tetrachloride or chloroform, at 25°C. in a thermostat. The flow-time of the solution and of the pure solvent at 25°C. were recorded.

In calculating the average molecular weight of the polymer (M) the following equations were used:-
(c.f. Gwyn Williams, J.Chem.Soc., (1938), 246).

$$\eta_{sp.} = \frac{\eta_{soln.} - \eta_{solv.}}{\eta_{solv.}}$$

$$\eta_{sp.}/c = K_m.M = an + b$$

$$= 2.5 \times 10^{-2} n \quad 0.2$$

$\eta_{sp.}$ = specific viscosity

$\eta_{solv.}$ = flow-time solvent

$\eta_{soln.}$ = flow-time solution

c = polystyrene concentration as mol. l^{-1} (C_8H_8).

The results of the polymerisation experiments are summarised in Tables XXVI, XXVII, XXVIII + XXIX and are discussed in Section III. The molecular weights of the polymers are given in Table XXIX. Experiments 11, 13, 21, 19, are quoted in full, in order to show the nature of the first and third order reactions obtained (Tables XXX, XXXI, XXXII, XXXIII Figs. XV, XVI) and rate curves for other experiments are shown (Figs. xxvi and xxvii)

SECTION III

DISCUSSION OF RESULTS.

A. The addition and halogen exchange reactions.

(1) Results.

In order to study the role of the catalyst in the addition of hydrogen halides to styrene in carbon tetrachloride at 20-25°C., hydrogen chloride and hydrogen bromide were used with stannic bromide and stannic chloride respectively. The products were isolated and analysed as described in Section II. The results are summarised in Tables VIII, IX, X.

In all experiments, mixtures of 1-phenylethyl halides were produced together with small amounts of low molecular weight polystyrenes. When a current of the hydrogen halide was continuously passed through the solution during the reaction, the amount of cross-halogenated product (i.e. containing the halogen of the catalyst) increased with increasing initial concentration of catalyst. The increase was not entirely regular, and this was believed to arise chiefly from the difficulty encountered in maintaining a completely constant flow of the hydrogen halide. That this could be the cause of the irregularity was indicated by a series of experiments (Table X) in which the supply of hydrogen bromide was stopped immediately after mixing the reagents, or was maintained at a rate much less than normal (1-2 bubbles/minute). In these experiments the amount of cross-halogenated product was much larger, and in fact represented the major part of the addition product, even at quite low catalyst concentration. It was noticeable that in several of these experiments (67, 69, 70, 71, 72) unusually large amounts of low molecular weight polystyrenes were produced.

The following halogen exchange reactions were then carried out in carbon tetrachloride at 20-25°C.:-

(a) Experiments with hydrogen halide (HX) and 1-phenylethyl halide (C_8H_9Y). The results (Table XI) showed that there was very little interchange of halogen (i.e. halogen exchange) between the reagents.

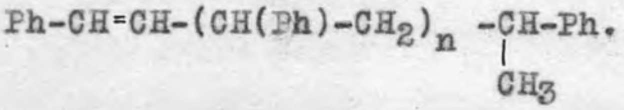
(b) Experiments with stannic halide (SnX_4) and 1-phenylethyl halide (C_8H_9Y). There was halogen exchange between stannic bromide and 1-phenylethyl chloride (X = Br, Y = Cl) and between stannic chloride and 1-phenylethyl bromide (X = Cl, Y = Br). This exchange was increased with increasing concentration of the tin halide and was diminished in the presence of hydrogen halide, HY. These results are summarised in Figs. xiia + xiib, xiiia + xiiib, and Tables XII, XIII.

(c) When styrene, 1-phenylethyl bromide and stannic chloride were allowed to interact for 4 hours, low molecular weight polystyrenes were formed, and there was some residual styrene and 1-phenylethyl halide (Table XV). The amount of halogen exchange which had occurred, as shown by analysis of the residual 1-phenylethyl halide, was less than would have occurred in the absence of styrene.

2. Discussion.

(a) Previous evidence.

It had previously been shown [52] that styrene reacts with hydrogen chloride in the presence of stannic chloride in carbon tetrachloride to form 1-phenylethyl chloride and di-, tri- tetra- and pentastyrenes, all of which were isolated and shown by ozonisation to have the structure



$Ph\text{-}CH{=}CH\text{-}(CH(Ph)\text{-}CH_2)_n\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}\text{-}Ph.$ A small amount of a saturated distyrene was formed also and was believed to be 1-phenyl-3-methyl indane. The polymers were formed in increasing proportion as the initial concentration of styrene was raised. Previous experiments had also shown

(i) that styrene and hydrogen chloride do not react together in the absence of a catalyst [60b].

(ii) that racemic 1-phenylethyl chloride does not undergo any substantial change under the influence of stannic chloride, 90% of the original material being recovered unchanged after contact for 140 minutes in carbon tetrachloride solution [60b.; cf. also 34].

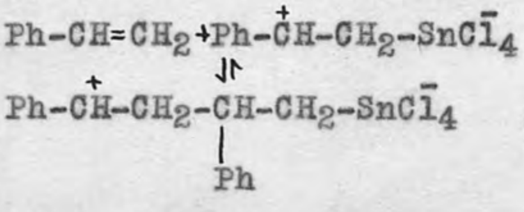
(iii) that distyrene does not change appreciably under the combined action of hydrogen chloride and stannic chloride except for a slow conversion to the saturated isomer [52]. but (iv) that in the presence of stannic chloride in carbon tetrachloride solution, 1-phenylethyl chloride reacts with styrene and, more slowly, with distyrene to form polymers [52]. Gwyn Williams showed [60b] that over a long period, the 1-phenylethyl chloride is completely consumed, viz.:

Starting materials	Stannic Chloride	Time (min.)	C_8H_9Cl recovered	$C_{16}H_{16}$ recovered	low polymer	Yield (%)
C_8H_8: 1.7 M C_8H_9Cl: 0.75 M	0.086 M	1500	0	20	66	86

To explain these results, and on the assumption [cf. Fairbrother, 32.b] that an alkyl halide and a metal halide form an ion-pair which is not necessarily dissociated into free ions in a solvent of low dielectric constant, the following interpretation of the addition reactions was suggested [52]:

Normal Polymerisation [cf. 74]

$$\text{Ph-CH=CH}_2\text{+SnCl}_4 \rightleftharpoons \text{Ph-}\overset{+}{\text{C}}\text{H-CH}_2\text{-Sn}\overset{-}{\text{Cl}}_4 \qquad (1)$$



$$\begin{array}{l} \text{Ph-CH=CH}_2\text{+Ph-}\overset{+}{\text{C}}\text{H-CH}_2\text{-Sn}\overset{-}{\text{Cl}}_4 \\ \qquad\qquad\quad \downharpoonleft\upharpoonright \\ \text{Ph-}\overset{+}{\text{C}}\text{H-CH}_2\text{-}\underset{\substack{|\\ \text{Ph}}}{\text{C}}\text{H-CH}_2\text{-Sn}\overset{-}{\text{Cl}}_4 \quad \text{, etc.} \end{array} \qquad (2)$$

In the presence of hydrogen chloride.

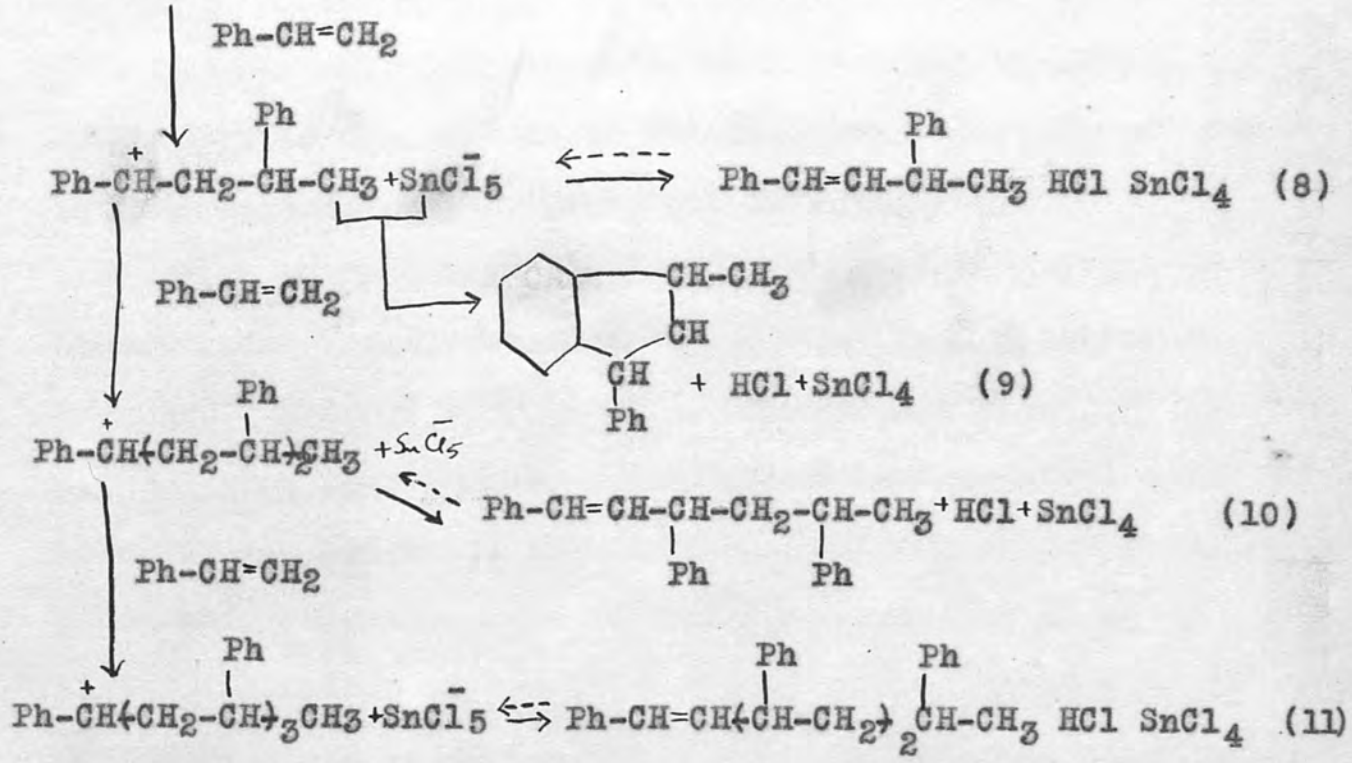
$$\text{HCl+SnCl}_4 \rightleftharpoons \overset{+}{\text{H}} + \text{Sn}\overset{-}{\text{Cl}}_5 \qquad (3)$$

$$\text{Ph-CH=CH}_2\text{+}\overset{+}{\text{H}} \rightarrow \text{Ph-}\overset{+}{\text{C}}\text{H-CH}_3 \qquad (4)$$

$$\text{Ph-}\overset{+}{\text{C}}\text{H-CH}_2\text{-Sn}\overset{-}{\text{Cl}}_4\text{+}\overset{+}{\text{H}} \rightarrow \text{Ph-}\overset{+}{\text{C}}\text{H-CH}_3\text{+SnCl}_4 \qquad (5)$$

$$\text{Ph-}\overset{+}{\text{C}}\text{H-CH}_3\text{+HCl} \longrightarrow \text{Ph-CH(Cl)-CH}_3\text{+}\overset{+}{\text{H}} \qquad (6)$$

$$\text{Ph-}\overset{+}{\text{C}}\text{H-CH}_3\text{+Sn}\overset{-}{\text{Cl}}_5 \rightleftharpoons \text{Ph-CH(Cl)-CH}_3\text{+SnCl}_4 \qquad (7)$$



This scheme envisages the initiation step in the normal polymerisation as occurring through the polarisation of the styrene double bond by stannic chloride. It was believed that such a polarisation might be operative in the addition reactions, followed by reactions (5) and (6). The scheme also provided an explanation for the observation [60b] that hydrogen chloride acts as an inhibitor of the long-chain polymerisation of styrene catalysed by stannic chloride, since the HCl would interfere with the normal polymerisation process through reactions (3) and (5).

The scheme also permits an alternative mechanism for the addition reactions, viz. reactions (3) and (4) followed by (6) or (7). Kinetic investigation [53] failed to distinguish between these mechanisms.

(b) <u>The present work</u>.

The present work was undertaken in order to obtain more exact information as to the relative importance of the various mechanisms previously put forward.

Since the addition of hydrogen bromide to styrene occurs quite rapidly even in the absence of a catalyst to give 1-phenylethyl bromide (e.g. Experiments 24,25,26, Table A, p. 74) the accompanying formation of 1-phenylethyl chloride when styrene interacts with hydrogen bromide in the presence of stannic chloride could possibly be explained by an exchange reaction of the type of (7). This point will be discussed again later (p. 106). But since hydrogen chloride does not add onto styrene in the absence of added catalyst (e.g. Expt. 20 p. 73) one must suppose that a catalyst is required to activate one or other of the reactants. In view of the affinity for electrons of metal halides, such as stannic halides, it seems that such activation will be of the type of (1) or (3) or both.

Evidence has been obtained from the Racemisation Experiments that under the conditions of these experiments, the extent of interaction of styrene and stannic chloride is very small in comparison with that of 1-phenylethyl chloride and stannic chloride, and it therefore seems unlikely that the former interaction (equilibrium (1), p.102) will act as the first stage in the addition reactions. This question is discussed further on p. 111.

On the other hand, the halogen exchange reactions show clearly that equilibria of the type of (3) and (7) are of importance under the conditions described.

The halogen exchange shown to occur between 1-phenylethyl halides and stannic halides is most probably due to equilibria of the type of (7), viz.:

$$\begin{array}{lcl} SnX_4 + PhCHYCH_3 & \rightleftharpoons & Sn\overset{-}{X}_4Y + Ph - \overset{+}{C}H - CH_3 \\ & & \qquad\quad \downarrow\uparrow \\ & & SnX_3Y + Ph - CHXCH_3 \end{array} \qquad (7a)$$

$$\begin{array}{lcl} SnX_3Y + Ph - CHYCH_3 & \rightleftharpoons & \overset{-}{SnX_3}Y_2 + Ph - \overset{+}{C}H - CH_3 \\ & & \qquad\quad \downarrow\uparrow \\ & & SnX_2Y_2 + Ph - CHX - CH_3 \\ & & \qquad\quad \text{etc.} \end{array} \qquad (7a)$$

The position of equilibrium will be governed by various factors, one of which will be the relative strengths of the Sn-halogen and C-halogen bonds.

The fact that for experiments with 1-phenylethyl halide (C_8H_9Y) and stannic halide (SnX_4) the extent of halogen exchange is markedly reduced in the presence of hydrogen halide (HY), can be explained if it is assumed that the hydrogen halide disturbs the equilibrium for interaction of the 1-phenylethyl halide and stannic halide, e.g. $C_8H_9Br + SnCl_4 \rightleftharpoons \overset{+}{C_8H_9} + Sn\overline{Cl_4}Br \rightleftharpoons C_8H_9Cl + SnBrCl_3$ (7b)

etc.

by interaction either with the 1-phenylethyl halide, viz.:

$$C_8H_9Cl + HBr \rightleftharpoons C_8H_9Br + HCl \qquad (13)$$

or with stannic chloride, viz.:

$$HBr + SnCl_4 \rightleftharpoons \overset{+}{H} + Sn\overline{Cl_4}Br \rightleftharpoons HCl + SnCl_3Br \qquad (3a)$$

etc.

or with a carbonium ion formed from (7a), viz.:

$$\overset{+}{C_8H_9} + HBr \rightleftharpoons C_8H_9Br + H^+ \qquad (6a)$$

Since it has been shown (Table XI) p.) that there is very little halogen exchange between hydrogen halides and 1-phenylethyl halides in carbon tetrachloride at room temperature, the first possibility is eliminated, and it therefore remains that the hydrogen halide may interact with the stannic halide as shown in (3a), and with carbonium ions as in (6a). If the former interaction (3a) holds, the concentration of free stannic halides is probably markedly decreased in the presence of hydrogen halides. This would agree with the results of Bohme [34] quoted in Section I (p.23).

The results of Table X . (p.) are also explicable on this basis if it is further assumed that the position of the equilibrium between HY and SnX_4 (3a) favours the formation of HCl. At the moment of mixing of the reagents in the experiments represented in Table X the HBr concentration is 0.3-0.4 M. In the normal addition reactions HBr is maintained at this concentration by the continued passage of the gas, and therefore true equilibrium conditions are not reached. But in the first two experiments shown in Table X, the supply of HBr was completely discontinued after the mixing, and in the remainder it was maintained at a very low rate. The high proportion of 1-phenylethyl chloride formed in these experiments can be explained in one of two ways. Either it is assumed that the addition of HBr to styrene is non-catalytic and that the 1-phenylethyl bromide produced yields 1-phenylethyl chloride by a halogen exchange reaction, or alternatively that equilibria (3a) and (7a) obtain and that addition occurs via (4) alone or by (4) and (6):

$$HBr + SnCl_4 \rightleftharpoons \overset{+}{H} + \overline{SnCl_4Br} \rightleftharpoons HCl + SnCl_3Br \qquad (3a)$$

etc.

$$Ph - CH=CH_2 + \overset{+}{H} = Ph - \overset{+}{C}HCH_3 \qquad (4)$$

$$Ph - CHCH_3 + Sn(\overline{Hal})_5 \rightleftharpoons Ph - \underset{\overset{|}{(Hal)}}{CH} - CH_3 + Sn(Hal)_4 \qquad (7a)$$

$$Ph - \overset{+}{C}H - CH_3 + H(Hal) \rightleftharpoons Ph - \underset{\overset{|}{(Hal)}}{CH} - CH_3 + \overset{+}{H} \qquad (6)$$

Since the results of Table X, and those of the halogen exchange reactions (Table XII) show that the amount of 1-phenylethyl chloride formed in the exchange reactions (except in the complete absence of HBr) is less than that obtained under comparable conditions in these addition experiments, it seems unlikely that halogen exchange between 1-phenylethyl bromide and stannic chloride would alone account for the amounts of 1-phenylethyl chloride formed in these addition experiments, and therefore the alternative explanation seems the more plausible. It is difficult to make a very close comparison since the halogen exchange reactions of Table XII were carried out either in the complete absence of HBr or at the saturation concentration of HBr, except for Experiment 95 which was performed under equilibrium conditions.

In the equilibria (3a) the position of equilibrium will probably favour the production of HCl, as indicated by the experiments of Besson (cf. Section I, p. 12). The saturation concentration of HCl in CCl_4 at 25°C. is 0.14 M [87] , and hence if it is formed at this concentration in the solution by halogen exchange between $SnCl_4$ and HBr it will probably escape from the solution by evaporation and the total concentration of hydrogen halides may therefore fall. This may limit the amount of 1-phenylethyl halide which can be formed, since the initial styrene and the HBr concentrations are approximately equal (0.3-0.4 M).

It is known ([60b] and Expt. 59, p. 75, Table XV) that 1-phenylethyl halides react with styrene in the presence of stannic halides to give low molecular weight polystyrenes. This reaction may become of considerable importance as the concentration of hydrogen halide falls, and may account for the unusually large amounts of low molecular weight polymers formed in these experiments.

These equilibria require further investigation, in particular that of the hydrogen halides and stannic halides, but the results of the addition and halogen exchange reactions indicate that equilibria (3a) and (7a) obtain under the experimental conditions described. Furthermore, it seems probable that the addition reactions proceed via (3), (4) and (7) possibly together with (6). The products from the halogen exchange reactions should then be identical with those from the addition reactions over comparable periods of time. There is quite a close agreement for the HBr experiments (Table XIV, figs. xii a&b, xiii b) For the HCl experiments (Tables VIII, XIII), Fig xiii a) the agreement is good at fairly low catalyst concentrations, but as the catalyst concentration is increased in the addition reactions the amount of 1-phenylethyl bromide in the products is greater than would be expected from the halogen exchange reactions. However, with stannic bromide as catalyst the addition of HCl to styrene is slow, and the reactions were usually stopped when the concentration of addition product was only 0.15-0.17 M (Table VIII), whereas in the halogen exchange experiments (Table XIII) a concentration of 1-phenylethyl halide of 0.3 M was used. From the one exchange experiment in which the concentration of 1-phenylethyl halide was 0.17 M, the product was similar in composition to those obtained from the addition experiments. Evidence was sought for the interaction of HCl and $SnCl_4$ in carbon tetrachloride using the method which Meerwein used for other non-aqueous media (see Section I, p. 12), namely following the colour change of p-dimethylaminoazobenzene indicator on mixing solutions of the two reagents. However, the method was found to be impracticable in carbon tetrachloride solution since hydrogen chloride itself gave a red colour with the indicator in this solvent at all dilutions.

The experiments under approximately anhydrous conditions were carried out partly with a view to determining the kinetics of the addition reactions under these conditions, and partly to see whether the cross-halogenated products were produced from hydrogen halide liberated from hydrolysis of the catalyst. The former project was temporarily abandoned in view of the difficulty of maintaining a steady stream of hydrogen halide. Unfortunately in these experiments low catalyst concentration was used, due to the limitation in size of the catalyst tubes which could be employed. However, the close agreement between the results obtained under approximately anhydrous conditions and normal conditions make it seem likely that hydrolysis of the catalyst was not responsible for the cross-halogenated products.

From the racemisation experiments it is evident that when 1-phenylethyl chloride, styrene and stannic chloride are present in carbon tetrachloride approximately in the proportions 0.2-0 .3 M, 0.4 M and 0.06 M respectively, any interaction between styrene and stannic chloride is not significant in comparison with interaction between the other components. But Expt. 59 (p. 75) indicates that when all three components are present in approximately equal proportions (approximately 0.16 M) there may be a significant amount of interaction between styrene and stannic chloride, since the extent of interaction between stannic chloride and 1-phenylethyl bromide under these conditions is reduced as shown by a reduction in the amount of halogen exchange occurring between them (cf. experiment 59, p. 75) and experiment , Table). Whether or not an associative equilibrium as shown below -

$$\mathrm{Ph - CH \underset{\substack{\downarrow \\ SnCl_4}}{=} CH_2 \rightleftharpoons Ph - CH = CH_2 + SnCl_4} \qquad (12)$$

would proceed to complete polarisation of the electrons of the styrene double bond so as to give (1) is not known.

It seems fairly certain, however, that for catalyst concentration equilibria of the type of (12) (and hence of (1)) have no importance and need not be considered in the addition experiments. At higher catalyst concentration an equilibrium of the type of (12) may have more importance, but whether or not it proceeds to (1) cannot be stated from these experiments. It is likely, as seen from the halogen exchange experiments, that the concentration of free stannic halide is greatly reduced in the presence of hydrogen halides, and hence an equilibrium of the type of (12) may not be of such importance, even at high catalyst concentration. The halogen exchange experiments indicate that the affinity of the metal halide for the three other components will decrease in the order hydrogen halide > 1-phenylethyl halide > olefin.

The possibility of the interaction of the catalysts and carbon tetrachloride has not yet been discussed. Such an interaction has been observed for aluminium chloride and CCl_4 in experiments conducted at 100°C. for 2 hours [35, cf. Section I, p. 24]. However, this exchange was shown to take place only on the surface of the metal halide and not at all in solution. A homogeneous mechanism was further excluded on energetic grounds, since to explain the observed activation energy of 19 k. cal. mol^{-1} for the overall reaction $CCl_4 + AlCl_3 \rightleftharpoons \overset{+}{C}Cl_3 + Al\overset{-}{C}l_4$, it was necessary to assume that the energy of binding of $\overline{Cl}$ to $AlCl_3$ to form $Al\overline{Cl}_4$ would be approximately 200 k. cal for a simple homogeneous reaction. Fairbrother had previously estimated [32a] that for $AlBr_3 + \overline{Br} \rightarrow Al\overline{Br}_4$ the energy is not greater than 100 k. cal, and it is unlikely that the energy will be much greater for the corresponding chlorides. In view of the fact that the electron affinity of $SnCl_4$ is probably less than that for $AlCl_3$, it seems very unlikely that there is any interaction between $SnCl_4$ (or $SnBr_4$) and CCl_4 in homogeneous solutions. On the other hand, Wallace and Willard took no account of the energy of interaction of $\overset{+}{C}Cl_3$ and $Al\overline{Cl}_4$. It nevertheless seems quite certain that such an exchange can only occur on the surface of the metal halide [35] and that it does not occur at all in homogeneous solutions.

B. Racemisation Experiments.

The most probable explanation for the racemisation of 1-phenylethyl chlorides in organic solvents in the presence of stannic chloride is that the two compounds interact to give an ionic complex composed of the planar carbonium ion $Ph - \overset{+}{C}H - CH_3$ and an anion, presumably $Sn\overline{Cl}_5$:

i.e. $$Ph - \overset{+}{C}H - CH_3 + Sn\overline{Cl}_5 \rightleftharpoons Ph - CHCl - CH_3 + SnCl_4 \quad (7).$$

Recombination of the carbonium ion with a halide ion will yield the $(\pm)$ organic halide, with a corresponding loss of rotatory power. It was of interest to know whether this phenomenon occurred in carbon tetrachloride solution for several reasons, one being that such an observation would indicate that the halogen exchange experiments could be explained by a carbonium ion mechanism.

(1) Results.

The experiments were conducted as described in Section II. The initial concentration of stannic chloride was not varied appreciably, but that of the (-)-1-phenylethyl chloride was varied from 0.0675 M to 0.3550 M. Styrene was present in some of these experiments.

The rotatory power of the (-)-1-phenylethyl chloride alone in CCl_4 was found to be unchanged after 48 hours (Table XVIa, p. 85). A fall in the rotatory power was observed in the presence of stannic chloride, and the rate of decrease could be represented as first order with respect to the (-)-1-phenylethyl chloride in the majority of the experiments. The results are summarised in Table XVI. Experiments 5,6,12 and 13 are quoted in full to show the reproducibility of individual velocity measurements (Tables XVII - XXII, figs. xx - xxiii) and also to show that added styrene (0.413 M in Experiments 6 and 13) does not affect the rate of racemisation.

The average value of the velocity constant was determined graphically using the first-order reaction equation:-

$$k_1 = \frac{2.303}{t_1 - t_2} \cdot \log_{10} \frac{a_{t_1} - a_\infty}{a_{t_2} - a_\infty},$$

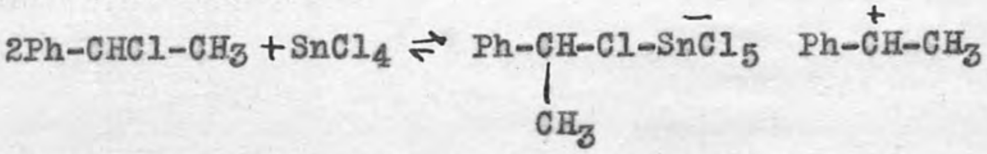
where $(a_{t_1} - a_\infty)$ and $(a_{t_2} - a_\infty)$ are, respectively, the observed rotations of the solutions at time t_1 and t_2.

The figures between the horizontal lines in Table represent series of racemisation experiments. In a particular series the same stock solutions of (-)-1-phenylethyl chloride and stannic chloride were used. At the beginning of a series a reaction was often found to be either of a mixed order, between first and second order, or of a high order with respect to the organic halide. Experiment 1 is quoted in full (p.   ) and is plotted as a first order (fig. xxiii a) and as a second order reaction (fig. xxiii b) to show the type of mixed order reaction encountered. Reaction 7 (Table XIX, fig. xxii) was a second order reaction, and reaction 15 a third order reaction (Table XXII, fig. XXIV). As described in Section II On. p. 86) there was good reason to believe that the high order reactions were observed when the polarimeter tube had been dried extra carefully. Prior to Experiment 15, the third order experiment, it was dried much more rigorously than in any other experiment.

(2) <u>Discussion.</u>

Since the stannic chloride concentration does not change during the reaction it is to be expected that if the racemisation reaction is represented by (7) it will be first order with respect to the organic halide.

However, it may be more correct to represent the reaction as -



$$2\text{Ph-CHCl-CH}_3 + \text{SnCl}_4 \rightleftharpoons \text{Ph-}\underset{\substack{|\\ \text{CH}_3}}{\text{CH}}\text{-Cl-}\overset{-}{\text{SnCl}_5} \quad \text{Ph-}\overset{+}{\text{C}}\text{H-CH}_3$$

Since it is known that the highest coordination number of tin is 6, and that it may be easier to effect the change from the tetrahedral compound SnCl_4 to the octahedral $\overset{-}{\text{SnCl}_5}\text{-Cl-R}$ than to $\overset{-}{\text{SnCl}_5}$. This would then account for the tendency to give rise to a second order reaction in the absence of water. In the presence of water another relationship might hold:

$$\text{Ph-CHCl-CH}_3 + \text{SnCl}_4 + \text{H}_2\text{O} \rightleftharpoons \text{Ph-}\overset{+}{\text{C}}\text{H-CH}_3 \quad \overset{-}{\text{SnCl}_5\text{OH}_2}.$$

This hypothesis would not explain the third order reaction (Experiment 15). Furthermore, it seems that $\overset{+}{\text{R}}\,\overset{-}{\text{SnCl}_5}$ can be formed since the polarisation of stannic bromide in cyclohexane (58.7 ±0.4c.c.) observed by Fairbrother [32b] was slightly higher than the value obtained by Coop and Sutton [85] for the vapour state and was presumed to be due to a flexing of the Sn-Br bonds in the solvent, or to a small extent of formation of an ionic autocomplex $\overset{+}{\text{SnBr}_3} - \overset{-}{\text{SnBr}_5}$ [32b]. Hence, this interpretation does not seem to be wholly satisfactory.

Any factor which will lower the potential energy of the ionic complex will obviously favour its formation in (7). As described in Section I (pp. 9 and 10) the heats of solvation of the anion and cation are important factors in determining whether or not an alkyl halide can ionise in a particular solvent. The same considerations will apply in the formation of the ionic complex in the racemisation reaction. In carbon tetrachloride the solvation energy for ions or for an ionic complex is probably low, but it is possible that if a more polar entity were present in the solution this might solvate the complex lowering the potential energy, and hence the activation energy for the formation of such a complex. Water might conceivably do this if it were present in small amounts. In the absence of water phenylethyl chloride might itself be the solvating entity, which might cause the order of the reaction to rise. This would agree with the observation of Bodendorf and Böhme [33] namely that the rate of racemisation is higher in solvents of higher dielectric constant.

The effect of styrene has already been discussed (pp. 104, 105). From the results in Table XVI it is clear that a reaction such as (1) is of no importance in these experiments. This was in accordance with experiments in which the rate of interaction of styrene and 1-phenylethyl chloride in the presence of stannic chloride was studied in carbon tetrachloride medium (Experimental Section, p.88,a,b Tables XXIII - XXV), and with those racemisation experiments (Table XVI) p. in which the styrene concentration was estimated during or after completion of racemisation. At concentrations comparable with those of the racemisation experiments (Tables XXIII XVI) the rate of disappearance of styrene was very low in comparison with the rate of racemisation, and therefore no correction was applied in the racemisation experiments for a decrease in the concentration of 1-phenylethyl chloride due to interaction with styrene. The results of these interaction experiments cannot be interpreted by any simple kinetic treatment, and it is likely that several stepwise reactions are taking place simultaneously, with the formation of varying amounts of di- tri- etc. styrenes. But it seems definite (Expt. 84, Table XXIII , fig. xviii) that at the concentrations used in the racemisations ~~the rate of~~ interaction of styrene and 1-phenylethyl chloride under the influence of stannic chloride is a slow process. Furthermore, 1-phenylethyl chloride does not appear to be an effective cocatalyst for the long-chain polymerisation of styrene, since when styrene is present (1.4 M) in excess over 1-phenylethyl chloride (0.17 M) an amount of styrene is used up at a rate which is of zero order with respect to styrene in an amount equivalent to the formation of small amounts of low molecular weight polystyrenes, and thereafter of disappearance of styrene is very slow (Expt. 86). If styrene, 1-phenylethyl chloride and stannic chloride interact to form low molecular weight polymers, the mechanism is probably that represented by equations 7-11 on p.103 and HCl and $SnCl_4$ (or $\overset{+}{H}\,\overset{-}{SnCl_5}$) will be liberated in the process. Equations 8-11 may be reversible, and if so the low molecular weight polystyrenes may increase gradually in molecular weight. But it seems much more likely that the $\overset{+}{H}\,\overset{-}{SnCl_5}$ attacks fresh styrene giving more 1-phenylethyl chloride. This will not occur rapidly since the concentration of HCl (or $\overset{+}{H}\,\overset{-}{SnCl_5}$) will probably be fairly low.

The question then arises of why the $\overset{+}{H}\,\overset{-}{SnCl_5}$ and the $Ph\text{-}\overset{+}{C}HCH_3\overset{-}{SnCl_5}$ do not initiate long-chain polymerisation in carbon tetrachloride medium, since it has been shown that HCl can function as a cocatalyst for the polymerisation of styrene with stannic chloride in ethyl chloride [71]. The explanation may lie in the comparative instability of the $\overset{-}{SnCl_5}$ anion which will limit the concentration of ion-pairs in the solution, and will limit still further the concentration of free ions. Unless some factor is introduced which will increase the stability of these ionic entities (cf. nitrobenzene experiments, pp.137-140) the lifetime of any growing chain will probably be too short to permit the formation of long-chain polymers. Furthermore, the tendency for the anion to unite with a proton of a carbonium ion at any stage in the reaction chain to yield an olefin, HCl and $SnCl_4$, is probably great, again owing to the relative instability of the $\overset{-}{\mathrm{Sn}}\mathrm{Cl}_5$ anion.

C. Polymerisation Experiments.

(a) Previous work.

Studies of the polymerisation of styrene in the presence of stannic chloride in carbon tetrachloride solution at 25°C. had previously shown [60]:

(a) that the overall rate equation was $\frac{-d(a-x)}{dt} = k.c.a.\ (a-x)^3$,

where 'a','c' are the initial concentrations of styrene and stannic chloride respectively, and (a-x) is the concentration of styrene at time 't',

(b) that the molecular weight of the polymer produced is proportional to 'a' but is independent of 'c',

and (c) that hydrogen chloride acts as an inhibitor of the long-chain polymerisation of styrene.

In these studies the molecular weights were calculated according to the Staudinger Equation, $\eta_{sp/c} = an + b$, where η_{sp} is the specific viscosity, 'c' is the polymer concentration in g. mols. $C_8H_8.l^{-1}$ and "a" and "b" are constants evaluated by Williams [60] from measurements by Staudinger [81, p.181; 88] for polystyrenes having cryoscopic molecular weights between 2,500 and 4,900. Pepper [69] has suggested that, if the equation derived by Dewar [59] for polystyrenes of molecular weights in the range 1,000 to 3,000 were used instead, then the molecular weights obtained by Williams would be proportional to "a".

This polymerisation was also studied in chloroform solution at 25°C. [89] when it was found:

(a) that the rate of polymerisation was approximately proportional to the catalyst concentration and was first order with respect to styrene. The first order relationship held only during the early stages of the reaction. Polymerisations with different initial concentrations of styrene suggested that the first order velocity constant rose slowly with initial concentration of styrene. These results were taken to indicate that the chloroform reaction might best be represented as a reaction of a mixed order.

(b) that the molecular weight of the polymer increased according to a fractional power of the monomer concentration and was independent of the catalyst concentration.

(c) that HCl inhibits the long-chain polymerisation of styrene in chloroform, and

(d) that occasional runs, for no apparent reason, gave results for which the rate of polymerisation was proportional to the third power of the styrene concentration.

The possible mechanism for the mixed first-third order reaction was considered to be the following:

<u>Mixed first-third order reaction</u>.

It was assumed that the following mechanism held, where M_n denotes a stable molecule of "n" monomer units, P_n denotes an active molecule of "n" monomer units, C denotes a catalyst molecule, and r_i, r_p, r_t are the rates of initiation, propagation and termination respectively:

Initiation: $M_1 + C \rightleftharpoons M_1C$

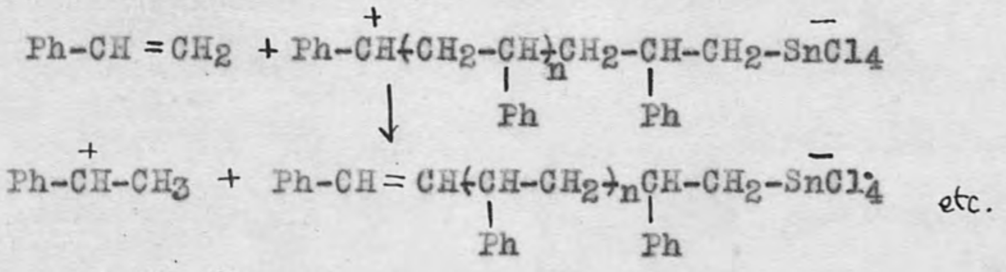
$M_1C + M = P_2C$

Propagation: $P_2C + M_1 = P_3C$ etc.

Termination: $P_nC = M_n + C$

or $M_1 + P_nC + M_1H^+ = M_{n+1} + C + M_1$

M_1H^+ was derived from an actively growing chain -



$$\mathrm{Ph{-}CH{=}CH_2 + Ph{-}\overset{+}{C}H{\leftarrow}CH_2{-}\underset{Ph}{CH}{\rightarrow}_n CH_2{-}\underset{Ph}{CH}{-}CH_2{-}\overset{-}{Sn}Cl_4}$$
$$\downarrow$$
$$\mathrm{Ph{-}\overset{+}{C}H{-}CH_3 + Ph{-}CH{=}CH{\leftarrow}\underset{Ph}{CH}{-}CH_2{\rightarrow}_n \underset{Ph}{CH}{-}CH_2{-}\overset{-}{Sn}Cl_4}\quad \text{etc.}$$

Putting $[M_1H^+] \propto [M_1]$ we have,

$$r_i = k_i [M_1]^2\, C$$
$$r_p = k_p [PC][M_1]$$
$$r_t = k_a [PC] + k_b [PC][M_1]^2$$

where P represents the sum of all the values of P_n, and k_p is independent of n.

For a stationary state, $r_i = r_t$, whence $[PC] = \frac{k_i[M_1]^2[C]}{P + [M_1]^2}$

Then, $r_{obs} = \frac{k[M_1]^3[C]}{p + [M_1]^2}$, where $k = \frac{k_i \cdot k_p \cdot}{k_t}$ and $p = \frac{k_a}{k_b}$.

If $[M_1]^2 \gg p$, $r_{obs} \triangleq k[M_1][C]$. If $[M_1]^2 \ll p$, $r_{obs} \triangleq \frac{k}{p}[M_1]^3[C]$.

This scheme did not explain the reason for the spasmodic occurrence of third order reactions which were observed in experiments using high initial styrene concentration (i.e. high values of M_1).

(b) Present Work.

The present studies sought to discover the reason for the occurrence of the mixed order reactions in chloroform and the high order reactions in carbon tetrachloride.

(1) Results.

It was found that by carefully drying the solvent and reagents, reactions which were third order with respect to styrene could be obtained quite readily in chloroform medium. In experiments 7, 22, 24, 25, 29 (Table XXVII) figs.) the chloroform was washed several times with water and dried twice over calcium chloride before distilling. The styrene was redistilled immediately before use after drying over calcium chloride.

these reactions were third order with respect to styrene.

On the other hand, when the solvent was only once dried over calcium chloride, reactions were obtained which were first order with respect to styrene (Experiments 23, 26, 27, Table XXVIII b).).

Further it was found that if carbon tetrachloride was not carefully dried first order reactions were obtained in this solvent also. In experiments 9-13 (Table XXVIIIa, figs. XV) ordinary Analar carbon tetrachloride was used and the reactions were first order with respect to styrene. When the CCl_4 was washed with water, dried twice over calcium chloride and distilled, and the styrene was washed with sodium hydroxide, water, dried over sodium sulphate and distilled immediately before use, the reactions were third order with respect to styrene (Experiments 1, 14, 15, 19, 21, 39, 44, 45, Table XXVI , figs. XVI).

It is clear from these experiments that the amount of water present in the system has a profound effect on the nature of the reaction taking place.

The results can be summarised as follows (Tables XXVI - XXVIII):

<u>Third-Order Reactions in Carbon Tetrachloride</u>. (Table XXVI)

The molecular weight appears to be independent of the catalyst concentration (Experiments 14 and 21) as was found previously [60] and for initial styrene concentration of approximately 1.7 M, $n = 22$-23. The third order rate constant for these polymerisations obtained graphically from the third order rate equation $\frac{-d(a-x)}{dt} = k\,(a-x)^3$ was in the region of 0.007-0.05, and was directly proportional to the catalyst concentration (fig. XVII).

First-Order Reactions in Carbon Tetrachloride (Table XXVIII a).

The rate of reaction and the molecular weight appear to be independent of the catalyst concentration and of initial styrene concentration. The first-order rate constants obtained graphically by plotting $\log(a-x)$ against time were of the order of 0.00115-0.00968, and n is of the order of 15-20.

Third-Order Reactions in Chloroform. (Table XXVII).

The third order rate constant determined as before had the value of 0.0143-0.059, and appeared to be independent of the catalyst concentration. The molecular weight decreased with decreasing initial monomer concentration and appeared to decrease with decreasing catalyst concentration.

First-Order Reactions in Chloroform. (Table XXVIIIb).

No data were obtained for the dependence of molecular weight on "a" and "c", but for initial styrene of approximately 1.7 M, n is of the order of 29. The first-order rate constant determined as before was in the region of 0.0066-0.00426 and was independent of the catalyst concentration.

Summarising, for "a" $\simeq$ 1.6-1.75 M, and "c" $\simeq$ 0.04-0.10 M,

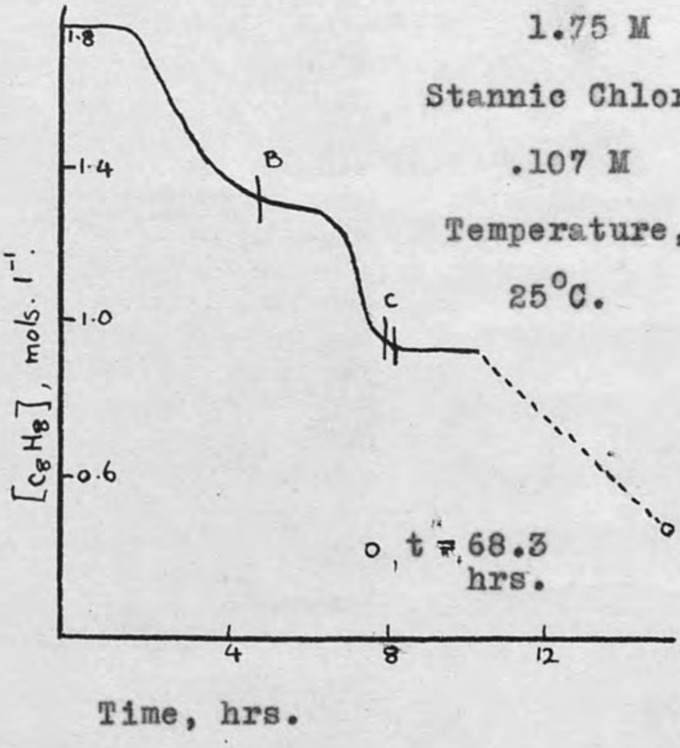
Solvent	Order with respect to Styrene	k_1 or k_3	n
CCl_4	3rd	0.015-0.050	22-23
$CHCl_3$	3rd	0.014-0.059	31-39
CCl_4	1st	0.012-0.0093	15-18
$CHCl_3$	1st	0.00426-0.00656	29

Thus, it seems that a change in the dielectric constant of the medium has a more pronounced effect on the molecular weight than on the rate for the polymerisations, although for the third order reactions the molecular weight and to a very slight extent the rate are increased with increasing dielectric constant of the medium.

In addition, one reaction was observed which was second order with respect to styrene (Expt. 8, fig. xxvii). The styrene used was commercial styrene redistilled without previous drying, and the solvent was chloroform which was washed with water, dried once over calcium chloride and distilled before use. Three other reactions (Expts. 5, 4, 28, figs. xxvi) were either very slow third order reactions ($k_3 = 11.5 - 9.2 \times 10^{-4}$) or of a mixed order.

(2) Discussion.

On the basis of other experiences with Friedel-Crafts polymerisations reviewed in Section I, and of the present findings on the effect of water on the polymerisations it seems likely that stannic chloride alone does not initiate the polymerisation of styrene but that the presence of a co-catalyst is required. Williams [60] passed moist air through a polymerisation solution and observed the fall of styrene concentration. The results are shown below in a diagram reproduced from his paper.

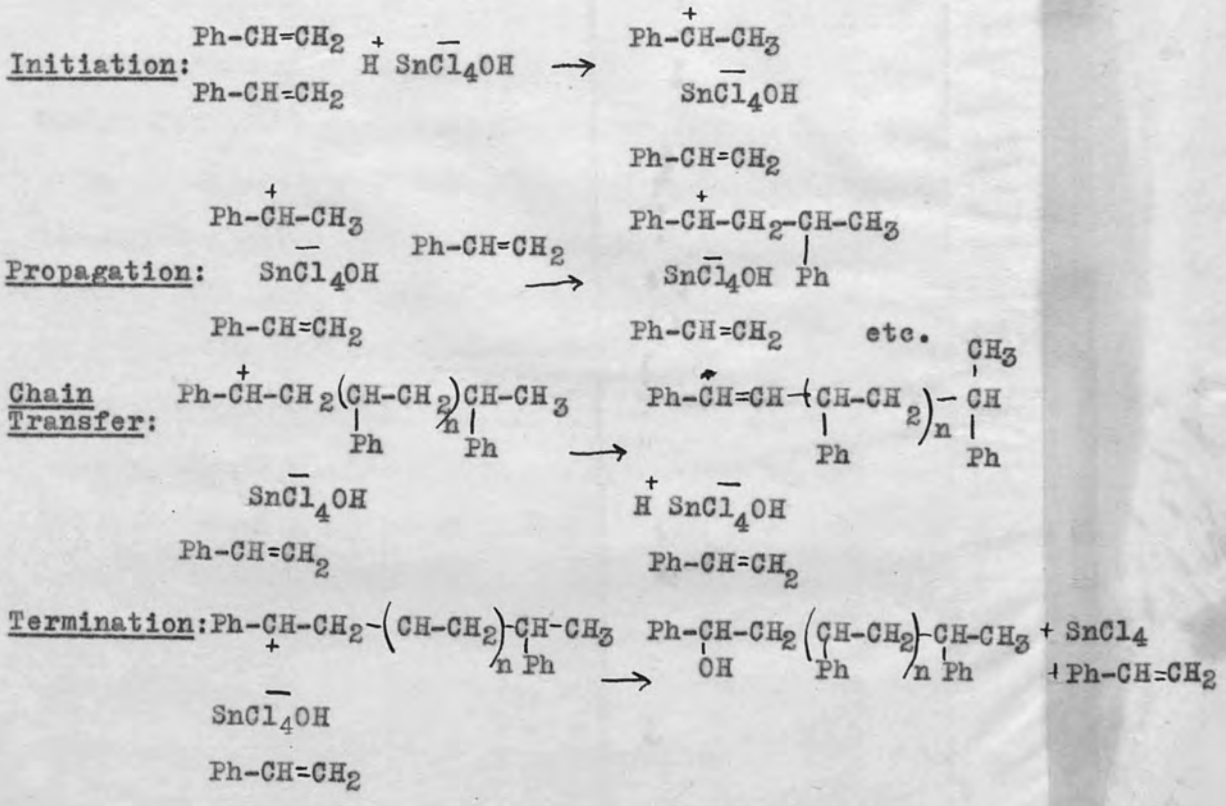


Plesch [84] has pointed out that this experiment indicates that water can function as a catalyst for stannic chloride in this system.

At B moist air was bubbled through the solution, and at C air which had passed through concentrated hydrochloric acid was used.

It is however impossible to make any definite statements on the basis of one experiment only. Norrish and Russel [68] showed that water was required as a co-catalyst for stannic chloride in the polymerisation of isobutene in ethyl chloride. If water does function as a co-catalyst for stannic chloride then one way in which the high order reaction can be explained is to postulate that a molecule of styrene functions as a solvating agent for the ionic complex formed from the catalyst, co-catalyst and monomer, and that the acid catalyst $\overset{+}{\text{H}}\,\overline{\text{SnCl}_4\text{OH}}$ is associated with two molecules of styrene in the transition state for the initiation reaction. Propagation should follow in the normal way, and termination would probably occur by a spontaneous mechanism, viz.:

$$\text{SnCl}_4 + \text{H}_2\text{O} \rightleftharpoons \overset{+}{\text{H}}\,\overline{\text{SnCl}_4\text{OH}}$$



Initiation:

$$\begin{matrix}\text{Ph-CH=CH}_2\\ \text{Ph-CH=CH}_2\end{matrix}\;\overset{+}{\text{H}}\,\overline{\text{SnCl}_4\text{OH}} \longrightarrow \begin{matrix}\text{Ph-}\overset{+}{\text{C}}\text{H-CH}_3\\ \overline{\text{SnCl}_4\text{OH}}\\ \text{Ph-CH=CH}_2\end{matrix}$$

Propagation:

$$\begin{matrix}\text{Ph-}\overset{+}{\text{C}}\text{H-CH}_3\\ \overline{\text{SnCl}_4\text{OH}}\\ \text{Ph-CH=CH}_2\end{matrix}\;\; \text{Ph-CH=CH}_2 \longrightarrow \begin{matrix}\text{Ph-}\overset{+}{\text{C}}\text{H-CH}_2\text{-}\underset{\text{Ph}}{\text{CH}}\text{-CH}_3\\ \overline{\text{SnCl}_4\text{OH}}\\ \text{Ph-CH=CH}_2\end{matrix}\quad \text{etc.}$$

Chain Transfer:

$$\begin{matrix}\text{Ph-}\overset{+}{\text{C}}\text{H-CH}_2\left(\underset{\text{Ph}}{\text{CH}}\text{-CH}_2\right)_n\underset{\text{Ph}}{\text{CH}}\text{-CH}_3\\ \overline{\text{SnCl}_4\text{OH}}\\ \text{Ph-CH=CH}_2\end{matrix} \longrightarrow \begin{matrix}\text{Ph-CH=CH-}\left(\underset{\text{Ph}}{\text{CH}}\text{-CH}_2\right)_n\text{-}\underset{\text{Ph}}{\overset{\text{CH}_3}{\text{CH}}}\\ \overset{+}{\text{H}}\,\overline{\text{SnCl}_4\text{OH}}\\ \text{Ph-CH=CH}_2\end{matrix}$$

Termination:

$$\begin{matrix}\text{Ph-}\underset{+}{\text{C}}\text{H-CH}_2\text{-}\left(\text{CH-CH}_2\right)_n\text{-}\underset{\text{Ph}}{\text{CH}}\text{-CH}_3\\ \overline{\text{SnCl}_4\text{OH}}\\ \text{Ph-CH=CH}_2\end{matrix} \longrightarrow \text{Ph-}\underset{\text{OH}}{\text{CH}}\text{-CH}_2\left(\underset{\text{Ph}}{\text{CH}}\text{-CH}_2\right)_n\text{-}\underset{\text{Ph}}{\text{CH}}\text{-CH}_3 + \text{SnCl}_4 + \text{Ph-CH=CH}_2$$

Then, using the same symbols as before -

$$r_i = k_i \left[M_1\right]^2 C \quad .$$

$$r_p = k_p \left[M_1\right]\left[PC\right] \, .$$

$$r_t = k_p \left[PC\right] \quad .$$

The condition for a stationary state is $r_i = r_t$,

$$\text{i.e.} \quad k_i\left[M_1\right]^2 C = k_p \left[PC\right] .$$

giving $\left[PC\right] = \frac{k_i}{k_p} \left[M_1\right]^2 C \quad .$

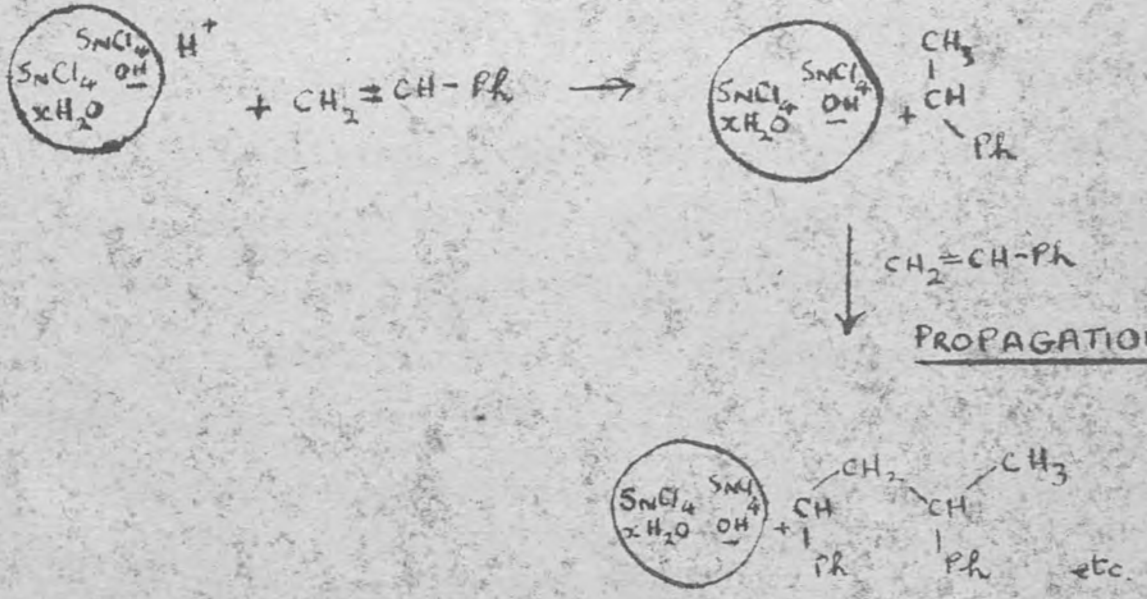
Also, $r_{obs} \simeq r_p = k_i \left[M_1\right]^3 C \quad .$

The degree of polymerisations $\propto \frac{r_p}{r_t} \propto \frac{k_i\left[M_1\right]^3 C}{k_i\left[M_1\right]^2 C} \propto \left[M_1\right]$.

The fact that for a third order reaction the molecular weight of the polymer and also to a very slight extent the rate of polymerisation increase with an increase in the dielectric constant of the medium may be explained if it is assumed that the potential energy of a carbonium ion-anion complex decreases with increasing polarity of the medium. If this is so, then k_i will increase, whereas k_p will decrease since it represents the interaction of an ion with a neutral molecule [cf. 54, p.105]. On the other hand k_t should decrease since the tendency for the elimination of a proton from a carbonium ion should be lowered. Hence, both the rate and degree of polymerisation should increase with increasing dielectric constant of the medium as is in fact observed. The order of the reaction falls to first or second order with respect to monomer in the solvents of still higher dielectric constant [69], which may be due to the fact that in such solvents the solvating entity is the solvent itself and not the monomer.

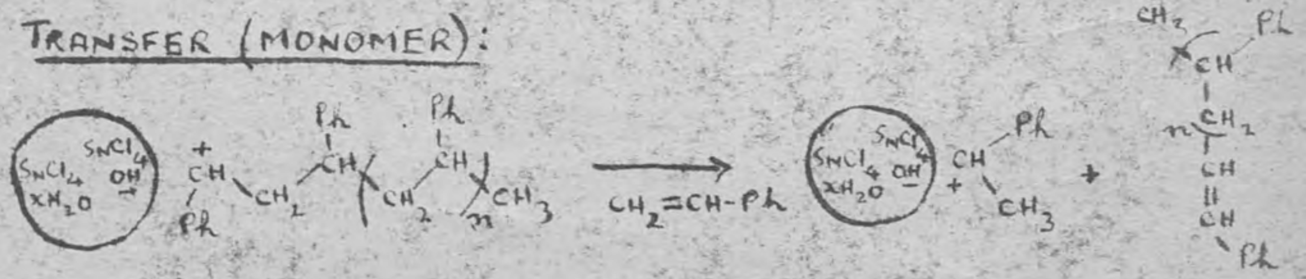
In the first order reactions there were probably somewhat larger amounts of water in the system, not however as great as 0.01 g. per 100 g. solvent, which is the saturation concentration of water (.0055 M) in carbon tetrachloride at 25°C [3]. Frequently traces of a crystalline substance, presumably $SnCl_4, 5H_2O$, separated out on the sides of the reaction vessel during the initial stages of the experiments. It seems likely therefore that within the solutions there were equilibria in existence between all the possible hydrates of stannic chloride, and that since the solubility of these hydrates in the non-polar solvent is probably very low, small crystal aggregates of the hydrates were dispersed throughout the medium. In such a system the rate of polymerisation could be governed solely by the rate of diffusion of styrene onto the surface of the aggregates where it would combine with any active hydrate (probably $SnCl_4.H_2O$) to give a carbonium ion and start a polymer chain. Combination between a monomer molecule and active hydrate to give an ion-pair, and subsequent combination of this with more monomer molecules would probably be rapid on the crystal surface, because of the surrounding ionic atmosphere, and hence the processes of chain initiation and propagation would probably be rapid relative to the slow process of diffusion of the monomer to the surface of the aggregates, and hence the rate of diffusion would become rate-determining for the polymerisation which would therefore be of low order, probably first order [2], with respect to styrene. On the crystal surface, initiation would probably be of first order with respect to styrene, and would be independent of catalyst concentration. Propagation would also take place at the surface of the catalyst and would be of low order with respect to styrene. Chain transfer could occur in several ways, as shown below. The most probable termination reaction is a spontaneous one, viz.:

INITIATION:



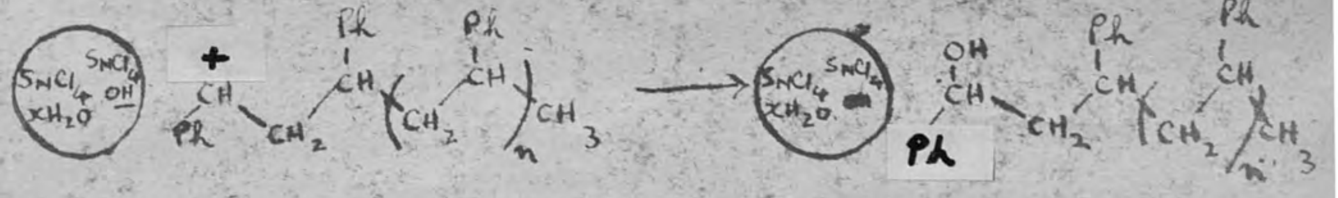
PROPAGATION:

TRANSFER (MONOMER):



TRANSFER (SPONTANEOUS):

TERMINATION (SPONTANEOUS):



If the rate of diffusion of the monomer is rate-determining, then the rate constants for the polymerisations should be independent of catalyst concentration and of the dielectric constant of the medium, as was in fact observed. This assumes that the rate of diffusion is not appreciably affected by the dielectric constant of the medium. On the other hand, the degree of polymerisation will be governed by the relative rates of the propagation and termination reactions, and the normal kinetic considerations apply, viz.:

$$r_i = k_i \left[M_1\right]$$
$$r_p = k_p \left[P\right]\left[M_1\right]$$
$$r_t = k_t \left[P\right]$$

For a stationary state, $r_i = r_t$, i.e. $k_i \left[M_1\right] = k_t \left[P\right]$

Hence $P = \dfrac{k_i . \left[M_1\right]}{k_t}$

Degree of polymerisation $\propto \dfrac{r_p}{r_t} \propto \dfrac{k_p . k_i}{k_t} . \left[M_1\right]^2 \dfrac{1}{k_i \left[M_1\right]}$

$$\propto \frac{k_p}{k_t} . \left[M_1\right].$$

Thus, the degree of polymerisation should be directly proportional to the initial monomer concentration. If, however, a monomer termination reaction or extensive transfer were taking place, the dependence on monomer concentration would become less than linear, and in fact might disappear entirely.

In such a reaction scheme, an increase in the dielectric constant of the medium would probably increase k_i slightly. Also, since in solvents of high dielectric constant solvation of ions by the solvent increases their stability and permits greater charge separation, the positively charged end of the polymer chain will be slightly further from the catalyst surface, and an approaching monomer molecule can more easily come into the correct position for addition onto the chain, hence k_p will probably increase slightly with increasing dielectric constant of the medium. Also, the termination reaction which involves the disappearance of ions will be retarded, and k_t will decrease. Hence the molecular weight of the polymers should increase with increasing dielectric constant of the medium, as is in fact observed.

Thus, a heterogeneous system is consistent with all the facts observed for the first order reactions in chloroform and carbon tetrachloride.

It is conceivable that if the concentration of active hydrate in the aggregates were high the rate of diffusion of styrene to these centres might be the limiting factor for the propagation step also, as there would be a great number of active centres distributed over the catalyst surface, and insufficient styrene might reach the whole of the surface for the propagation reaction to take place with the usual rapidity. Then the observed rate would be approximately equal to the rate of propagation -

$$\text{i.e. } r_{obs} \bumpeq r_p = \frac{k_p \cdot k_i}{k_t} \cdot \left[M_1\right]^2 .$$

The reaction should then become of second order with respect to monomer, as was in fact observed in one instance (Experiment 8).

It is likely that increasing the water content of the medium above a certain low value will not greatly affect the rate of polymerisation and may even cause a decrease in rate, since the equilibrium concentration of active hydrate (probably $SnCl_4.H_2O$) is probably reached at a low water content. Increasing the water content above this value merely leads to the formation of the stable, inert, $SnCl_4.5H_2O$. This would explain the observations of Eley and Richards [78b] and of Pepper [69] for added water. At the high water contents used by them the reactions might quite well have been heterogeneous.

If the assumptions made are valid, the factor which determines whether the polymerisation reactions will be of third order, second order or first order with respect to styrene will be the concentrations of hydrates of stannic chloride in the reaction medium, which will in turn be governed by the amount of water present in the system. It is reasonable to suppose that under certain conditions reactions will be encountered which are apparently of a mixed order, where both heterogeneous and homogeneous mechanisms are operating simultaneously.

The induction periods observed at the beginning of the third order polymerisations may be due to the gradual uptake of water from the atmosphere during the withdrawal of samples from the solution. Those occurring in the first order experiments may represent the period required for equilibrium to be established between the various hydrates of stannic chloride.

It is recognised that these suggestions are of a speculative character, and require substantiation by further experimental work. In particular it would be of great interest to know whether polymerisation does in fact occur in these systems under completely anhydrous conditions, and following that, to study the effects of the addition to the systems of known, small amounts of water. Insufficient evidence is available to establish with any certainty that a heterogeneous mechanism is operating in the first order reactions, but it seems a possible mechanism, and one which will satisfactorily account for the first order nature of the reactions.

D. Nitrobenzene Experiments.

Addition of hydrogen chloride to styrene in the absence of added catalyst was found to take place rapidly in nitrobenzene solution (Expt. 63, p. 89) to give 1-phenylethyl chloride and a very small amount of low molecular weight polymer. Evidently in this solvent the dissociation of the HCl is sufficient to enable attack of a proton on the olefinic double bond. The organic halide will also be solvated by the nitrobenzene, so that the situation differs from that encountered in dilute aqueous solutions [cf. 40 , p. 271] where addition of hydrogen halides to olefins is slow because of solvation of the proton to give the comparatively inert $H_3\overset{+}{O}$. Furthermore, in aqueous medium there is no solvation energy for the products of the hydrogen halide addition.

In the presence of stannic chloride, however, a very rapid and vigorous reaction occurs (Expt. 64, p. 91), the products being low molecular weight polystyrenes. It is likely that in nitrobenzene solution all the HCl and $SnCl_4$ will interact to give the ions $\overset{+}{H}$ and $\overset{-}{SnCl_5}$ which then promote the reactions shown on p. 102-3. Owing to the polar nature of the solvent and the consequent lowering of the potential energy of any ions in the solution, these reactions will take place very rapidly. Since the concentration of the active catalyst is probably quite high, only low molecular weight polymers are formed.

With approximately identical initial styrene concentration, and in the presence of stannic chloride only in nitrobenzene solution, a long-chain polymerisation occurs which appears to be first-order with respect to styrene (Expt. 91, Table XXXIV, fig. xix). It is impossible to say what the initiating entity is. Possibly in a solvent of high dielectric constant stannic chloride itself may be effective, or if there are traces of water present in the solution the catalyst may be the acid hydrate $\overset{+}{H}\,\overset{-}{SnCl_4OH}$. In either case, the initiation step would be first order with respect to monomer and would probably be very rapid since the solvent would provide the necessary solvation energy for the process. Then, if termination is due to the usual spontaneous mechanism the kinetic relations would be as follows:

$$r_i = k_i\,[M_1][C].$$

$$r_p = k_p\,[M_1][PC].$$

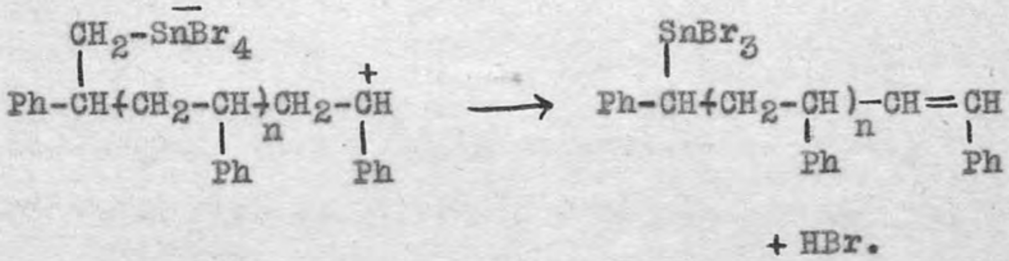
$$r_t = k_t\,[PC]$$

whence $[PC] = \dfrac{k_i[M_1][C]}{k_t} = \dfrac{k_i}{k_t}\,.\,[C][M_1]\,.$

Then, since $r_{obs} \hat{=} r_p = \dfrac{k_p . k_i}{k_t}\,C[M_1]^2\,.$

i.e. the reaction should be of second order with respect to monomer. The only reasonable explanation for the observed first order relationship appears to be that the initiation reaction becomes extremely rapid in the solvent of high dielectric constant, and that the rate observed is a measure of the propagation step only, which will then be of first order with respect to monomer, and which will tend to be relatively slow in a solvent of high dielectric constant, being an interaction of an ion with a neutral molecule.

Some information relating to the initiation process for the polymerisation of styrene in nitrobenzene catalysed by stannic bromide has recently been offered by Landler [85], who, using catalyst containing radioactive bromine detected radioactivity in the polymers produced. Estimation of this radioactivity and determination of the molecular weight of the polymer showed that one polymer molecule in three contained $-SnBr_3$. Thus initiation was believed to occur by polarisation of the styrene double bond under the influence of stannic chloride (reaction (1), p. 102), followed in the propagation steps by addition of monomer molecules (as in reaction (2), p. 102), the termination reaction occurring by elimination of HBr from a growing chain, viz.:



$$\overset{\mathrm{CH_2-\overline{Sn}Br_4}}{\mathrm{Ph-CH}}\left(\mathrm{CH_2-}\underset{\mathrm{Ph}}{\mathrm{CH}}\right)_n\mathrm{CH_2-}\underset{\mathrm{Ph}}{\overset{+}{\mathrm{CH}}} \longrightarrow \overset{\mathrm{SnBr_3}}{\mathrm{Ph-CH}}\left(\mathrm{CH_2-}\underset{\mathrm{Ph}}{\mathrm{CH}}\right)_n\mathrm{-CH=}\underset{\mathrm{Ph}}{\mathrm{CH}} + \mathrm{HBr}.$$

Doubt is thrown onto the reliability of this work, however, since the molecular weights of the polymers were found to be about 46,000, which is a value far greater than any other recorded for Friedel-Crafts polymerisations. The possibility of free radical polymerisations, initiated by atoms or radicals produced by radiations in the solutions cannot therefore be overlooked. In the present work, a polymerisation of styrene with stannic bromide in nitrobenzene proceeded fairly rapidly and gave a polymeric product of average (viscosimetric) molecular weight 2,704 (Expt. , Table , fig.).

Although it is not possible to state the exact nature of the initiation and termination processes for polymerisation in nitrobenzene, it is evident that both polymerisation and addition reactions of styrene do proceed with great ease in this solvent. The difficulties encountered in other solvents are no doubt due to the non-polar nature of the medium which does not favour reactions proceeding by ionic mechanisms.

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TABLE Ia.

Calculation of total halogen for mixtures of 1-phenylethyl halides:

Compound or mixture.	Wt. g.	No. of equivalents of Ag used (Volhard)	Wt. Ag-halide produced (g.) (Gravimetric)	Amount of halogen liberated (g.) (Weiler & Strauss Analyses).
C_8H_9Cl	100	0.7163	102.4	25.3
C_8H_9Cl C_8H_9Br	98 2	0.7020 0.0109 Tot. = 0.7129	100.6 2.05 Tot. = 102.65	24.89 0.873 Tot. = 25.76
C_8H_9Cl C_8H_9Br	92 8	0.6591 0.0469 Tot. = 0.7028	94.45 8.205 Tot. = 102.66	23.36 3.49 Tot. = 26.85
C_8H_9Br	100	0.5461	102.6	43.30
C_8H_9Br C_8H_9Cl	98 2	0.5351 0.0143 Tot. = 0.5494	100.5 2.053 Tot. = 102.55	42.77 0.500 Tot. = 43.27
C_8H_9Br C_8H_9Cl	92 8	0.5025 0.0573 Tot. = 0.5598	94.37 8.212 Tot. = 102.58	39.23 2.03 Tot. = 41.26

Calculations were similarly made for values of carbon and hydrogen.

TABLE Ib.

Calculated deviations from the theoretical values for the 3 methods of analysis for total halogen, and for carbon and hydrogen.

Compound or mixture.	Wt. g.	Deviation for Volhard(%)	Deviation for Gravimetric(%)	Deviation for direct halogen (Weiler & Strauss)	C %	H %
C_8H_9Cl C_8H_9Br	98 2	-0.5	+0.25	+0.4	-1	0
C_8H_9Cl C_8H_9Br	92 8	-2.0	+0.26	+4.0	-2.2	.03
C_8H_9Cl C_8H_9Br	2 98	+0.6	- .05	- .01	+ .6	+.5
C_8H_9Cl C_8H_9Br	8 92	+2.8	- .02	-5	+2.4	+2

TABLE II.

Values for total halogen and for carbon and hydrogen for products from the addition experiments.

(Analyses by Drs. Weiler and Strauss)

Name of Compound	Found:			Theoretical:			% impurity	
	C%	H%	Halogen%	C%	H%	Halogen%	Found	Calculated
KM/10	53.33	5.09	42.3	51.9	4.9	43.2	3.7	5
KM/11	54.06	5.09	41.15	51.9	4.9	43.2	12.8	9
KM/13	67.75	6.34	26.2	68.3	6.4	25.3	6.4	7
KM/14	66.09	6.57	27.7	68.3	6.4	25.3	9.85	12
KM/18	67.55	6.64	26.3	68.3	6.4	25.3	5.96	8
KM/21	52.4	4.98	42.9	51.9	4.9	43.2	4.45	3
KM/22	52.38	4.87	42.41	51.9	4.9	43.2	0.1	5
KM/23	53.49	5.69	40.82	51.9	4.9	43.2	1.4	12
KM/24	67.33	6.44	26.54	68.3	6.4	25.3	11.62	10
KM/25	67.54	6.63	26.1	68.3	6.4	25.3	6.37	7
KM/26	67.17	6.44	26.4	68.3	6.4	25.3	4.47	8

TABLE III.

Estimation of bromide in 1:3 sulphuric acid medium (8-9N).

Volume of 0.1016N bromide	Volume of 0.8318N chloride	Volume of As_2O_3(0.2011N) in flask B.	Volume of As_2O_3(0.2011N) in flask C.	Titre of B with 0.1034N iodine.	Titre of C with 0.1034N iodine	Norm. of bromide found
20	-	20	10	19.82	19.65	0.0997
20	-	20	10	19.94	19.67	0.0998
5	-	20	10	34.37	19.65	0.1010
5	10	20	10	33.49	19.64	0.1186
5	10	20	10	34.27	19.62	0.1029
5	10	20	10	34.07	19.63	0.1072
5	10	20	10	34.10*	19.96*	0.1062

*0.1023N iodine.

TABLE IV.

Estimation of bromide in 7N sulphuric acid.

5	10	20	10	34.29*	19.61*	0.1025
5	10	20	10	34.41*	19.65*	0.1001
5	10	20	10	34.42*	19.68*	0.1001
5	-	20	10	34.56*	19.64*	0.0969
-	10	20	10	39.47*	19.74*	-
-	10	20	10	39.39*	19.68*	-

TABLE V.

Estimation of bromine in mixtures of synthetic 1-phenylethyl halides.

(The titre of iodine for flask C is not quoted as it agreed in every case with the theoretical value).

Wt. 1-phenyl-ethyl bromide. (g.)	Wt. 1-phenyl-ethyl chloride. (g.)	Titre of B with 0.1006N iodine. (ml.)	Wt. 1-phenyl-ethyl bromide found (g.)	%Br_2 found	% C_8H_9Br present Found	% C_8H_9Br present Theoret.
0.2836	-	25.16*	-	41.3	-	-
0.2569	-	28.37*	-	39.6	-	-
0.3634	-	21.00*	-	41.79	-	-
0.3199	-	21.79	-	41.37	-	-
0.2971	-	22.55	-	41.94	-	-
0.2823	-	23.00	-	42.68	-	-
0.2712	-	23.44	-	43.2	-	-
0.2762	-	23.56	-	42.65	-	-
0.4546	-	14.50	-	42.48	-	-
0.0663	0.3204	35.20	0.0395	-		
0.3236	0.0407	21.09	0.3180	-	88.62	88.81
0.1804	0.1673	28.16	0.1784	-	51.60	51.88
0.1316	0.3042	30.56	0.1311	-	30.11	30.19
0.0439	0.2345	34.99	0.0436	-	15.70	15.77

Normality of the As_2O_3 = 0.1981. (* = 0.2011)

TABLE VIa.

"Compound"	Wt. taken (g.)	Titre of B with 0.1006N iodine. (ml.)	Wt. C_8H_9Br found (g.)	%C_8H_9Br present in "compound"		Average
KM/10	0.3667	19.15	0.3558	97.00	1·50	96.4
KM/10	0.2486	24.94	0.2408	96.70		
KM/10	0.2362	25.76	0.2258	95.50		
KM/11	0.2453	26.38	0.2131	86.95	0·85	87.13
KM/11	0.3263	22.55	0.2883	87.80		
KM/11	0.3834	20.29	0.3339	87.00		
KM/13	0.2140	36.50	0.01356	6.34	0·74	6.38
KM/13	0.2620	36.40	0.01578	6.03		
KM/13	0.2552	36.32	0.0173	6.77		
KM/14	0.1538	36.40	0.01579	10.28	0·87	9.85
KM/14	0.3309	35.69	0.03179	9.41		
KM/15	0.2606	36.21				
KM/15	0.2879	36.16				

Total halogen estimations for these compounds given in Table VIb. (As_2O_3 is 0.1981N).

Table VIb.

"Compound"	Wt. taken (g.)	Wt. Silver halide formed (g)	Vol. NH_4CNS titre (ml.) (0.1075N)	$AgNO_3$ (0.1960N) used by compound (ml.)	% Halogen Found	% Halogen Theoret. (* for C_8H_9Cl) (for C_8H_9Br)
KM/10	0.2742	-	22.49	7.66	42.75	43.2
		0.2809	-	-	43.59	"
KM/10	0.2957	0.3008	-	-	43.38	"
		-	21.56	8.17	43.28	"
KM/11	0.3040	0.3112	-	-	43.56	"
		-	20.43	8.79	45.29	"
KM/11	0.3314	0.3376	-	-	43.38	"
		-	19.18	9.48	44.81	"
KM/13	0.2524	0.2567	-	-	25.17	25.3*
		-	20.09	8.96	24.70	"
KM/13	0.2472	0.2528	-	-	25.36	"
		-	20.30	8.86	24.90	"
KM/14	0.2053	0.2099	-	-	25.30	"
		-	23.25	7.24	24.51	"
KM/14	0.1798	0.1843	-	-	25.36	"
		-	25.01	6.27	24.23	"
KM/15	0.2423	0.2480	-	-	25.33	"
		-	20.84	8.57	24.59	"
KM/15	0.2292	0.2353	-	-	25.41	"
		-	21.60	8.15	24.09	"

Table VIII

Expt. No.	Initial C_8H_8 M.	$SnBr_4$ M.	Time of Expt. (hrs.)	%Styrene recovered as:- C_8H_8	C_8H_9X	$(C_8H_8)_2$ and $(C_8H_8)_n$	Total	Analysis of C_8H_9X %Brom cpd.	%Total Halide (Calc. C_8H_9Cl)	%Total Halide (Gravim.)	%Total Halide (Volhard)
18	0.34	0.0048	41	46	33.3	8.3	87.6	6.38	25.3	25.24	24.81
†19	0.34	0.0167	14	0	36	0	36	9.85	25.33	25.33	24.37
23	0.34	0.0264	48	15.6	35.5	22.7	73.8	7.24	25.3	25.34	24.59
*54	0.329	0.0136	24½	29.8	20.9	12.0	62.7	11.62	25.3	24.42	-
*55	0.371	0.0173	29¾	31.6	75.9	0	(107.5)	6.37	25.3	24.66	24.12
87	0.333	0.1616	10¾	48.6	33.1	7.8	89.5	63.0‡	-	-	-
88	0.333	0.1699	10¾	34.7	47.2	10	91.9	52.4‡	-	-	-
89	0.333	0.1051	12¼	64.5	29	6.7	(100.2)	45.5‡	-	-	-
90	0.333	0.2207	10¾	35.21	42.3	17.8	95.31	54.0‡	-	-	-

Interaction of Styrene with HCl and $SnBr_4$.

Solvent: CCl_4 (†Chlorobenzene). Temp. 20-25°C.
Dry hydrogen chloride was led through the solutions. (Conc. of HCl = 0.14N).
*Reactions performed under approximately anhydrous conditions.
‡Density method of analysis.

Table IX.

Expt. No.	Initial C_8H_8 M.	$SnCl_4$ M.	Time of Expt. (hrs.)	%Styrene recovered as:- C_8H_8	C_8H_9X	$(C_8H_8)_2$ and $(C_8H_8)_n$	Total	%Brom-cpd.	Analysis of C_8H_9X. %Total halide (Calc. C_8H_9Br)	%Total halide (Gravim.)	%Total halide (Volhard)
16	0.34	0.035	3¼	0	69.2	16.7	85.9	96.4	43.3	43.41	43.01
17	0.34	0.186	4¾	0	63.5	16.7	80.2	87.15	43.3	43.47	45.05
*51	0.389	0.0202	3	0	78.7	15.8	94.5	98.6	43.3	-	-
*52	0.527	0.0104	2¾	8.6	59.34	15.33	83.27	99.9	43.3	43.36	43.12
*53	0.793	0.562	4	22.82	54.2	17.2	94.22	95.55	43.3	43.30	43.20
73	0.34	0.0857	2½	0	71.5	14.7	86.2	99.0	(By Density Method)		
°74	0.34	0.0857	2½	0	85.5	0	85.5	76.5	(" " ")		
77	0.34	0.0857	7	0	89.4	0	89.4	82.5	(" " ")		
78	0.34	0.3428	2¾	0	80.1	9.4	89.5	50.5	(" " ")		
79	0.34	0.3428	3	0	81.4	9.4	90.8	60.1	(" " ")		
81	0.34	0.0685	2	0	86.4	0	86.4	99.0	(" " ")		

Interaction of Styrene with HBr and $SnCl_4$.

Solvent: CCl_4. Temp. 20-25°C.
Dry hydrogen bromide led through the solutions throughout (Conc. HBr = 0.3-0.4N).
*Reactions performed under approximately anhydrous conditions.
°HBr stopped for short while.

Table X

Expt. No.	Initial C_8H_8 M.	$SnCl_4$ M.	Time of Expt. (hrs.)	%Styrene recovered as:- C_8H_8	C_8H_9X	$(C_8H_8)_2$	$(C_8H_8)_n$	Total	%Brom-cpd. in C_8H_9X by Density Method.
°65	0.34	0.3428	2¼	0	72.2	1.70	5.4	94.4	4.6
°67	0.34	0.1714	4¾	5.0	57.0	25.3	7.3	94.6	35.7
*69	0.34	0.1714	5¼	5.0	27.2	36.5	32.2	100.9	2.03
*70	0.34	0.174	3¼	18.4	34.22	42.9		96.0	4.7
*71	0.34	0.3428	3	0	49.7	39.5		89.2	2.3
*72	0.34	0.0857	3¼	40.0	26.3	34.3		100.6	11.1
†75	0.34	0.175	6¼	35.7	36.0	12.9		84.6	28.5
‡76	0.34	0.175	4	27.9	68.4	0		96.3	20.0

Interaction of Styrene with HBr and Stannic Chloride, ctd.

Solvent CCl_4. Temp. 20-25°C.
°HBr discontinued immediately after addition of C_8H_8 and $SnCl_4$.
*Very slow current of HBr maintained, 1-2 bubbles/minute.
† HBr stopped after 15 min.
‡ HBr stopped after 40 min.

Table XI

Expt. No.	Initial C_8H_9Cl M.	Initial C_8H_9Br M.	Time of Expt. (hrs.)	Hydrogen halide used.	%C_8H_9X recovered	Other products	Total yield %.	%Brom-cpd. in C_8H_9X by Density Method.
82	-	0.33	4	HCl	95.3	None	95.3	99.9
83	-	0.33	20	HCl	83.1	None	83.1	98.7
86	0.355	-	5	HBr	91.2	None	91.2	5.0

Interaction of 1-phenylethyl halides with Hydrogen Halides.

Solvent CCl_4. Temp. 20-25°C.

A current of the hydrogen halide used was maintained throughout the experiment.

Table XII

Expt. No.	Initial C_8H_9Br M.	$SnCl_4$ M.	Time of Expt. (hrs.)	%C_8H_9Br recovered as:- C_8H_9X	Other products	Total %	Analysis of C_8H_9X:- %Brom-cpd.	Total halide (Calcd.)	Total halide found (grav.)
56	0.33	0.164	6	91.1	0	91.1	4.47	25.3	25.51
*57	0.33	0.164	13½	80.4	0	80.4	56.7	-	-
*58	0.33	0.164	6	88.7	0	88.7	88.5	-	-
*60	0.33	0.0164	4	68.2	0	68.2	96.6	43.3	-
†95	0.33	0.164	4	94.3	0	94.3	45.5	–	–

Interaction of 1-phenylethyl bromide with $SnCl_4$.

Solvent CCl_4. Temp. 20-25°C.

*Dry hydrogen chromide led through the solutions. HBr Conc. = 0.3-0.4M.

† Reagents added to solvent saturated with HBr, then supply of gas discontinued

Table XIII

Expt. No.	Initial C_8H_9Cl M.	$SnBr_4$ M.	Time of Expt. (hrs.)	%C_8H_9Cl recovered as:-			Analysis of C_8H_9X:-		
				C_8H_9X	Other products.	Total %	%Brom-cpd.	Total halide Calc.	Total halide found Grav.
33	0.30	0.036	12	78.1	-	78.1	5.96	25.3	25.2
*62	0.30	0.0331	48	73	-	73	10.9	-	-
65	0.34	0.0211	50	97.2	-	97.2	9.5	-	-
92	0.30	0.1137	12	96.7	-	96.7	24.4	-	-
93	0.30	0.1105	12	94.6	-	94.6	21.9	-	-
*94	0.17	0.242	12	92.5	-	92.5	39.7	-	-

Interaction of 1-phenylethyl chloride with $SnBr_4$.

Solvent CCl_4. Temp. 20-25°C.
*Dry hydrogen chloride led through the solution. HCl Conc. = 0.14M.

Table XIV.

%1-phenylethyl bromide in products from exchange experiments (Figs.i and ii)		%1-phenylethyl bromide in products from the addition experiments (Table II)		$[SnCl_4]$ M.
% C_8H_9Br	Time of Expt.	%C_8H_9Br	Time of Expt.	
95.5	4hr.	95.55	4hr.	0.056
99.5	4hr.	99.9	2¾hr.	0.0104
98.5	4hr.	98.6	3hr.	0.0202
97.5	4hr.	96.4	3¼hr.	0.035
84.7	4hr.	87.15 82.5	4¾hr. 2¾hr.	0.186
72.0	4hr.	50.5 60.1	2¾hr. 3hr.	0.343

Comparison of products from exchange reactions and addition experiments.

Table XII

Expt. No.	Starting Materials.	$SnCl_4$ M.	Time of Expt. (hrs.)	C_8H_9X	%Styrene recovered as:- C_8H_8	$C_{16}H_{16}$	$(C_8H_8)_n$	Total	%C_8H_9Br found in product.
59	0.1982M C_8H_8 0.165M C_8H_9Br	0.164	4	19.7	14.8	23.5	35.2	93.2	72.31

Interaction of Styrene, 1-phenylethyl bromide and $SnCl_4$.

Solvent CCl_4. Temp. 20-25°C.

1 ml styrene to 20 ml reaction mixture →

ⓧ Correct for styrene i.e. × $\frac{20}{21}$

Table XVI.
Racemisation Experiments in Carbon Tetrachloride at 25°C.

Wt hal. in 100 ml.	No. of Racemisation Expt.	c_0	$[\alpha]_D$ of C_8H_9Cl used.	Total C_8H_9Cl	C_8H_9Cl	$SnCl_4$	C_8H_8	k_1 Initial Curve	k_1 Final Curve.
0.9998	1		-50.05	0.1396	0.1350	0.0712	-	0.0273	0.00645*
0.9998	2		″	0.0698	0.0675	0.0712	-	0.0175	0.0175
2.4235	3	4.847	″	0.3383	0.3265	0.0712	-	0.05066	0.0039*
″	4	4.847	″	0.3383	0.3265	0.0712	-	(0.0691	0.1152)
3.0741	5	2.244	-36.5	0.2145	0.1510	0.0584	-	0.0461	0.0461
3.0741 × $\frac{20}{21}$	6	ⓧ 2.244	″	0.2043	0.1438	0.0556	0.413	0.0461	0.0461
								(2nd order, see fig. xii)	
2.5801	7	2.409	-46.7	0.1801	0.1625	0.0600	-	0.02303	0.0042
sty ″ × 20/21	8	2.409	″	0.1716	0.1583	0.0572	0.413	0.0173	0.0092*
″ × 20/21	9	2.409	″	0.1716	0.1583	0.0572	0.413	0.0265	0.0101*
″	10	2.409	″	0.1801	0.1625	0.0600	-	0.0599	. 0.0599
2.9102	11	2.630	-45.26	1/2 0.4062	0.3550	0.0739	-	0.03685	0.03685
″	12	″	″	0.4062	0.3550	0.0739	-	0.06909	0.06909
″ × 20/21	13	″	″	0.387	0.3380	0.0704	0.413	0.06576	0.06576
″ 20/21	14	″	″	0.387	0.3380	0.0704	0.413	0.06909	0.06909
								3rd order (fig.)	
1.7575	15	1.773	-51.9	0.1226	0.1226	0.0778	-		
″	16	″	″	0.1226	0.1226	0.0778	-	0.0622	0.0622
″ × 20/21	17	″	″	0.1167	0.1167	0.0741	0.413	0.0739	0.0739
″ 20/21	18	″	″	0.1167	0.1167	0.0741	0.413	0.076	0.076
1.6076	19	1.669	″	0.1121	0.1121		-	0.0490	0.0490
″ × 20/21	20	″	″	0.1068	0.1068		0.413	0.0652	0.0652
″ 20/21	21	″	″	0.1068	0.1068		0.413	0.0594	0.0594
″	22	″	″	0.1121	0.1121		-	0.0550	0.0550

*Reactions of a mixed order. Expt. 1 is plotted as a 1st order (fig.) and as a 2nd order (fig.) to illustrate.

Table XVI ctd.

Styrene concentration, estimated by bromine absorption, after completion of racemisation:-

Expt.No.	Time of Sampling. (min.)	C_8H_8 (M.)
17	90	0.3938
18	75	0.385
20	21} 54}	0.419} 0.393}

Table XVII , fig. xx.

Expt. No.5. Temperature 25°C.

Initial pure (-)-1-phenylethyl chloride = 0.1510M.

Stannic chloride = 0.0584M.

$a_{t_1} - a_{\alpha} = -1.86$ k_1(from graph) = **0.0461**

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Time (min.)	∞	$(a_{t_2} - a_{\alpha})$		$\log\frac{(a_{t_1} - a_{\alpha})}{(a_{t_2} - a_{\alpha})}$
5.25		1.60	0·2041	0.0654
7.17		1.52	~~0·201~~ 0·1818	0.0777
8.00	1·41	~~1.11~~	~~0·0453~~ ·1492	0.1203
9.10		1.32	0·1206	0.1489
9.50		1.27	0·1038	0.1557
11.20		1.23	0·0899	0.1796
12.40		1.17	0·0682	0.2013
14.50		1.06	0·0253	0.2442
15.55		1.00	0	0.2695
17.10	$\bar{1}$·9685	0.93		0.3010
18.40	9294	0.85		0.3401
21.15	8751	0.75		0.3944
23.00	8451	0.70		0.4244
25.25	7853	0.61		0.4842
29.10	7243	0.53		0.5452
30.35	7076	0.51		0.5619
31.45	6532	0.45		0.6163
33.50	6128	0.41		0.6567
37.40	5563	0.36		0.7132
40.40	4771	0.30		0.7924
41.50	3979	0.25		0.8716
45.00	3424	0.22		0.9271
51.15	2788	0.19		0.9907
54.00	2041	0.16		1.0654
63.05	0792	0.12		1.1903
67.00	$\bar{2}$·8451	0.07		1.4244

Table XVIII , fig. XX .

Expt. No. 6. Temperature 25°C.

Initial pure (-)-1-phenylethyl chloride = 0.1436M.

Stannic chloride = 0.0556M.

Styrene = 0.413M.

$a_{t_1} - a_{\alpha} = -1.86$. k_1 (from graph) = 0.0461

	Time (min.)		$(a_{t_2} - a_{\alpha})$		$\log\frac{(a_{t_1} - a_{\alpha})}{(a_{t_2} - a_{\alpha})}$	
	7.30		1.60	1.2041	0.0654	
	9.55		1.49	1.1732	0.0963	
	11.30		1.40	1.1461	0.1234	
	14.10		1.14	1.0569	0.2026	
	15.15		1.02	1.0086	0.2609	
	16.20		1.00	10	0.2695	
	18.30		0.94	0.973	0.2694	
	19.50		0.80	903	0.3664	✓ X
	21.45		0.74	869	0.4003	
	24.00	0.64	0.80		0.4664	X ≡ 2.927
	25.00		0.69	839	0.4307	✓
	26.30		0.65	813	0.4566	
	27.35		0.55	740	0.5291	
?	31.00		0.49	690	0.5713	
	30.00		0.41	613	0.6567	
	33.40		0.47	672	0.5974	
	34.45		0.41	613	0.6567	
	38.05		0.40	602	0.6674	
	39.40		0.31	491	0.7781	
	44.30		0.29	462	0.8071	
	49.35		0.19	279	0.9907	
	50.30		0.22	342	0.9271	
	54.00		0.20	301	0.9685	
	123.00		0.04		1.6674	

Table XIX, fig.xxii.

Expt. No.7. Temperature 25°C.

Initial pure (-)-1-phenylethyl chloride = 0.1625M.

Stannic chloride = 0.0600M.

$a_{t_1} - a_\alpha = -1.83.$ k_2 (from graph) = 0.00566

t_2	$\frac{1}{a_{t_2} - a_\alpha}$	$(a_{t_2} - a_\alpha)$	$\log\frac{(a_{t_1} - a_\alpha)}{(a_{t_2} - a_\alpha)}$
6.20	0.574	1.74	0.0220
7.10	0.613	1.63	0.0503
9.00	0.636	1.57	0.0666
10.10	0.645	1.55	0.0722
11.40	0.662	1.51	0.0835
12.45	0.679	1.47	0.0952
15.30	0.714	1.40	0.1164
19.45	0.735	1.36	0.1290
21.40	0.751	1.33	0.1386
25.00	0.793	1.26	0.1621
27.10	0.812	1.23	0.1726
48.10	0.892	1.12	0.2133
50.00	0.934	1.07	0.2331
99.10	1.113	0.90	0.2669
104.10	1.179	0.85	0.3331
114.50	1.251	0.80	0.2669
161.40	1.390	0.72	0.4052
164.00	1.540	0.65	0.4496
207.25	1.670	0.60	0.4843
208.30	1.755	0.57	0.5075
209.30	1.789	0.56	0.5143
243.20	2.022	0.49	0.5723
244.00	2.00	0.50	0.5635
272.00	2.022	0.43	0.6290
273.25	2.022	0.43	0.6290

Table XX, fig.xxi.

Expt. No. 12. Temperature 25°C.

Initial pure (-)-1-phenylethyl chloride = 0.3550M.

Stannic chloride = 0.0739M.

$(a_{t_1} - a_\alpha) = -1.60$. k_1 (from graph) = 0·06909

t_2 (min.)	$(a_{t_2} - a_\alpha)$	$1 + \log a_t$?	$\log\frac{(a_{t_1} - a_\alpha)}{(a_{t_2} - a_\alpha)}$	
6.05	1.53	1·1847	0.0194	0·00321
7.05	1.43	1·1553	0.0488	339
8.05	1.36	1·1335	0.0706	
9.05	1.22	1·0864	0.1177	
10.40	1.10	1·0414	0.1627	0·0156
11.50	1.01	1·0043	0.1998	
13.20	0.90	0·954	0.2499	
15.35	0.82	0·914	0.2903	
16.50	0.79	0·898	0.3065	
17.45	0.65	0·813	0.3912	
20.45	0.60	0·778	0.4259	0·0208
21.50	0.52	0·716	0.4881	
22.50	0.45	0·653	0.5489	
25.45	0.40	0·602	0.6020	
28.30	0.34	0·532	0.6726	
30.10	0.30	0·477	0.7370	0·0245
32.20	0.20	0·301	0.9031	
35.25	0.19	0·279	0.9253	
36.10	0.14	0·146	1.0620	
37.20	0.17	~~0·176~~ 0·230	0.9737	
38.45	0.15	0·176	1.0280	
58.50	0.01		2.2041	

$$-51\cdot9 = \frac{a_0 \times 1000}{2 \times 0\cdot3550 \times 140\cdot6}$$

$$a_0 = \frac{-51\cdot9 \times 0\cdot3550 \times 140\cdot6}{1000} \quad \text{(×2)}$$

$$= 5\cdot18 \ ? \qquad 2\cdot59$$

$a_0 = 2.47$

Table XXI , fig. xxi

Experiment 13. Temperature 25°C.

Initial [pure(-)-1-phenylethyl chloride] = 0.3380M

Stannic chloride = 0.0704M

Styrene = 0.413M

$a_t - a_\alpha = -1.53$

k_1 (from graph) = 0.06576

t_2	$(a_{t_2} - a_\alpha)$		$\log \frac{a_{t_1} - a_\alpha}{a_{t_2} - a_\alpha}$
8.45	1.18	1.0719	0.1128
9.35	1.12	1.0492	0.1355
11.15	0.94	0.973	0.2018
13.05	0.80	0.903	0.2762
14.35	0.79	0.898	0.2871
15.45	0.71	0.851	0.3334
17.25	0.64	0.806	0.3785
20.30	0.55	0.740	0.4443
22.35	0.52	0.716	0.4687
23.35	0.46	0.653	0.5219
25.45	0.39	0.591	0.5936
27.55	0.34	0.532	0.6532
29.40	0.32	0.505	0.6796
30.15	0.28	0.447	0.7375
34.10	0.26	0.415	0.7697
36.40	0.20	0.301	0.8837
39.40	0.19	0.279	0.9059
45.30	0.15	0.176	1.0086
62.10	0.09	-0.046	1.2305
66.05	0.09		1.2305

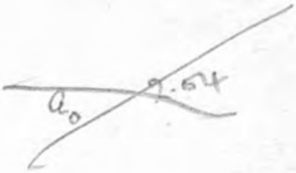


Table $\overline{\text{XXII}}$, fig. xxiv

Expt. No. 15. Temperature 25°C.

Initial pure (-)1-phenylethyl chloride = 0.1226M.

Stannic chloride = 0.0778M.

$a_{t_1} - a_{\infty} = -1.06$ k_3 (from graph) = 0.0837

t_2	$(a_{t_2} - a_{\infty})$	$\log \frac{(a_{t_1} - a_{\infty})}{(a_{t_2} - a_{\infty})}$	$\frac{1}{(a_{t_2} - a_{\infty})^2}$
7.30	1.02	0.0167	0.96
8.20	1.04	0.0083	0.925
11.10	1.00	0.0253	0.00
12.00	0.95	0.0476	1.11
14.30	0.85	0.0959	1.382
16.30	0.82	0.1115	1.488
18.25	0.77	0.1388	1.805
22.20	0.74	0.1561	1.825
26.35	0.70	0.1702	2.11
29.30	0.64	0.2191	2.44
33.10	0.61	0.2400	2.68
35.50	0.57	0.2694	3.08
50.30	0.52	0.3093	3.70
60.50	0.46	0.3625	4.72
67.40	0.41	0.4125	5.94
76.20	0.43	0.3918	5.40
83.50	0.39	0.4342	6.57
91.15	0.35	0.4812	8.15
97.30	0.35	0.4812	8.15
108.20	0.38	0.4455	8.93
177.30	0.30	0.5482	11.11
180.00	0.29	0.5589	16.0
182.00	0.26	0.6103	14.8
183.00	0.26	0.6103	14.8
221.45	0.22		20.6
222.45	0.22		20.6

Table XXVI

Experiment No.	Initial (C_8H_8) M.	Initial ($SnCl_4$) M.	k_3, min.$^{-1}$	n.
1	1.71	Not known	0.021	22
14	1.73	0.1391	0.050	23
15	1.675	0.1462	0.036	-
19	1.710	0.0717	0.0208	-
21	1.724	0.0515	0.0213	23
39	1.83	0.0347	0.0088	-
44	1.71	0.0172	0.0074	-
45	1.69	0.0712	0.015	

Third Order Reactions in carbon tetrachloride.

Temp. 25°C.

Table XXVII

Experiment No.	Initial (C_8H_8) M.	Initial ($SnCl_4$) M.	k_3, min.$^{-1}$	n.
7	1.67	0.0443	0.0352	-
22	1.76	0.0919	0.0143	33
24	1.76	0.1042	0.036	39
29	0.883	0.052	0.0345	22
25	1.64	0.0881	0.059	31

Third Order Reactions in chloroform.

Temp. 25°C.

Table XXVIIIa

Experiment No.	Initial (C_8H_8) M.	Initial $(SnCl_4)$ M.	k_1, min.$^{-1}$	n.
9	1.78	0.0516	0.00576	17
10	1.717	0.1559	0.00968	-
11	1.772	0.152	0.009212	-
12	0.8680	0.0152	0.00541	-
13	0.8607	0.0950	0.00925	-
17	1.715	0.1524	0.00115	15
20	1.727	0.1327	0.00276	18

First Order Reactions in carbon tetrachloride.

Temp. 25°C.

Table XXVIIIb

Experiment No.	Initial (C_8H_8) M.	Initial $(SnCl_4)$ M.	k_1, min.$^{-1}$	n.
23	1.702	0.1221	0.0061	29
26	1.714	0.0539	0.00656	-
27	1.729	0.0478	0.00426	-

First Order Reactions in chloroform.

Temp. 25°C.

Table XXIX.

Expt. No.	Wt. $(C_8H_8)_n$ taken (g.)	Volume of solution (ml.)	c	Flow time solvent (sec.)	Flow time solution (sec.)	n.
4	0.3463	100	.004048	965.6	999.5	34
1	0.2107	50	.004048	965.6	995.0	22
14	0.3581	100	.00344	965.6	989.5	23
16	0.2210	50	·00425	965.6	992.5	18
23	0.3407	100	·00328	965.6	995.2	29
22	0.6512	100	.00626	974	1040	36
22	0.9968	100	.0104	980.5	1082.5	35
21	0.1902	100	.001829	976.7	992.5	27
21	0.3055	100	.002938	974	993.9	20
21	0.6005	100	.005774	976.7	1017.6	21
17	0.3844	100	.00368	965.6	986.3	15
24	0.3428	100	·00333	965.6	1002.8	39
9	0.3458	100	.003322	965.6	985.6	17
25	Concn. from titre,		.0340	612.5	632.8	31
29	" "	" ,	.0290	610.0	622.6	22

Table XXX. (Fig. xv).

Experiment No. 11.

k_1 (from graph) 0.009212.

Initial Styrene 1.772 M.

Stannic chloride 0.152 M.

Temperature 25°C.

Solvent: carbon tetrachloride

Time (min.)	Styrene (M)	log(a-x).
8.5	1.772	0.2484
18.5	1.772	0.2484
90.5	1.772	0.2484
118.4	1.649	0.2173
126.55	1.570	0.1969
156.85	1.190	0.0752
169.55	1.057	0.0241
241.65	0.545	-0.2636
244.55	0.4789	-0.3197
350.0	0.3468	-0.4599

Table XXXI (Fig. xv).

Experiment No. 13.

k_1 (from graph) 0.00925.

Initial Styrene 0.8607

Stannic chloride 0.0950

Temperature 25°C.

Solvent: carbon tetrachloride.

Time (min.)	Styrene (M)	log(a-x).
16.5	0.8607	-0.0651
78.35	0.8607	-0.0651
202.45	0.8487	-0.0712
235.6	0.8368	-0.0774
243.65	0.8294	-0.0812
253.95	0.8151	-0.0888
331.55	0.4568	-0.3402
343.75	0.4039	-0.3937
360.3	0.3679	-0.4343
369.05	0.3390	-0.4698
455.05	0.2572	-0.5896
498.51	0.2284	-0.6413

Table XXXII (Fig. xvi).

Experiment No. 19.

k_3 (from graph) = 0.0208

Initial Styrene = 1.710 M.

Stannic Chloride = 0.0717 M.

Temperature = 25°C.

Solvent: carbon tetrachloride.

Time (min.)	Styrene (M)	$\frac{1}{(a-x)^2}$
17.90	1.710	0.342
33.90	1.710	0.342
94.90	0.8128	1.532
103.65	0.7671	1.730
113.25	0.7286	1.88
120.25	0.7070	2.00
131.00	0.6735	2.21
143.20	0.6397	2.45
156.95	0.6108	2.68
165.80	0.6084	2.71
186.60	0.5652	3.13
204.40	0.5459	3.35
239.45	0.4830	4.29
368.30	0.3728	7.24
384.35	0.3619	7.67

Table XXXIII. (Fig. xvi)

Experiment No. 21.

k_3 (from graph) = 0.0213

Initial Styrene = 1·724

Stannic chloride = 0·0515

Temperature = 25°C.

Solvent: carbon tetrachloride.

Time (min.)	Styrene (M)	$\frac{1}{(a-x)^2}$
16.25	1.724	0.338
24.70	1.724	0.338
44.15	1.460	0.469
51.30	1.208	0.685
60.20	1.13	0.782
67.40	1.019	0.9650
74.80	0.948	1.113
83.00	0.878	1.329
89.95	0.842	1.427
97.85	0.811	1.45
174.90	0.555	3.25
182.85	0.532	3.53
240.05	0.464	4.65
267.95	0.438	5.21

Table XXXIV (Fig. xix)

k_1 (from graph) = 0.0143.

Initial styrene = 0.392 M.

Stannic chloride = 0.03072 M.

Temperature = 25°C.

Time (min.)	Styrene (M.)	log (a-x)
2.0	0.391	-.4078
4.0	0.362	-.4413
9.0	0.3063	-.5139
11.66	0.286	-.5436
24.5	0.2581	-.5882
37.25	0.225	-.6478
44.17	0.2045	-.6893
100.17	0.0625	-1.2041
121.5	0.0565	-1.2480
131.17	0.0459	-1.3382
180.5	0.0284	-1.5467
194.75	0.0224	-1.6498

The molecular weight of the solid product was determined viscosimetrically in carbon tetrachloride solution ($n = 26$):–

Flow-time solvent = 148.8 secs.
Flow-time solution = 156.0 secs.
Concentration of solution = 0.05635 g. mols. styrene/litre.
Hence,

$n = 26.$

FIGURES.

i. Distillation of Stannic Chloride 1.

ii. Distillation of Stannic Bromide.

iii. Apparatus for the addition of hydrogen chloride (normal conditions).

iv. Apparatus for the addition of hydrogen bromide (normal conditions).

v. Distillation of Stannic chloride 2.

vi. Apparatus for hydrogen halide production (approximately anhydrous conditions).

vii. Apparatus for dry nitrogen supply (approximately anhydrous conditions).

viii. Reaction vessel for addition reactions (approximately anhydrous conditions).

viiia. Stopper holder.

ix. Pycnometer.

x. Density and composition of mixtures of 1-phenylethyl halides.

xi. Polarimeter tube. xia. Syphon tube.

xiia. & b. Halogen exchange for 1-phenylethyl bromide and stannic chloride.

xiii~~a~~b Halogen exchange for 1-phenylethyl bromide and stannic chloride.

xiii~~b~~a Halogen exchange for 1-phenylethyl chloride and stannic bromide.

xiv. Apparatus for the estimation of bromine.

xv. Polymerisation experiments 11, 13.

xvi. Polymerisation experiments 19, 21.

xvii. Catalyst concentration and k_3 for polymerisation experiments in carbon tetrachloride.

xviii. Interaction of styrene and 1-phenylethyl halide, experiments 84, 85, 86.

xix. Polymerisation of styrene in nitrobenzene.

xx. Racemisation experiments 5, 6.

xxi. Racemisation experiments 12, 13.

xxii. Racemisation experiment 7.

xxiiia. & b. Racemisation experiment 1.

xxiv. Racemisation experiment 15.

xxva. & b. Interaction of styrene and 1-phenylethyl chloride, experiment 84.

xxvi. Polymerisation experiments 4, 5, 28.

xxvii. Polymerisation experiment 8.

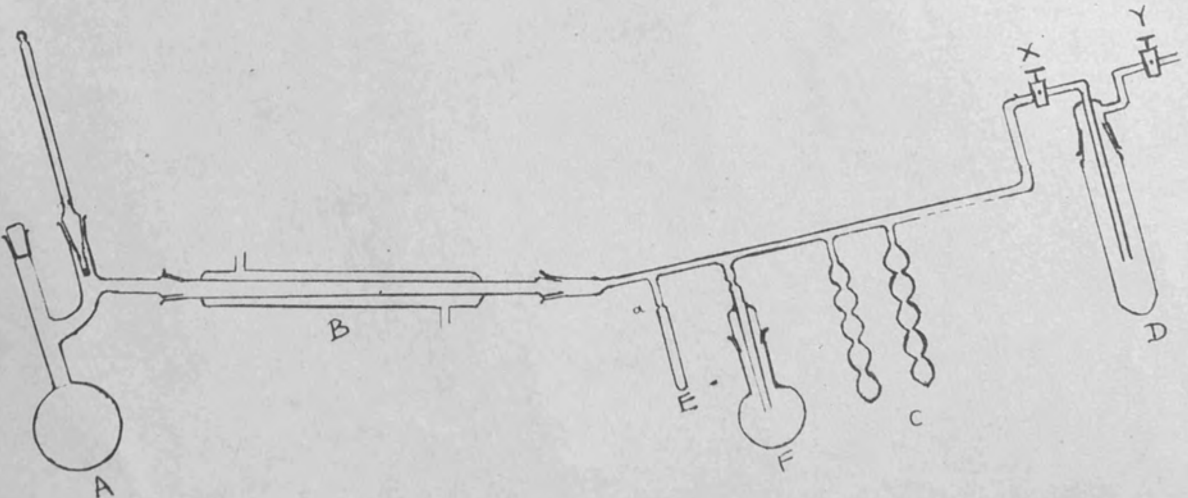
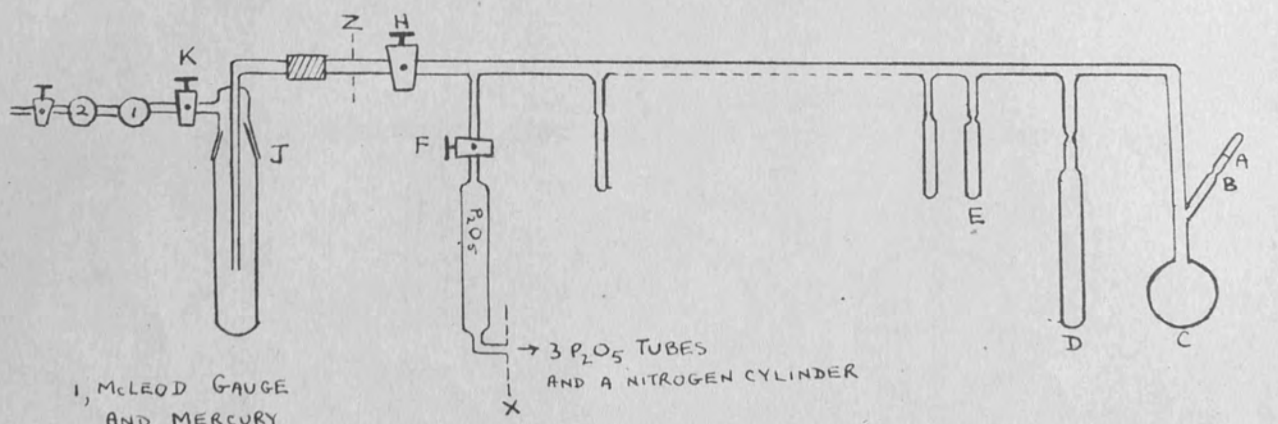


Fig i



1, McLEOD GAUGE AND MERCURY DIFFUSION PUMP

2, ROTARY PUMP

Fig. ii.

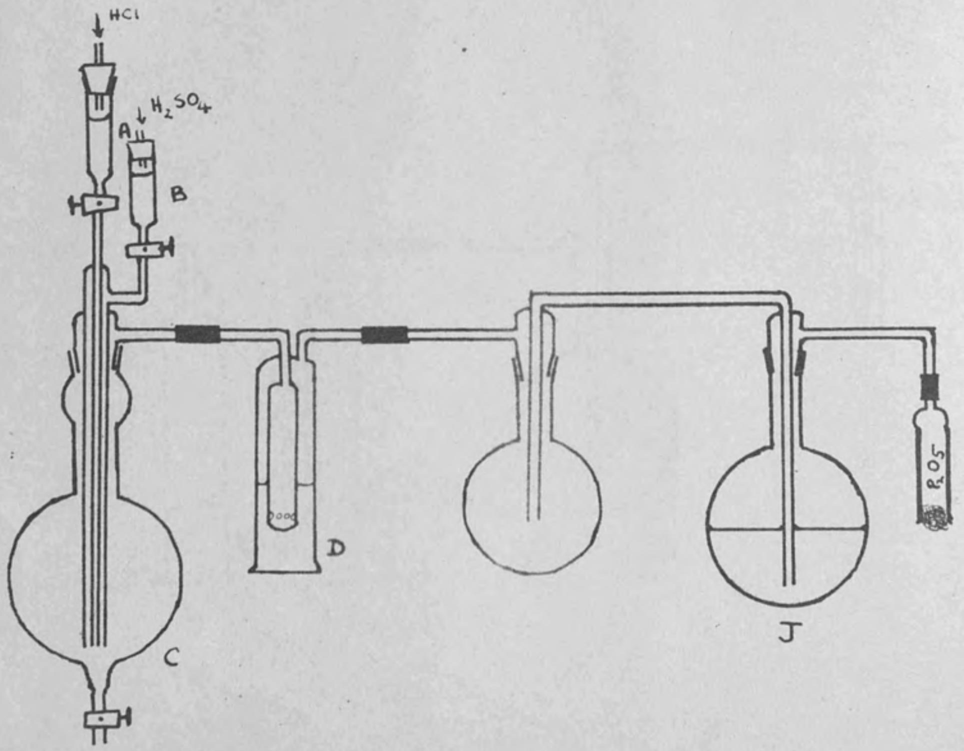


Fig iii

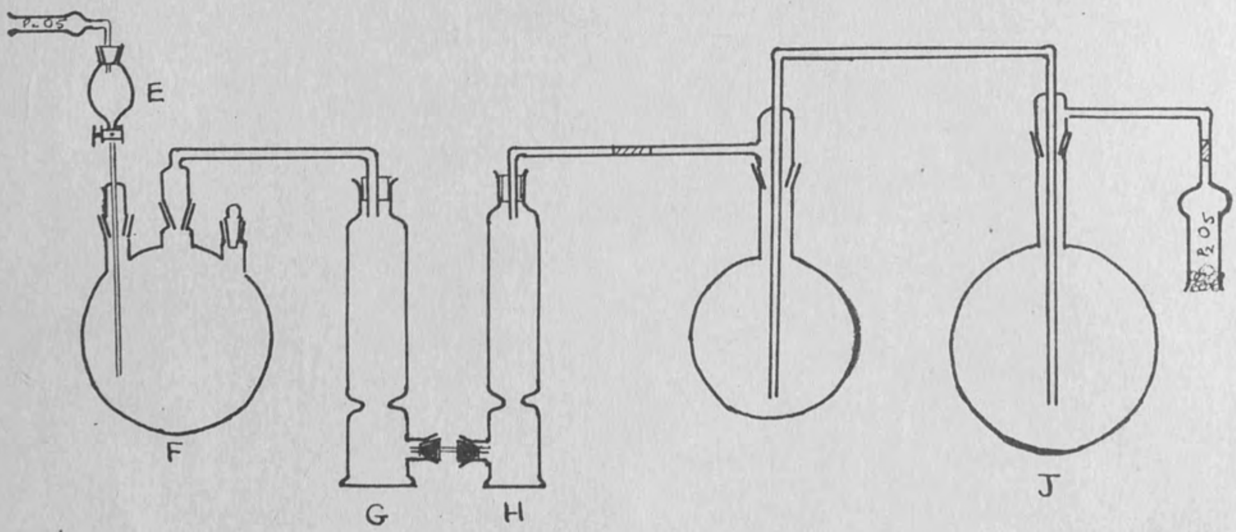


Fig. iv.

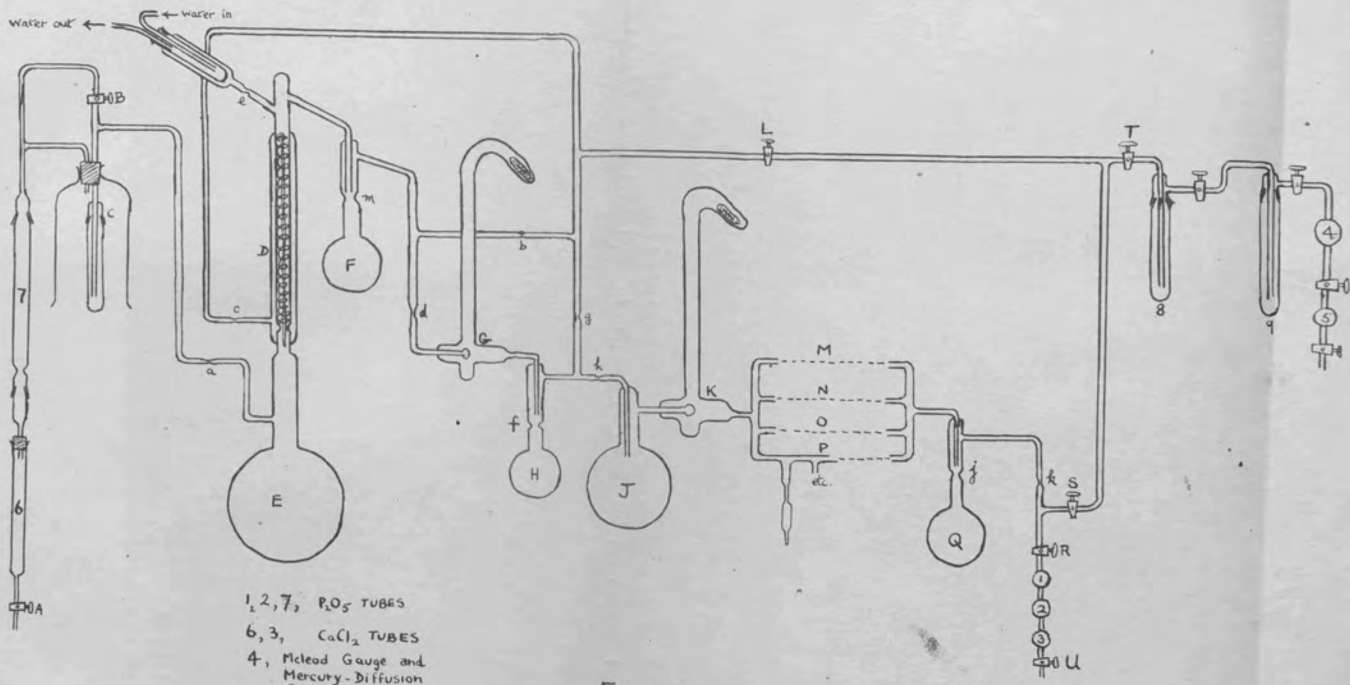

Water out
Water in
B
C
7
6
A
e
D
m
F
b
c
a
E
d
G
g
h
f
H
J
K
L
T
M
N
O
P
etc.
j
Q
k
S
R
1
2
3
U
8
9
4
5
1, 2, 7, P_2O_5 TUBES
6, 3, $CaCl_2$ TUBES
4, Mcleod Gauge and Mercury-Diffusion Pump
5, Rotary Pump
8, 9, Liquid Air Traps.

Fig. V.

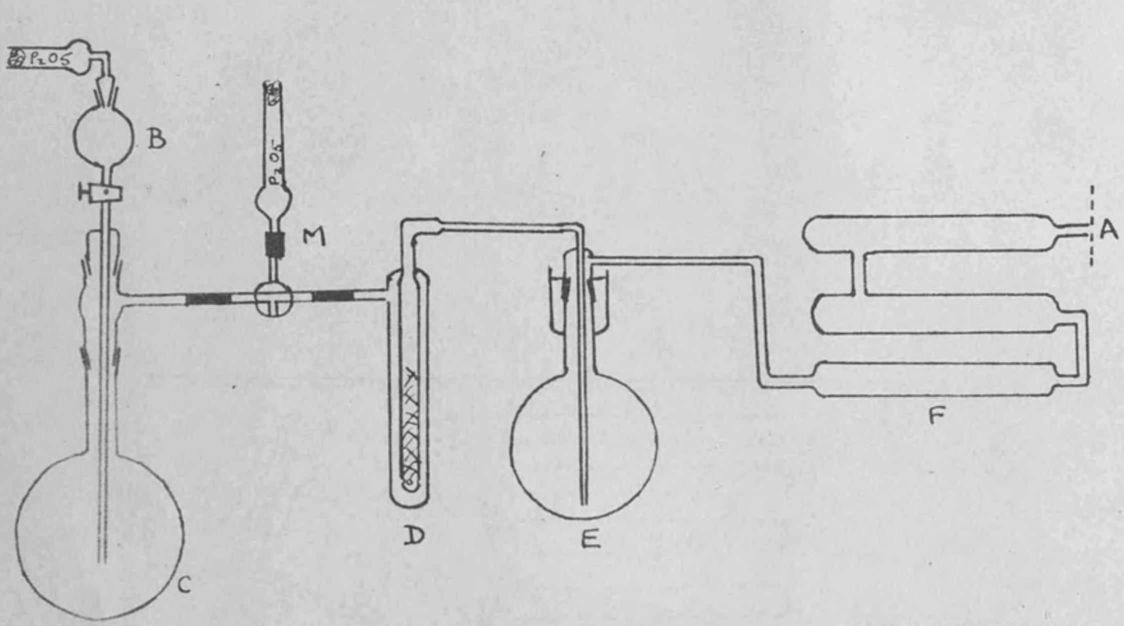


Fig. vi

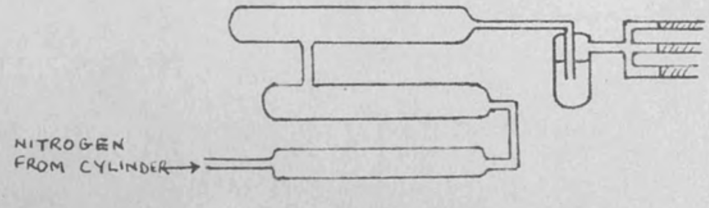


Fig. vii.

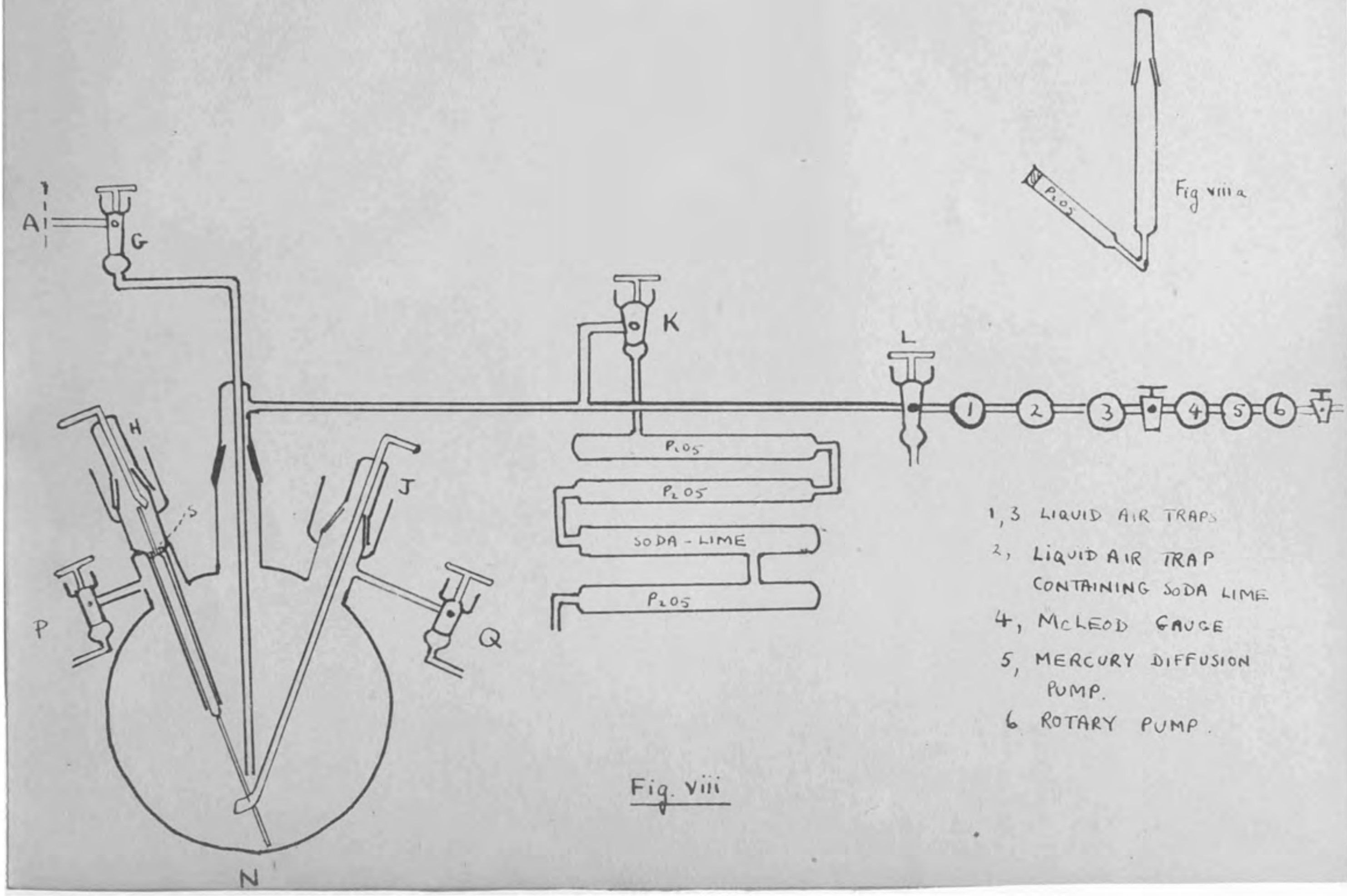


Fig viii a

Fig. viii

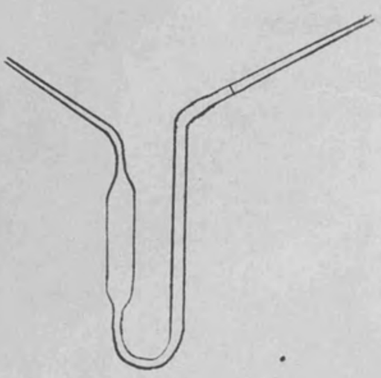


Fig.ix.

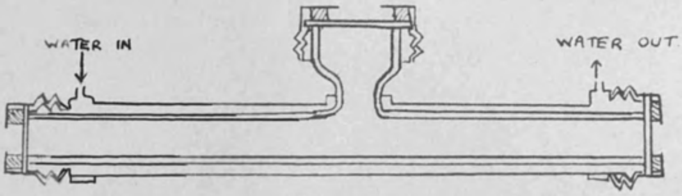


Fig. xi

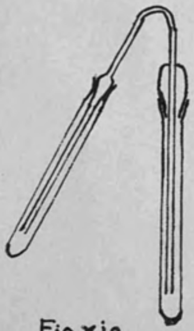


Fig.xia

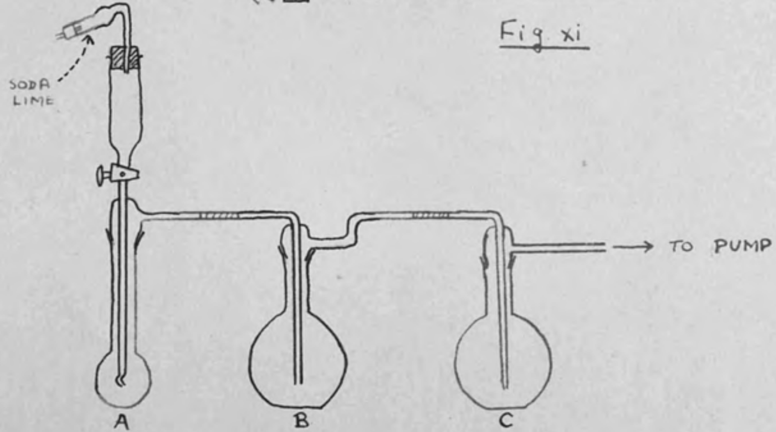


Fig.xiv.

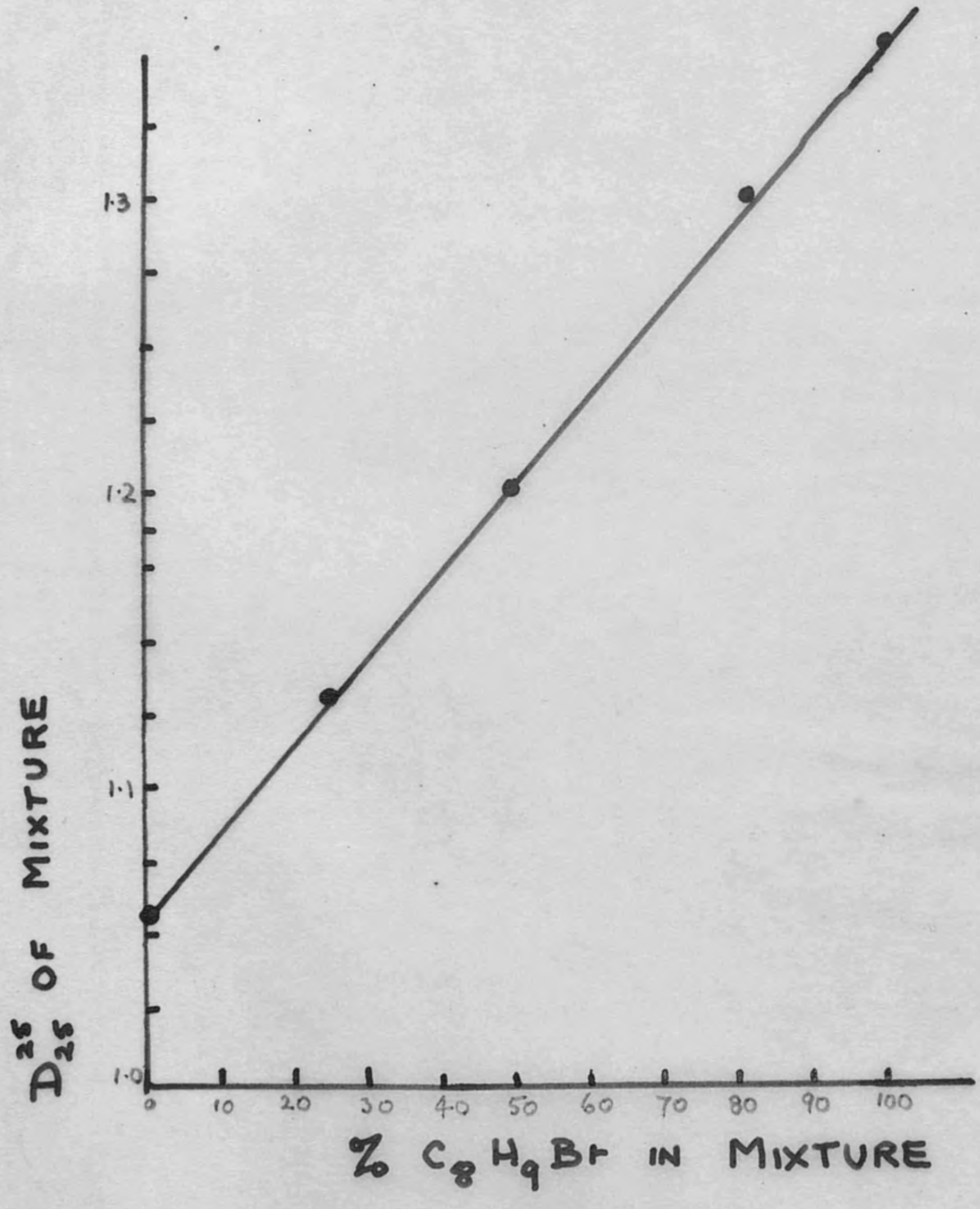

D^{25}_{25} OF MIXTURE
1·0
1·1
1·2
1·3
0
10
20
30
40
50
60
70
80
90
100
% C_8H_9Br IN MIXTURE

Fig. X.

SYSTEM: C_8H_9Br, HBr, $SnCl_4$ IN CCl_4

ROUGH ESTIMATE FROM GRAPH
OF HALOGEN EXCHANGE AFTER 4HRS:-

$[SnCl_4]$ (M)	% C_8H_9Br (calc)	% C_8H_9Br (FOUND)
0.056	95.5	95.55 (4 hr)
0.0104	99.5	99.9 (2¾ hr)
0.0202	98.5	98.6 (3 hr)
0.035	97.5	96.4 (3¼ hr)
0.186	84.7	87.15 (4¾ hr)
0.34	72.0	

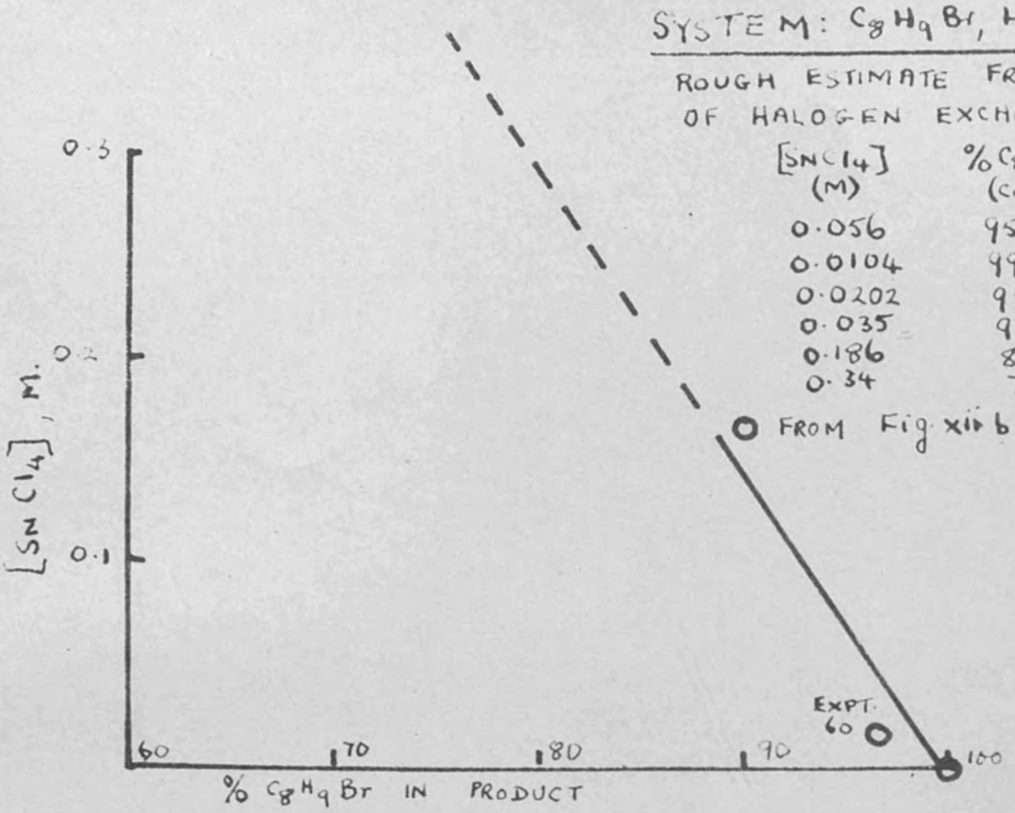
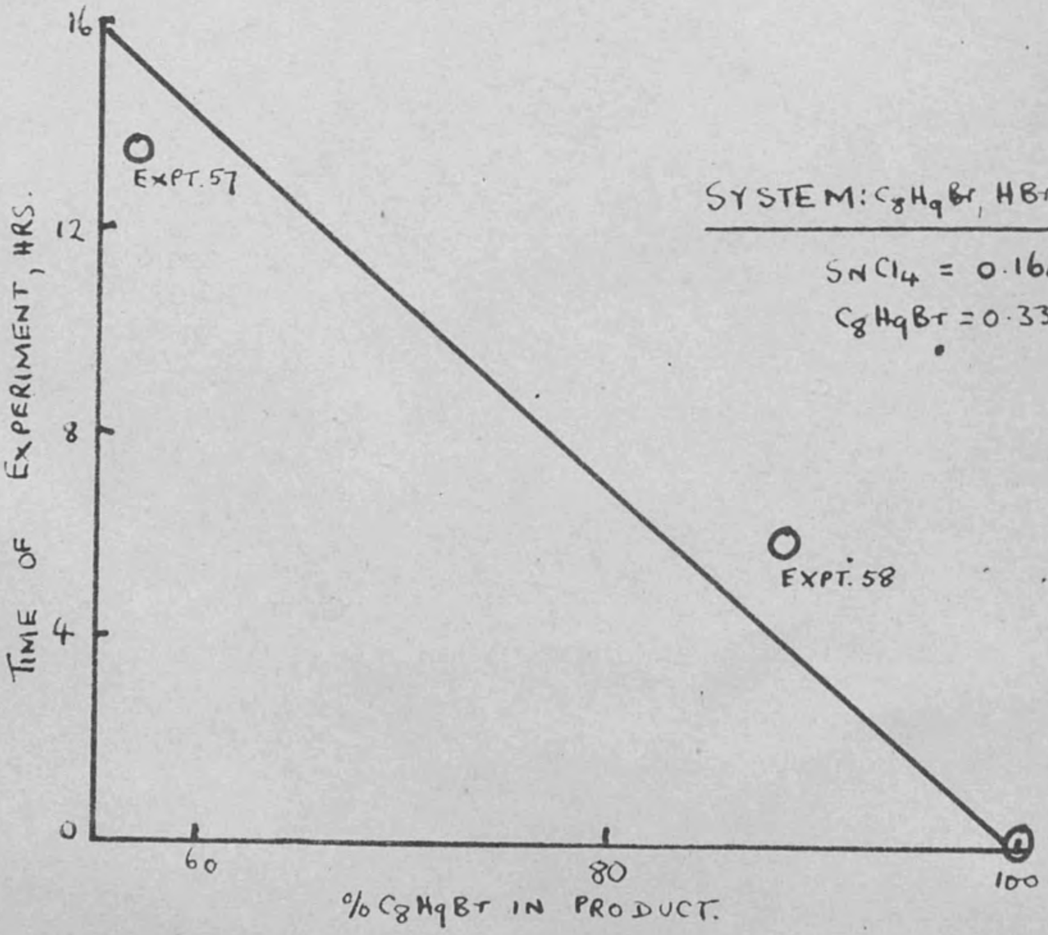


Fig. xii a



SYSTEM: C_8H_9Br, HBr, $SnCl_4$ IN CCl_4

$SnCl_4$ = 0.164 M.

C_8H_9Br = 0.33 M.

Fig. xii b.

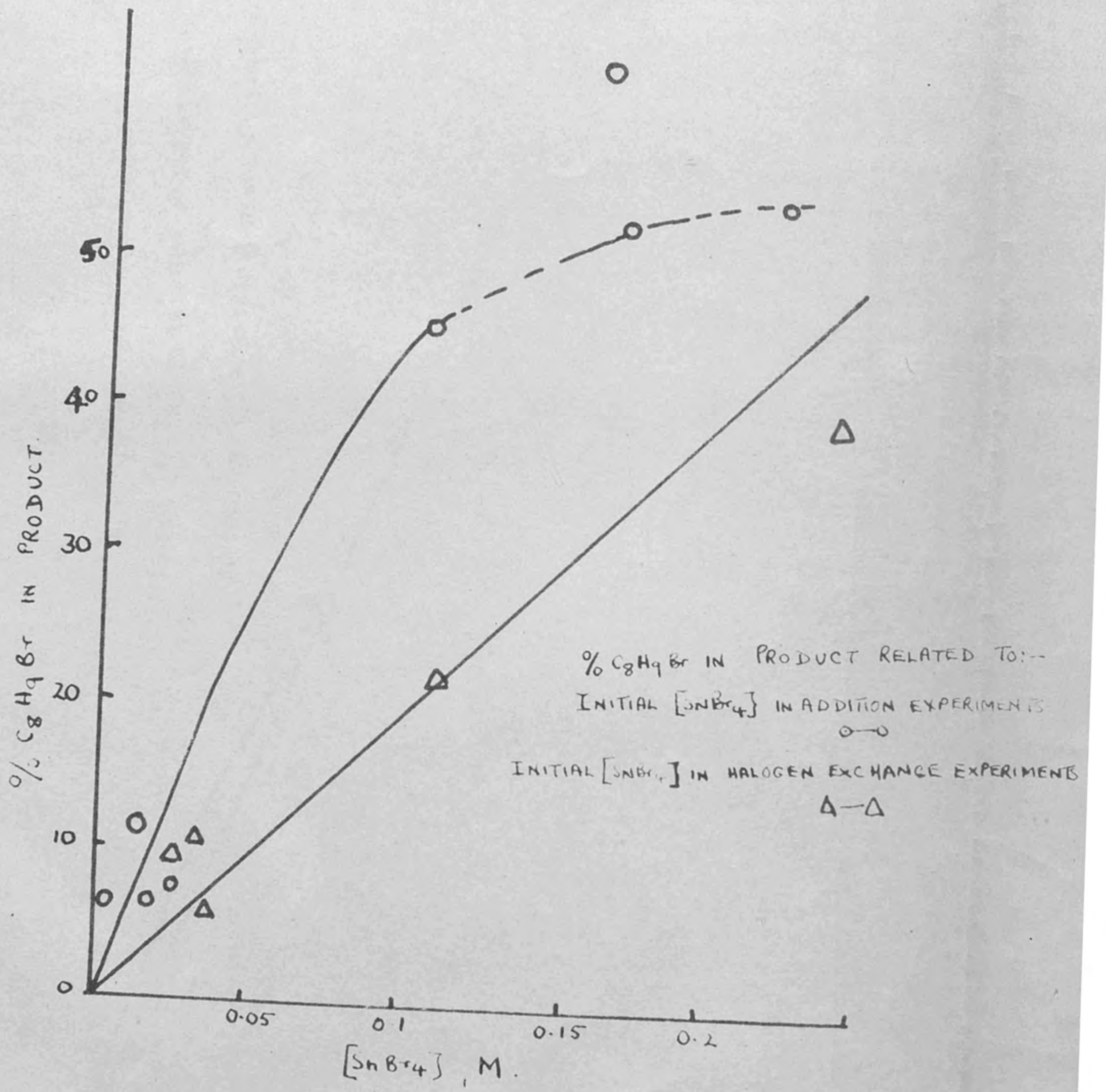
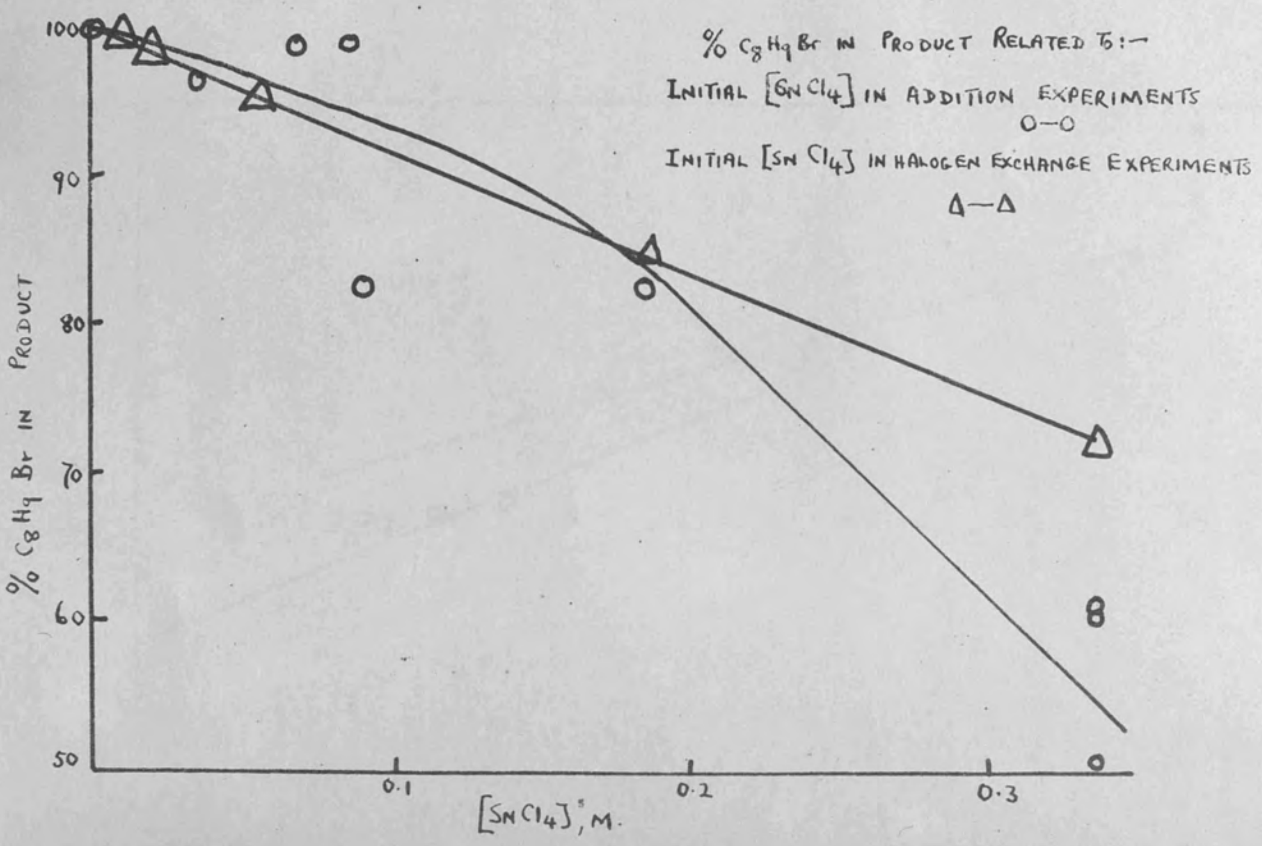

% C_8H_9Br IN PRODUCT
50
40
30
20
10
0
0.05
0.1
0.15
0.2
$[SnBr_4]$, M.
% C_8H_9Br IN PRODUCT RELATED TO:--
INITIAL $[SnBr_4]$ IN ADDITION EXPERIMENTS
o—o
INITIAL $[SnBr_4]$ IN HALOGEN EXCHANGE EXPERIMENTS
Δ—Δ

Fig xiii a

Fig. xiii b.


% C_8H_9Br in Product related to:–
Initial $[SnCl_4]$ in addition experiments O–O
Initial $[SnCl_4]$ in halogen exchange experiments Δ–Δ
100
90
80
70
60
50
% C_8H_9Br in Product
0·1
0·2
0·3
$[SnCl_4]^s$, M.

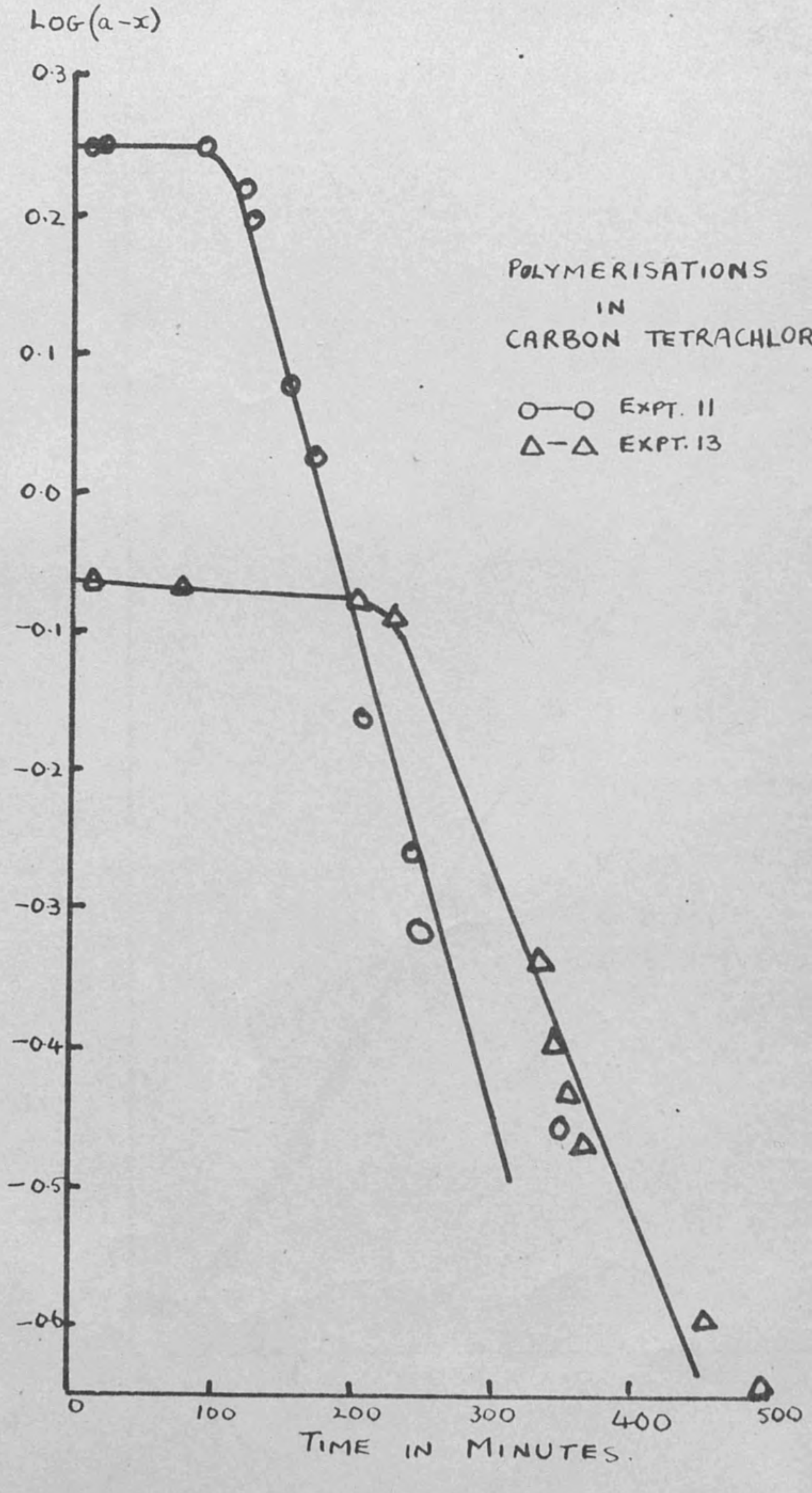

LOG(a−x)
0·3
0·2
0·1
0·0
−0·1
−0·2
−0·3
−0·4
−0·5
−0·6
0
100
200
300
400
500
TIME IN MINUTES.
POLYMERISATIONS
IN
CARBON TETRACHLORIDE
O—O EXPT. 11
Δ−Δ EXPT. 13

Fig. XV.

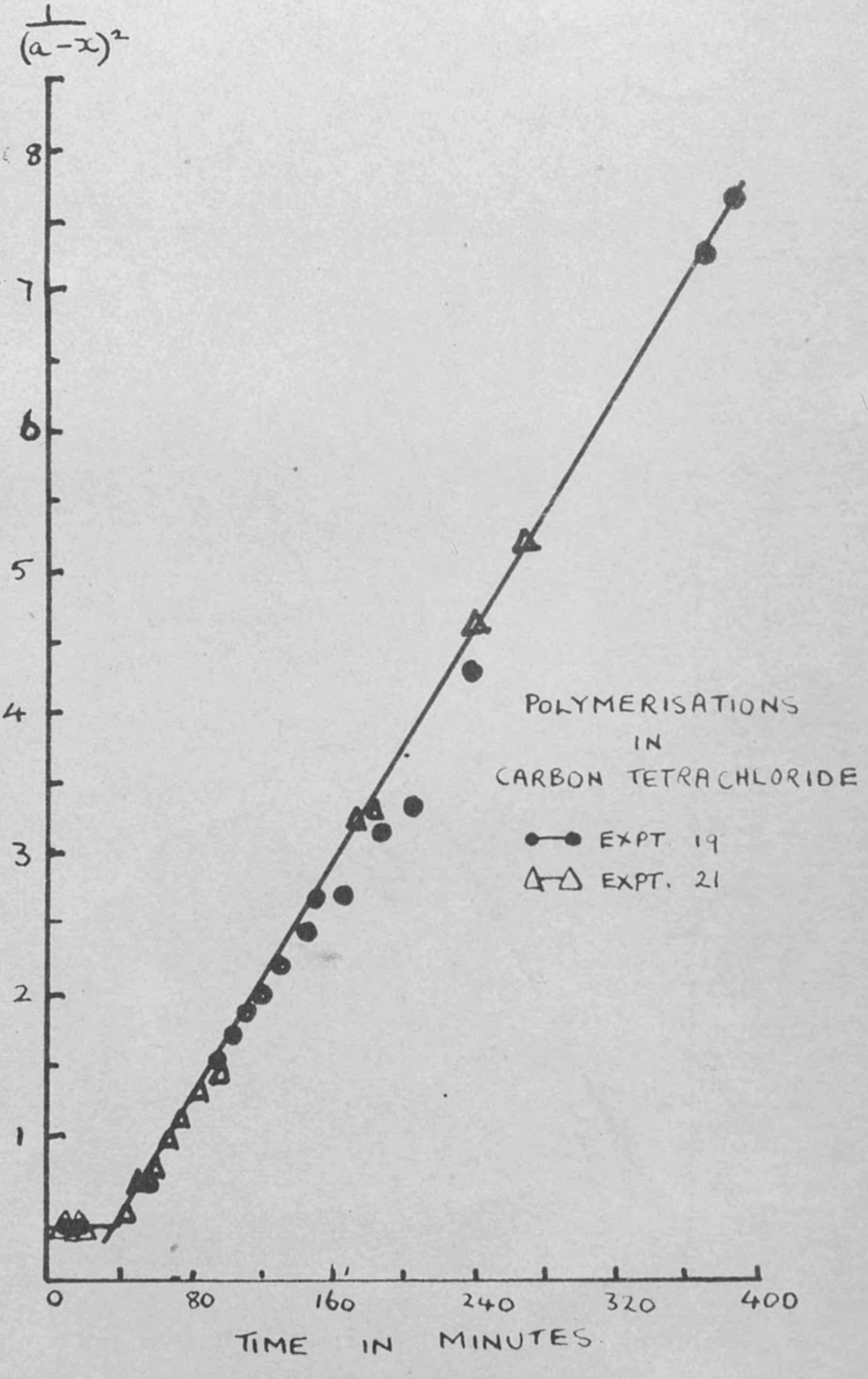

$\frac{1}{(a-x)^2}$
8
7
6
5
4
3
2
1
0
80
160
240
320
400
TIME IN MINUTES
POLYMERISATIONS IN CARBON TETRACHLORIDE
●—● EXPT. 19
△—△ EXPT. 21

Fig. XVi

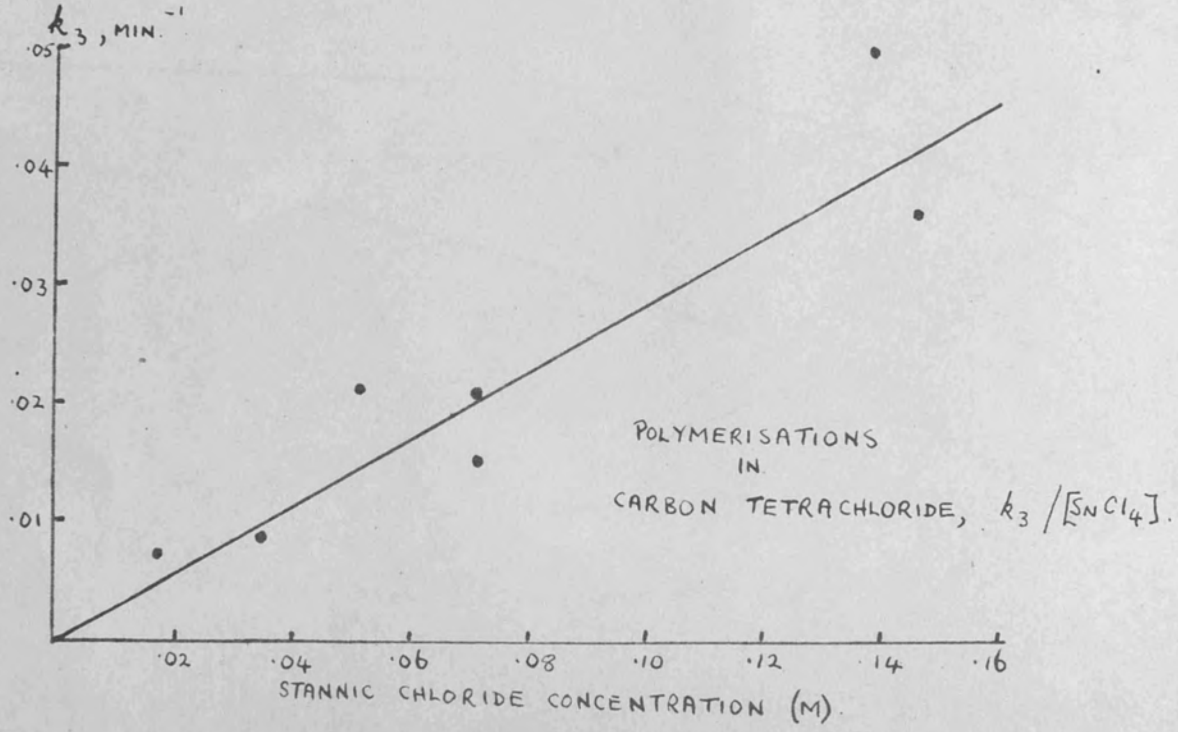
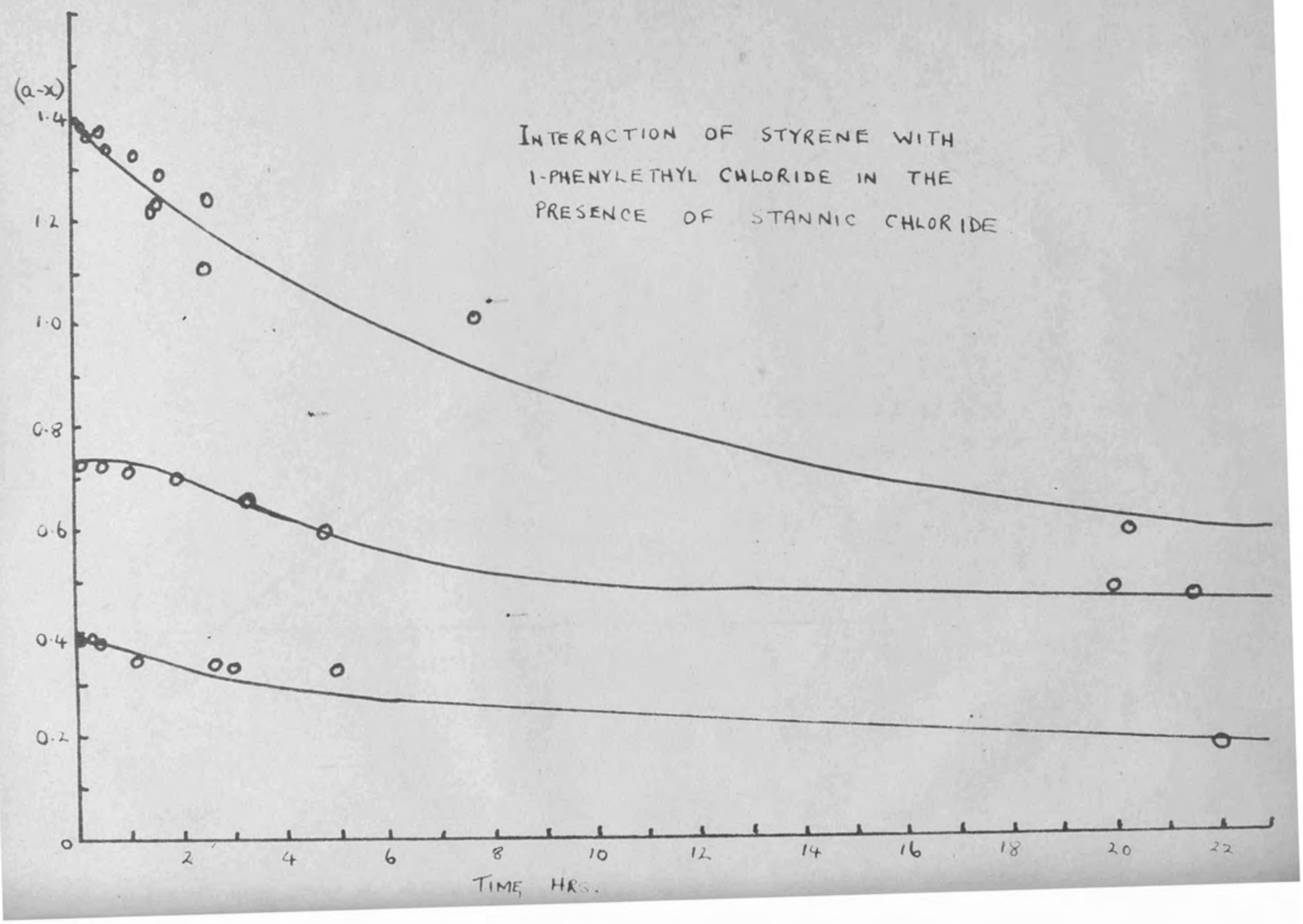

k3, MIN.⁻¹
·05
·04
·03
·02
·01
·02
·04
·06
·08
·10
·12
·14
·16
STANNIC CHLORIDE CONCENTRATION (M).
POLYMERISATIONS
IN
CARBON TETRACHLORIDE, k3/[SnCl4].

Fig. xvii


INTERACTION OF STYRENE WITH
1-PHENYLETHYL CHLORIDE IN THE
PRESENCE OF STANNIC CHLORIDE
(a-x)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
2
4
6
8
10
12
14
16
18
20
22
TIME, HRS.

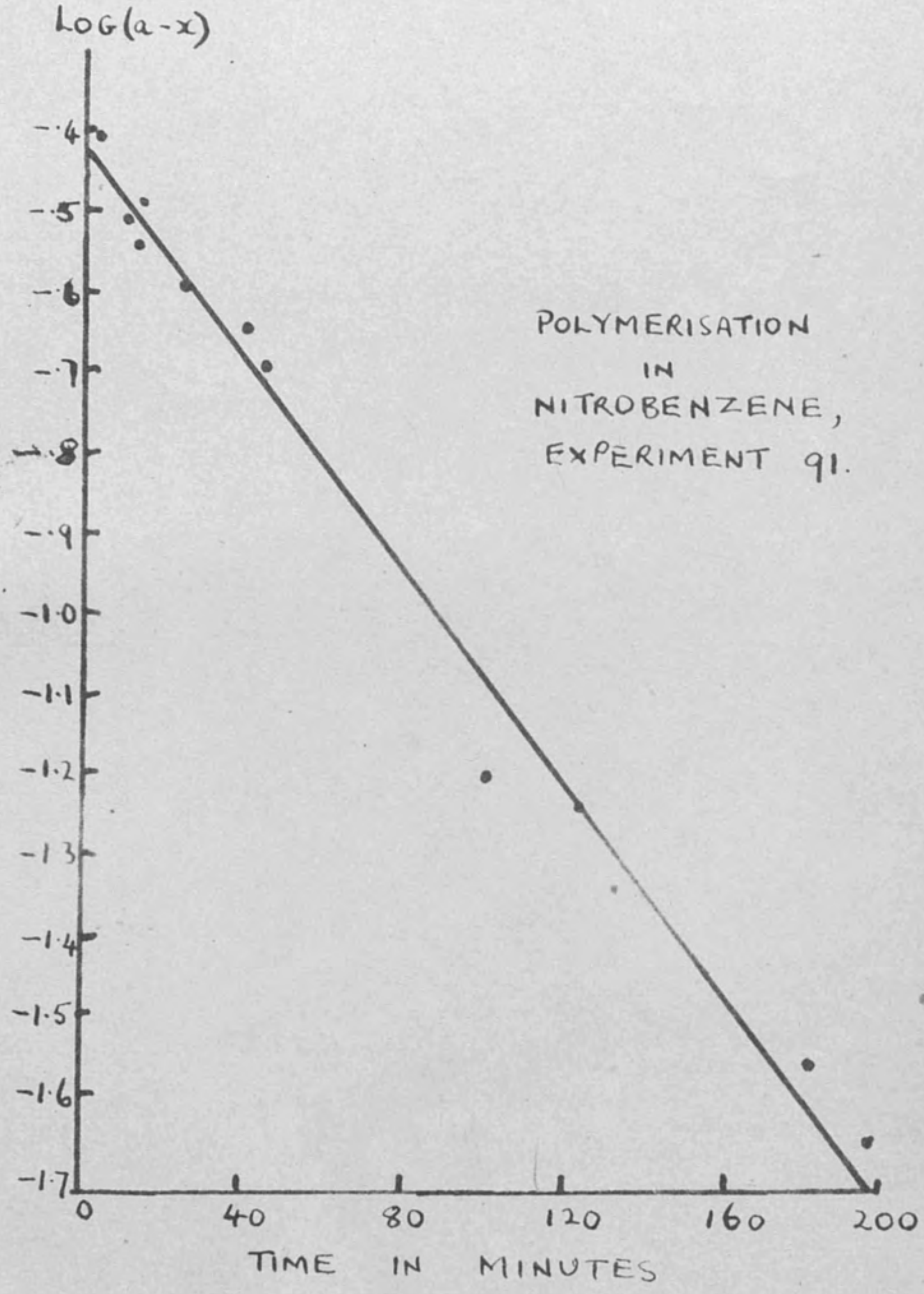

LOG(a-x)
-·4
-·5
-·6
-·7
-·8
-·9
-1·0
-1·1
-1·2
-1·3
-1·4
-1·5
-1·6
-1·7
0
40
80
120
160
200
TIME IN MINUTES
POLYMERISATION
IN
NITROBENZENE,
EXPERIMENT 91.

Fig. xix.

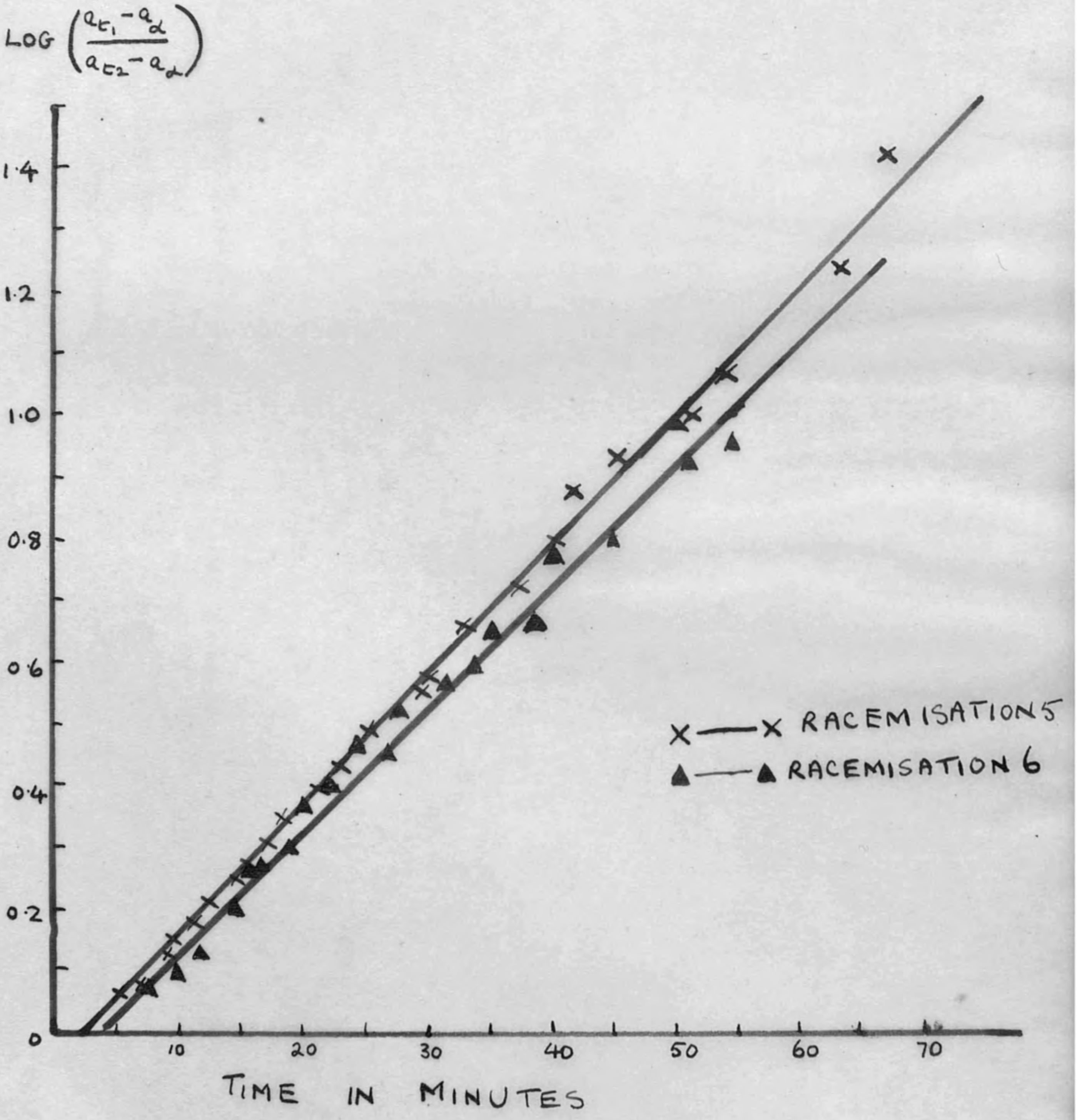

LOG $\left(\frac{a_{t_1} - a_\alpha}{a_{t_2} - a_\alpha}\right)$
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
10
20
30
40
50
60
70
TIME IN MINUTES
× —— × RACEMISATION 5
▲ —— ▲ RACEMISATION 6

Fig. XX.

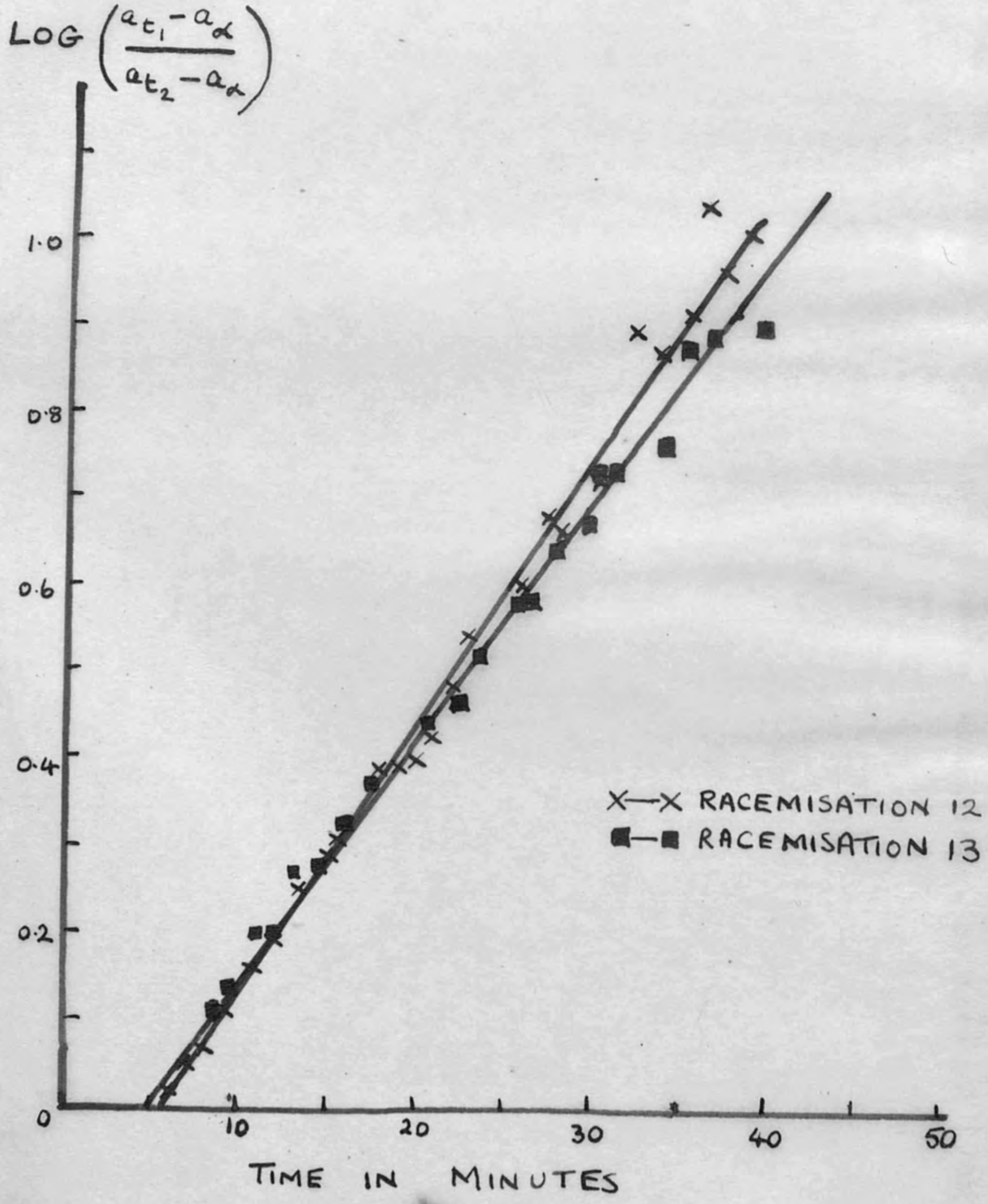

$\log\left(\frac{a_{t_1}-a_\alpha}{a_{t_2}-a_\alpha}\right)$
1.0
0.8
0.6
0.4
0.2
0
10
20
30
40
50
TIME IN MINUTES
X—X RACEMISATION 12
■—■ RACEMISATION 13

Fig xxii.

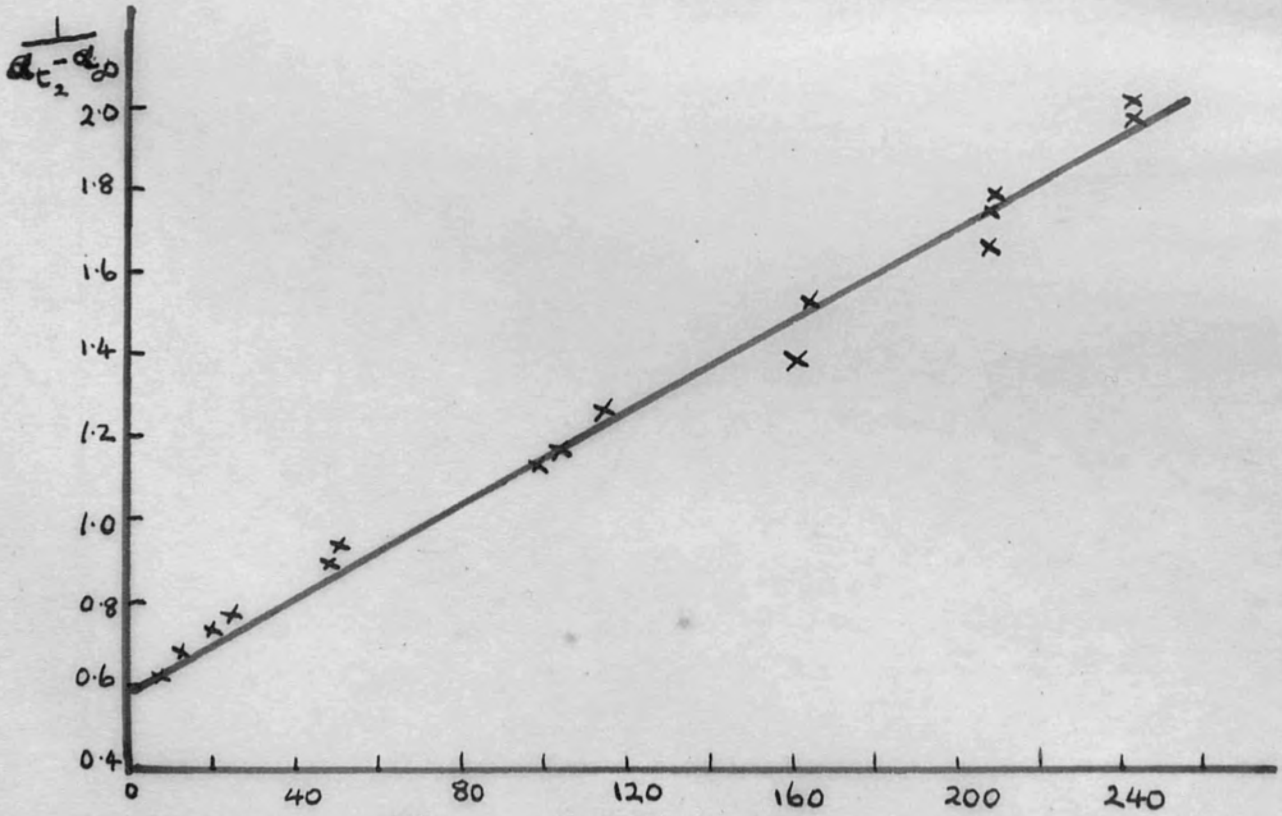

$\frac{1}{\alpha_{t_2}-\alpha_\infty}$
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0
40
80
120
160
200
240
TIME IN MINUTES.

Fig. XXII

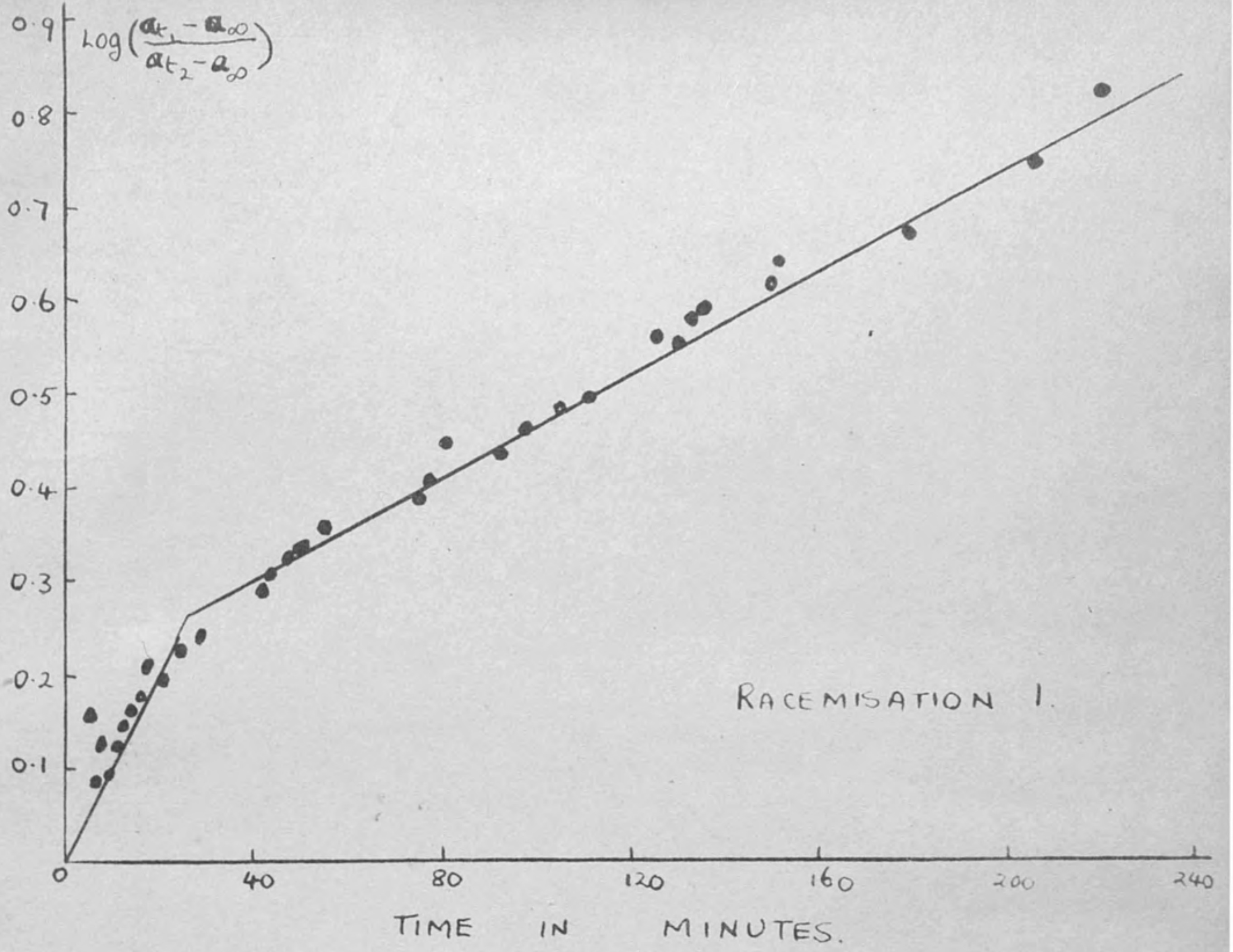


Fig. XXiiia

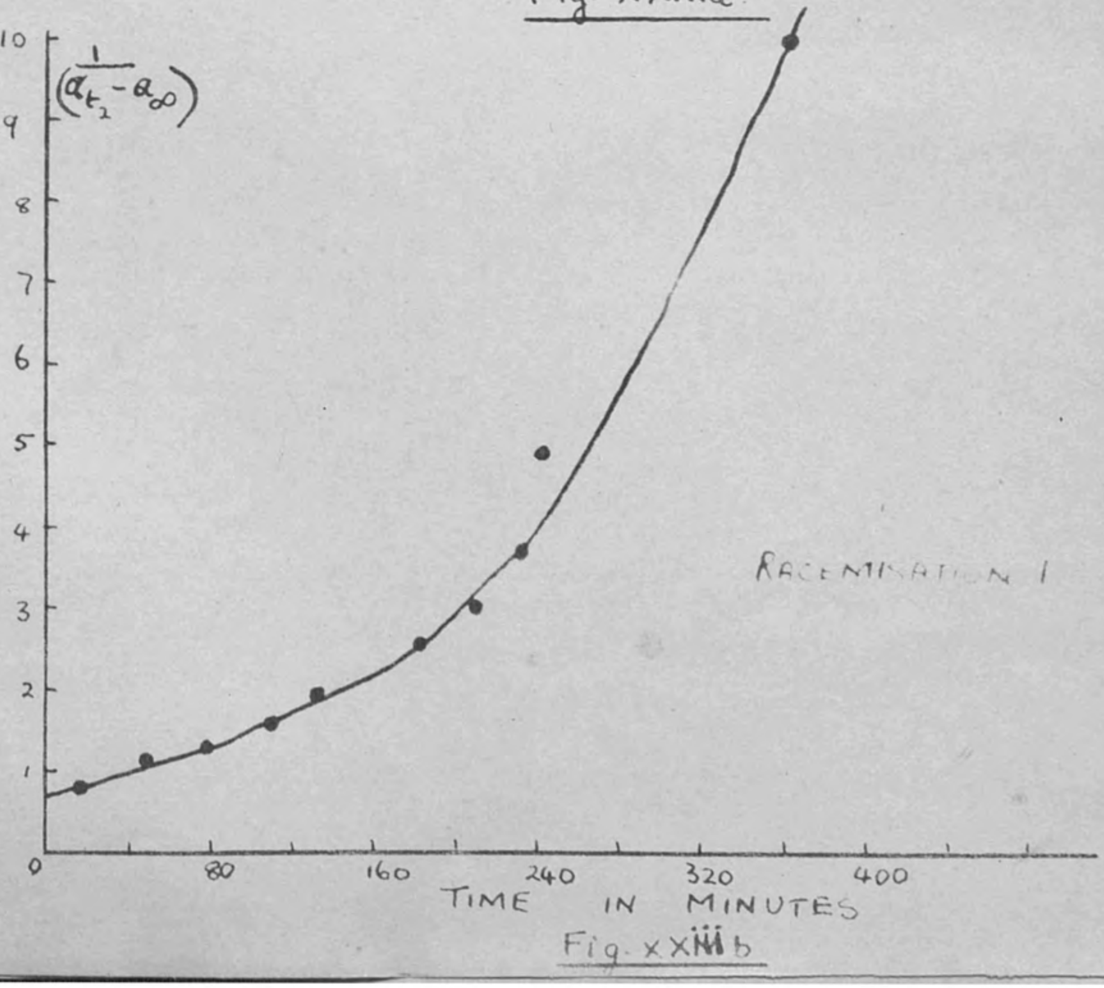


Fig. XXiiib

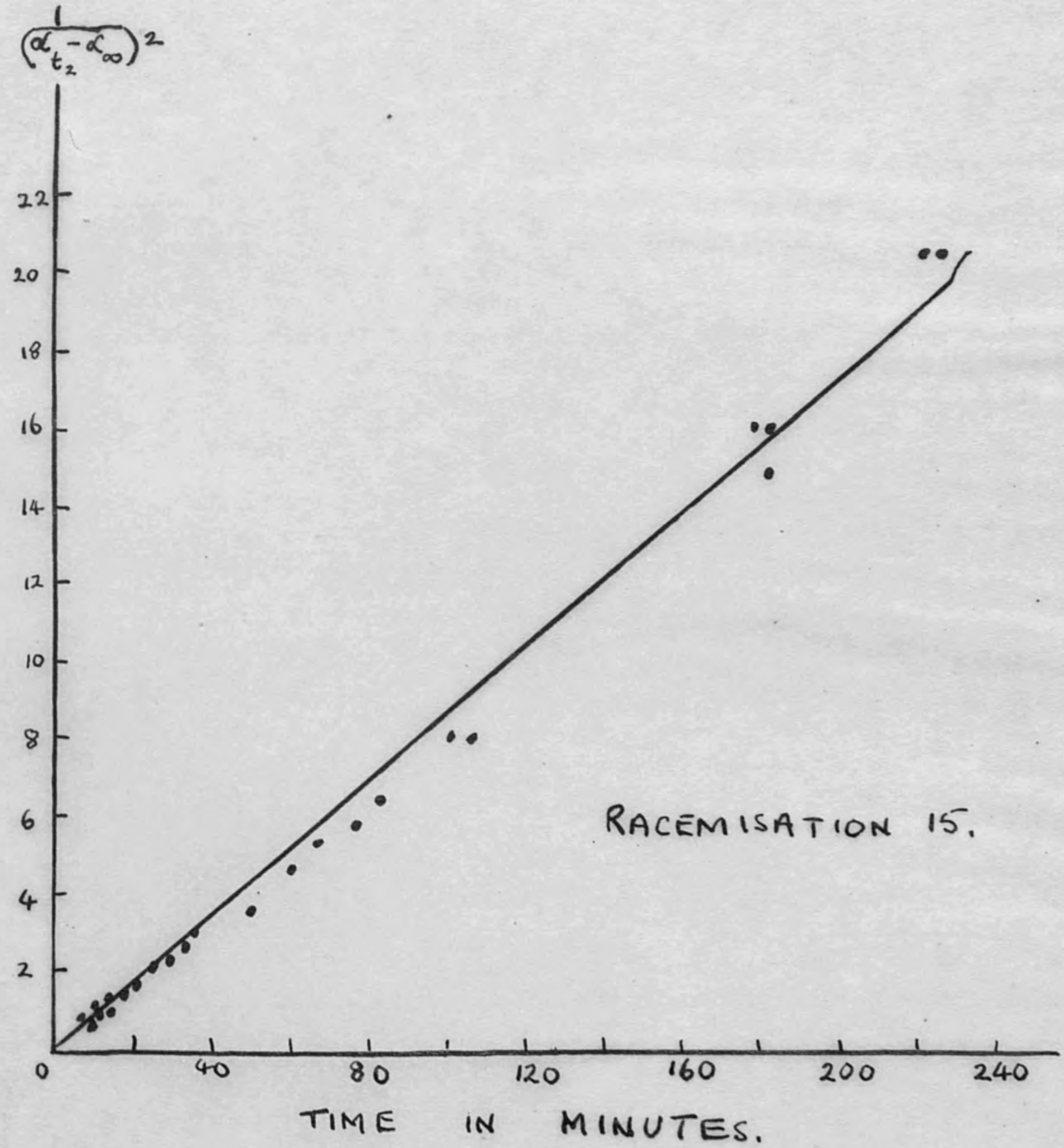
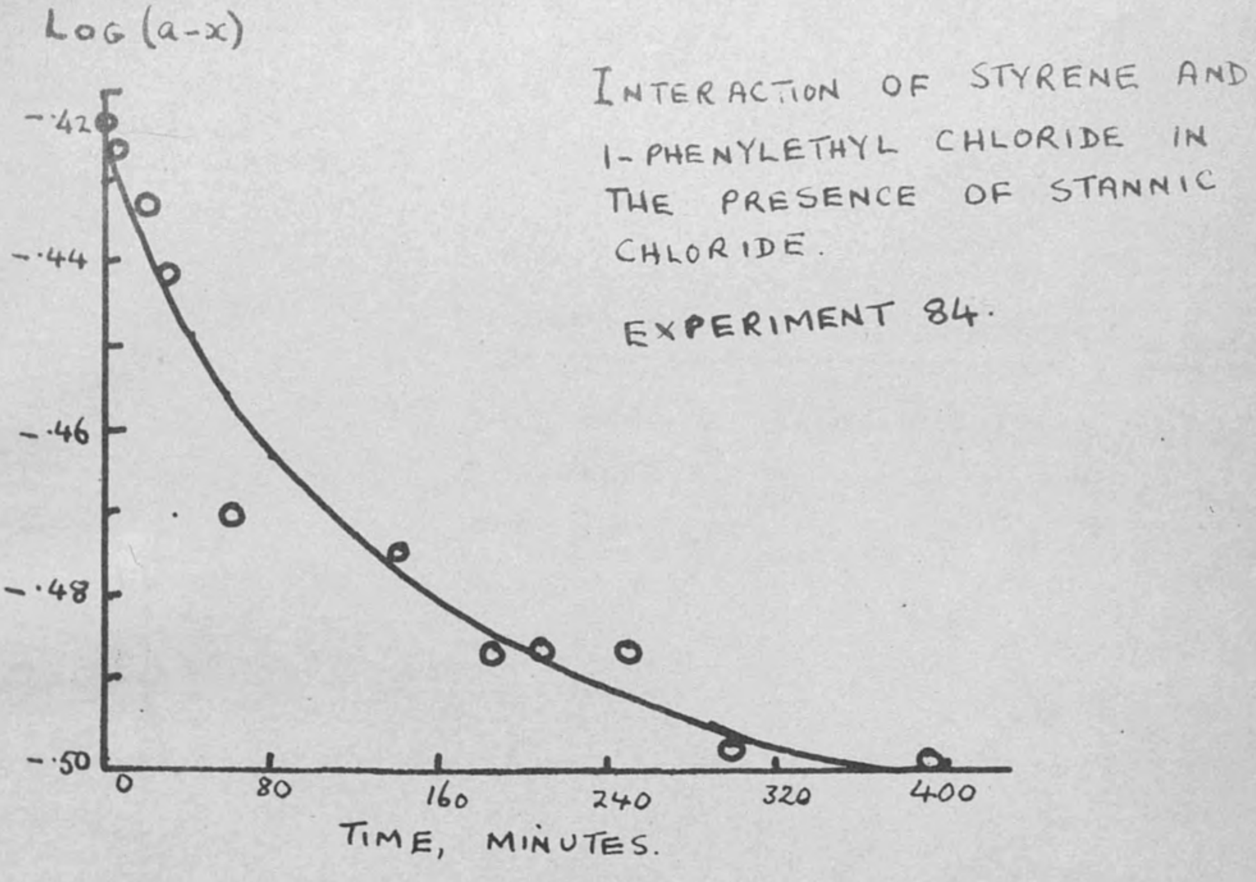

$\frac{1}{(\alpha_{t_2}-\alpha_\infty)^2}$
22
20
18
16
14
12
10
8
6
4
2
0
40
80
120
160
200
240
TIME IN MINUTES.
RACEMISATION 15.

Fig. XXIV.


INTERACTION OF STYRENE AND 1-PHENYLETHYL CHLORIDE IN THE PRESENCE OF STANNIC CHLORIDE.

EXPERIMENT 84.

Fig. XXV a.

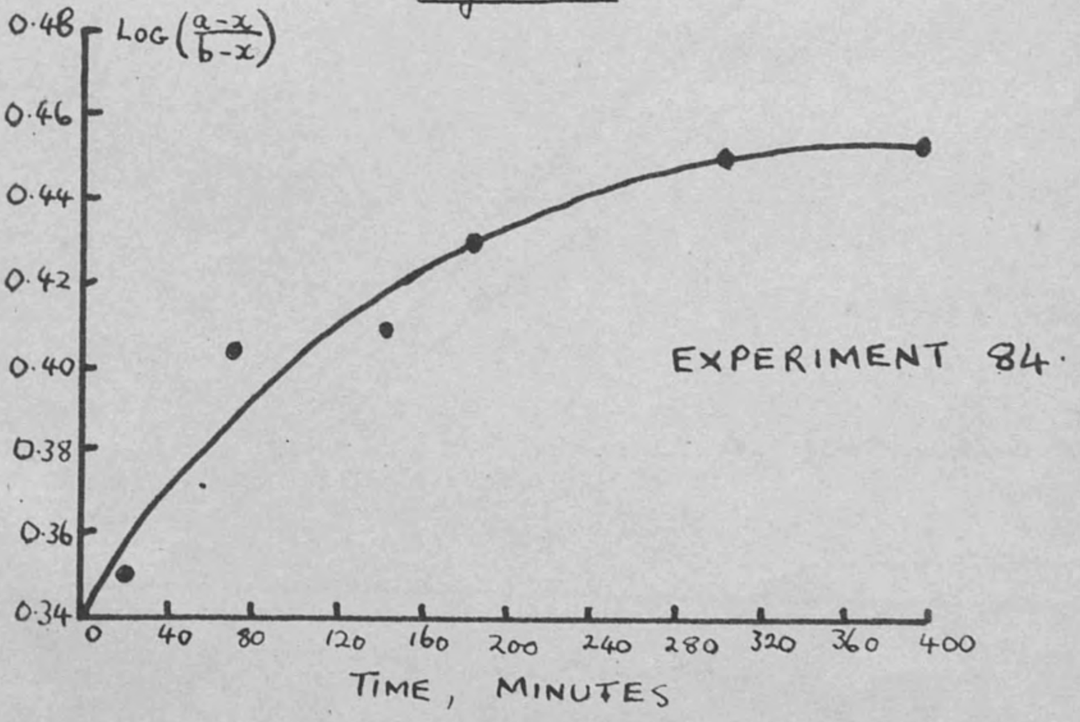

EXPERIMENT 84.

Fig. XXV b.

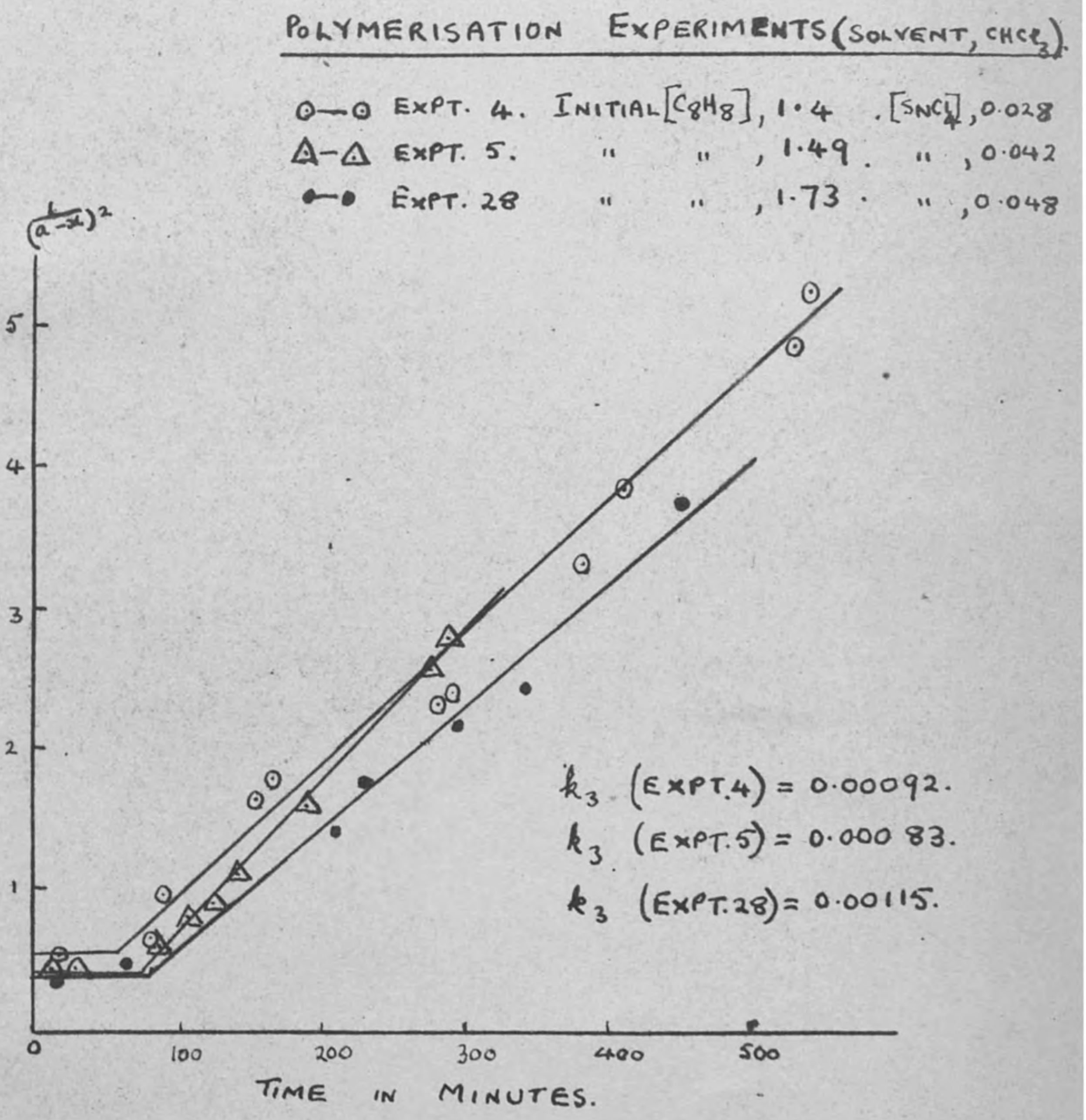
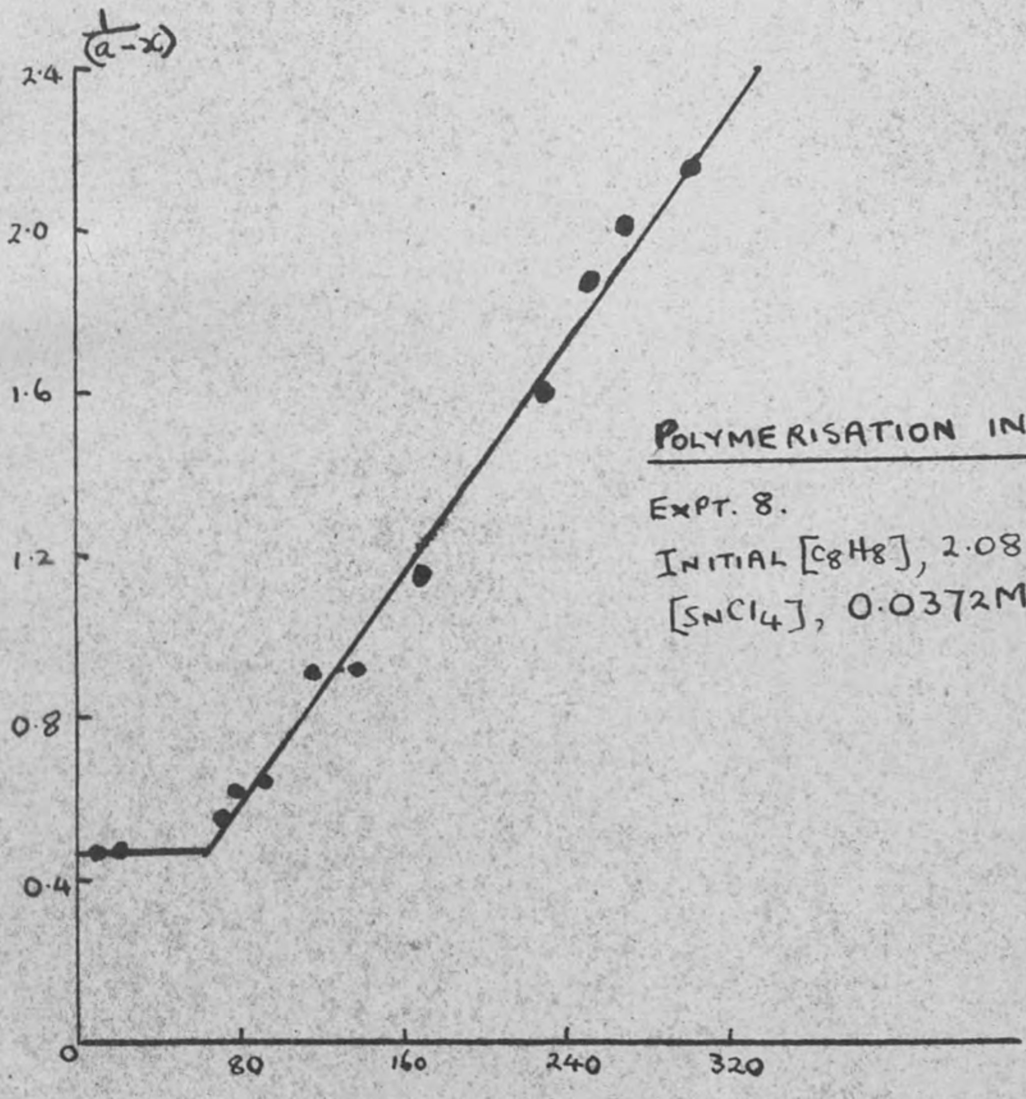

POLYMERISATION EXPERIMENTS (SOLVENT, CHCl3).
EXPT. 4. INITIAL [C8H8], 1·4 . [SnCl4], 0·028
EXPT. 5. " " , 1·49 . " , 0·042
EXPT. 28 " " , 1·73 . " , 0·048
1/(a−x)²
5
4
3
2
1
0
100
200
300
400
500
TIME IN MINUTES.
k3 (EXPT.4) = 0·00092.
k3 (EXPT.5) = 0·000 83.
k3 (EXPT.28) = 0·00115.

Fig. XXVI



POLYMERISATION IN $CHCl_3$.

EXPT. 8.
INITIAL $[C_8H_8]$, 2.08M.
$[SnCl_4]$, 0.0372M.

Fig. xxvii.