"CATALYTIC ADDITION REACTIONS OF STYRENE"

Thesis

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by

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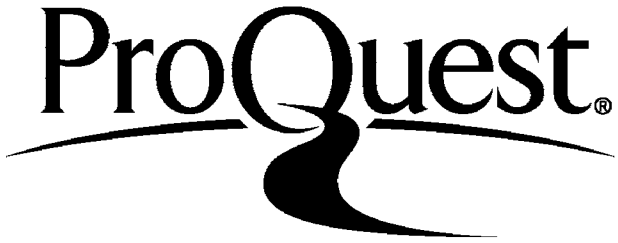

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THE CATALYTIC ADDITION REACTIONS OF STYRENE.

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Hydrogen chloride inhibits the long chain polymerisation of styrene catalysed by stannic chloride. Styrene reacts with hydrogen chloride in the presence of stannic chloride and in carbon tetrachloride medium to form α-phenylethyl chloride and low molecular weight polymers. To support the main kinetic investigations the products ot the reaction have been examined. The reactions are compared with the short chain polymerisation of styrene in the presence of strong acids and are consistent with the mechanism in which a proton, derived from the interaction of hydrogen chloride and stannic chloride, attaches itself to the styrene molecule or may grow by the accretion of monomeric styrene until stabilised to form short chain polymers.

The reaction rate is measured by following the fall in styrene concentration. It is shown that, provided the hydrogen chloride is initially in excess over styrene and stannic chloride, some simple kinetic relationships are discernible.

The effects of varying the styrene and catalyst concentrations are investigated by 'flow' experiments. It appears that the addition is first order with respect to styrene and there is good evidence to show that over the range of styrene concentration 0.05 to 0.2 M the rate of consumption is proportional to the concentration of styrene.

Also up to 0.015 M stannic chloride the first order reaction constant k_1 is directly proportional to the catalyst concentration. However above 0.015 M this simple relationshipdoes not hold.

At high styrene concentration the experimental evidence is conflicting. There is some evidence that there is a lowering of the reaction order, but on the occasions when the reaction obeys the usual first order reaction, k_1 is proportional to the square of the catalyst concentration.

Experiments varying the initial hydrogen chloride concentration show that the rate of consumption of styrene is proportional to the hydrogen chloride concentration provided the latter is in excess over styrene and stannic chloride. However when the stannic chloride chloride becomes equal to or falls below the acid concentration there is again a lowering of the reaction order.

The simple thoery mentioned earlier is discussed in the light of kinetic evidence. The catalyst may form a complex with (a) hydrogen chloride (b) styrene but kinetic evidence does not clearly between the alternatives. (a) is favoured when the hydrogen chloride is in considerable excess over styrene and stannic chloride. However, its application is limited and as styrene or stannic chloride increase in concentration it is probable that the styrene complex plays a part. Also the reaction is complicated by the formation of low polymers.

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Abbreviations used in text

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

Z.Phys.Chem. - Zeitschrift fur Physikalische Chemie.

J.C.S. - Journal of the Chemical Society.

Chem.Revs. - Chemical Reviews.

Ann.Repts. - Chemical Society Annual Reports.

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

Ann. - Justus Leibig's Annalen der Chemie

Can.J.Res. - Canadian Journal of Research.

Comp.Rend. - Comptes rendus de l'Académie des Sciences.

Rec.Trav.Chim. - Recueil des travaux chimiques des Pays-Bas.

B., or Ber. - Berichte der Deutschen Chemischen Gesellschaft.

J.Prakt.Chem. - Journal fur Praktische Chemie.

Ann.Chim.Phys. - Annales de Chimie et de Physique.

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

Bull.Soc.Chim.-Bulletin de la Societé Chimique de France.

Chem. and Ind.- Chemistry and Industry.

PART I

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Section I

At the lowest styrene concentrations the main product of the reaction of stannic chloride and hydrogen chloride on styrene in carbon tetrachloride solution was α-phenylethyl chloride, so some account of the mechanisms that have been discussed for additions at the C-C double bond is relevant.

A - Nature of the Chemical Bond.

According to the modern concept of a simple chemical bond, two electrons of two atoms (e.g. H_2) are of opposite spin and will pair to form a stable bond between two atoms. In the resultant molecule, however, the electrons cannot be definitely located nor can they be assigned definite orbits. There is merely a certain probability of finding them in any particular spot, a probability which is relatively high in the region between the two nuclei. In essence these hypotheses could be considered elaborations of G. N. Lewis's electron pair hypothesis (J.Am.Chem.Soc. 1916 38 762). The electron distribution round these bonds would be symmetrical and there would therefore be no force in the bond to restrict free rotation.

In the double bond there is a different situation which is reflected in its high chemical reactivity compares with similar saturated molecules. In this bond - in addition to the primary bond between the C-atoms (symmetrical) - there is a supplementary electron pair bond for which the bounding

energy is less (approx. 70% of the first). This second pair, often called π electrons, is asymmetrically distributed about the bond axis concentrating above and below the plane containing the C-H Bonds, with a consequent loss of cylindrical symmetry, It is the tending towards a ribbon-like band between the two atoms which tends to prevent free rotation. This second pair of electrons, less firmly held between the two nuclei, is more exposed to external influences and is therefore responsible for the high polarisability and chemical reactivity of unsaturated compounds.

B - Addition to double bonds in solution.

(i) Introduction. It has long been thought that chemical reactions were necessarily preceded by some process of molecular activation (e.g. Arrhenius, Z. Phys. Chem. 1889, 4, 226; 1899, 28, 317). Lowry suggested (J.C.S.1923, 822) that while a single bond in organic chemistry could be either an electrovalency or a covalency, a double bond in organic chemistry usually reacted as if it contained one covalency and one electrovalency - e.g. ethylene could be written as $C\overset{+}{H}_2 - C\overset{-}{H}_2$. Bonds of this character were described as "mixed double bonds.' Their existence could be justified on the basis of the electronic theory of valency by assigning a complete octet to each negatively charged atom and a sextet of electrons to each positively charged atom. (cf. G. N. Lewis, J.Am.Chem.Soc. 1916, 38, 775). This view found support by many workers - it was considered necessary as an explanation of the high temperature

coefficients exhibited by most reactions. Although there were diverse views as to the mechanism of this activation it seemed generally agreed that the reaction would involved an absorption of energy by the molecule so that the activated form was in a more highly energised state than the non-reactive resting form. Many examples had been recorded of inert substances becoming active by the addition of a trace of some polar substance. In other words, many chemical reactions seemed to be catalytic in nature. (Norrish, J.C.S. 1923, 123, 3006). This theory had been tested experimentally, e.g. by investigation of the reaction of ethylene and bromine (Norrish loc. cit.) It was shown that the dried gases practically ceased to react when enclosed by non-polar walls of paraffin wax, but that they reacted rapidly when enclosed by a polar surface of glass, stearic acid or cetyl alcohol. These experiments agreed with the hypothesis that the activation of the ethylene molecule was due to the polarisation induced in the molecule by association with some polar catalyst.

Later this and a mass of other examples were correlated and explained by what has become known as the electronic theory of organic reactions, and before proceeding with a more specialised account of additions to double bonds it seems of interest to give a general picture of the essentials of this now well-known theory. (Ingold, Chem. Rev., 1934, 15, 225: Robinson, Electronic theory of the course of organic reactions.)

(ii) Brief survey of current theories of nature of organic reactions. Conventions (based on the electronic theory of valency - G. N. Lewis, J.A.C.S. 1913, 35, 1448) have been adopted to represent the structures of organic molecules. The ordinary literal symbols represent the atomic kernels without the electrons of the valence shells. Bonds are represented, either fully, showing all the electrons of the valency shell or in the usual abbreviated form, e.g. -C-C- represents a pair of shared electrons between the two C-atoms. Ionic centres are labelled + and - . The notation $\delta+$ and $\delta-$ is used to denote the partial acquisition of polarity through electron displacement. Also Sidgwick's notation ($\longmapsto$) for molecular dipole is often used.

In a bond such as $R_3C - CR_3$ - a symmetrical arrangement - the sharing of the electrons would be equal. However, in a bond such as C - Cl equal sharing would not be likely. Experiments on dipole moments have proved, in many cases, that these displacements occur (cf. Lewis, J.A.C.S. 1916, 38, 762: Ingold, Ann. Repts. 1926, 23, 129).

Any application of the electronic theory as a basis for the development of an electrical conception of reactions would require the preservation of stable electron groups. There are two ways in which electron pairs could undergo displacements without disturbing their octets or altering the original arrangement of the atomic nuclei. In the first (G. N. Lewis, Valence and structure of molecules, p.139)

the electrons remained in their original octets and the electrical disymmetry caused by the unequal attractions of the two linked groups was propagated along the molecule by a mechanism analogous to electrostatic induction. It was a permanent condition, and was called the inductive effect (Ingold, Ann. Repts. 1926, 23, 129).

$$Cl \xleftarrow{a} C \xleftarrow{b} C \xleftarrow{c} C$$

The arrowhead attached to the bond sign indicated the direction towards which the electrons were concentrated. The effect could be transmitted along a chain but diminished in magnitude as it receded from the source.

The second method, characterised by the substitution of one pair of electrons for another in the same atomic orbit (e.g. T. M. Lowry, J.C.S., 1923, 822), showed how the entrance into an octet of an unshared pair of electrons possessed by a neighbouring atom could cause the ejection of another pair which would then either remain unshared or initiate a similar change further along the molecule. This was not wholly a permanent condition but merely an activation mechanism and was termed the electromeric effect (Ingold, J.C.S. 1926, 1310). It was represented by curved arrows pointing from the pair in the direction in which the displacement was assumed to occur. A simple example, $CH_2=\overset{\curvearrowright}{O}$ implied that to some extent the electrons of the double bond were breaking from the carbon atom and remaining wholly attached to the oxygen atom.

The idea of a permanent state associated with this mode of electronic displacement was introduced by Ingold and Ingold (J.C.S., 1926, 1310). It was supposed to be intermediate between the non-polar and the final polar states of the molecule - this they called the mesomeric effect. The mesomeric effect of Ingold and Robinson was closely related to what is known as Resonance. This postulates that when a molecule may be represented by two or more electronic arrangements, differing little in energy and steric configuration, the molecule actually behaves like a hybrid of the two and is more stable than either. An important phase in the development of the subject was concerned with the ~~continuation~~ COMBINATION of the inductive and electromeric effects showing how the former might assist and give direction to the latter, e.g. in the activation of olefines in their addition reactions. (e.g. Ingold, Chem.Revs. 1934, 15, 225).

Every worker in the field of the electrochemical theory has found it necessary to classify reagents according to their polarity relative to dher reagents (Robinson: 'Electronic theory of course of organic reactions').

In connection with modern theories of organic reactions, an attempt was made to formulate an explanation of phenomena such as orientation in the benzene ring and direction of addition to double bonds from a different approach, based

sdely on a direct field effect. (Price, Chem. Revs. 1941, 29, 37). From X-ray and electron diffraction data available in the literature, bond distances and bond angles for simple organic molecules were accurately estimated. Correlation of this information with Dipole Moment data leads to the assignment of bond moments to individual covalent bonds in a molecule. The charge separation for each bond is simply related to the bond moment so that it was thus possible to ascribe a definite charge to each atom in the group. Then from an accurate scale model, it was possible to calculate the coulombic electrical force which the substituent would exert on an electron located in an adjacent double bond.

Supporting evidence was found in the study of the orientation influence of various substituents in the benzene ring - there was good agreement between predictions based on the calculations and the actual orientations for many groups.

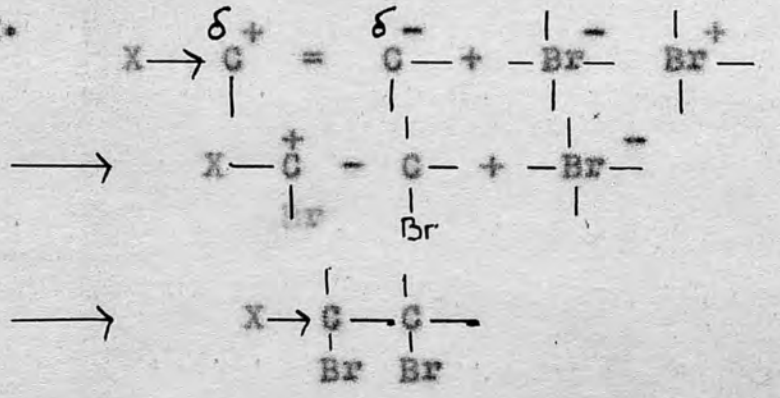
"The essential contrast to the resonance hypothesis as an explanation of the influence of nearly all structural changes in organic reactions is that, although mesomerism can and does play an important role in many molecules, the polarity of a molecule is more profitably considered as an electrical distortion of the bonds rather than as a resonance hybrid between ionic and purely covalent forms." (Price, "Addition to the $\diagdown C = C \diagup$ double bond").

(iii) Special reference to addition to double bonds.

In the light of this electronic theory of reactions, it followed that additions at double bonds would be preceded by some degree of polarisation (Ingold, J.S.C., 1928, 904; Robinson, "Outline of an electrochemical theory of the course of organic reactions" Inst.of Chem. 1932). It was the electromeric effect which became important: the electrons from one of the C-atoms would actually dissociate themselves and become attached to the other. The system $\diagdown C = C \diagup$ should be polarisable in either of two directions, $C \overset{\curvearrowright}{=} C$ or $C = \overset{\curvearrowleft}{C}$ (Ingold, Chem.Revs. 15, 225, 1934). In the presence of a substituent with electron repelling properties one of these directions became important, e.g. $X \longleftrightarrow C \overset{\curvearrowright}{=} C$. If X were electron attracting the opposite effect would be true. Also electron repelling groups would be expected to increase the overall availability of electrons and thus increase the reaction rate with an electrophilic reagent (Ingold, J.C.S. 1931, 2354; Anantakrishnan and Ingold, ibid. 1935, 984, 1396). Theoretically, the known effect of a particular substituent in one reaction could be used to predict its effect in another case. However, in practice it was not so simple.

Numerous kinetic investigations recorded in the literature emphasised that the mechanisms involved in addition reactions were more complicated than might be expected if the reaction occurred by the simple union of two molecules. For

example, in the case of halogen addition, which is very amenable to treatment, it seemed well established that addition took place with impact of the positive atom of the polarised halogen (e.g. $-\overset{+}{Br}-\overset{-}{Br}-$) on the negative carbon of the ethylenic system, thereupon the resulting positive charge on the second carbon was neutralised by the negative bromine (Burton and Ingold, J.C.S. 1928, 904; G. Williams, Trans.Far.Soc.1941, 749) (e.g.



The view held by some workers (eg Ogg, J.A.C.S. 1935, 57, 2727; ibid, 1939, 61, 1946) that the initial attack was by negative halogen was considered (Hughes, Trans.Far.Soc. 1941, 763) to be based on a misrepresentation of the stereochemical data (Roberts and Kimball, 1937, 59, 947).

This type of reaction would be expected to be facilitated by a polar environment. The solvents, even if themselves only slightly ionised, would compete with the negatively charged halogen, e.g. in bromine addition in water, the bromohydroxy derivative was formed almost exclusively (Read and Read, J.C.S. 1928, 745), and if such an ion as nitrate

were present, this would add in preference to OH (Francis, J.A.C.S. 1925, 47, 240). Similarly, in the presence of methylalcohol some bromomethoxy derivative was formed (Jackson, J.A.C.S. 1926, 48, 2166).

Kinetic results in dissociating solvents were homogeneous, reproduceable and insensitive to catalysis, e.g.

Bythel and Robertson J.C.S. 1938, 179

White and Robertson J.C.S. 1939, 1509

Walker and Robertson J.C.S. 1939, 1915

In the case of halogen additions, evidence pointed to an ionic mechanism in strongly dissociating solvents, and by a two stage molecular mechanism in dissociating solvents such as acetic acid. (G. Williams, loc. cit.)

In non-dissociating solvents such as carbon tetrachloride, the results were much less reproduceable and very sensitive to catalysts especially to light (e.g. Sudborough and and Thomas, J.C.S. 1910, 715, 2450; D. M. Williams and James, J.C.S 1928, 343).

C - Hydrogen halide addition.

(1) Introduction.

In addition to symmetrical olefines, it is clear that there could only be one product, e.g.

$$CH_2 = CH_2 + HBr \longrightarrow CH_3 - CH_2Br.$$

However, in the case of an unsymmetrical olefine, there would

be two alternatives, e.g.

$$CH_3.CH{:}\ CH_2 + HI \rightarrow \begin{cases} CH_3CHICH_3 \\ CH_3CH_2CH_2I \end{cases}$$

The well-known orientation rule of Markownikoff (Ann. 1870, 153, 256) stated that in the addition of a halogen acid to an olefine linkage the halogen became attached to the C-atom carrying the smallest number of H-atoms.

Michael (Ber. 1906, 39, 2138) sought to generalise on the basis of the principle of maximum neutralisation, according to which the electronegative group of the addendum became attached to the more electropositive of the unsaturated atoms.

However, it has become evident that the orientation as well as the velocity of reaction (see B) would be affected by the neighbouring group by reason of their influence upon the electron of the double bond (Lucas, J.A.C.S. 1924, 46, 2475; 1925, 47, 1459) and (Kharasch, Chem. Revs. 1298, 5, 571), e.g. in a compound such as CHR = CHR' either the polarisation CHR = CHR' or CHR = CHR' would be favoured by the groups R and R', e.g. in acrylic and vinyl acetic acids the bromine of HBr added at the β and γ positions respectively, owing to the effect of the COOH group (which was known to have electron attracting properties) although this would be contrary to the Markownikoff rule.

$$CH_2 = CHCOOH + HBr \rightarrow CH_2BrCH_2COOH$$

$$CH_2 = CHCH_2COOH + HBr \rightarrow CH_2BrCHCH_2COOH$$

External factors such as medium temperature and illumination were also considered to play a part.

A great many conflicting results are recorded in the literature concerning the products of additions to some olefines.

Investigations by Kharasch (J.A.C.S. 55, 2468 (1933); 60,3097 (1938)) and his collaborators did much to explain this lack of consistency. In a series of studies of hydrogen halides to olefine compounds they discovered the peroxide effect. It was discovered during an investigation of the addition of HBr to allyl bromide. This could take either of two courses,

$$CH_2 = CHCH_2Br + HBr \begin{cases} \rightarrow CH_3CHBrCH_2Br & (1) \\ \rightarrow CH_3BrCH_2CH_2Br & (2) \end{cases}$$

If the reagents were pure and freshly prepared, and if oxygen was excluded from the reaction vessel, then (1) took place exclusively (Abraham and Smith, J.C.S. 1936,1605). If the reaction occurred in the presence of small quantities of oxygen or a peroxide were introduced deliberately or by using old allyl bromide, 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. (Mayo and Walling, Chem.Revs. 1940, 27, 358). The effects of these peroxides was supposed to arise out of their ability to initiate chain reactions in which atoms or free radicals acted as chain carriers. The so-called solvent effects and

inhibitory effects of traces of various materials were best interpreted as a result of their effects on chain reactions. (Mayo and Walling loc. cit.).

(iii) The normal addition.

The normal addition was defined by Mayo (Chem. Revs. 1940, 27, 354) as that which took place in the case of hydrogen chloride or iodide, since these always gave a single product - that predicted by Markownikoff's rule. A large number of additions were carried out using hydrogen chloride, and in many cases peroxides were employed with the object of altering the reaction products. With very few exceptions they yielded only one product thus supplying convincing evidence that they always added in the same way.

In a series of researches Maas and his associates studied the addition of hydrogen chloride to olefines in the absence of solvents (Coffin and Maas, Can. J. Research, 3, 526, (1930) - they found that those which (as indicated by the melting point curves of the mixtures) formed 1:1 complexes with halogen acids at low temperatures gave addition products more easily (around room temperature) than those which did not form complexes, also that the additions were complicated by dimerisation reactions so that rate equations could not be established, also that excess halogen acid was more effective than excess alkene in accelerating the addition.

For example, they studied the freezing point curves of propylene and ethylene with hydrogen bromide: these indicated that propylene molecules had a greater attraction for hydrogen bromide than had ethylene. They related this to the fact that propylene and hydrogen bromide reacted chemically in the absence of a catalyst giving isopropyl bromide. They also showed that a side reaction involving the formation of hexylbromide took place. In kinetic studies with hydrogen chloride they found that similar reactions occurred, giving isopropyl chloride (main reaction) and a chlorohexane (side reaction.)

In excess the hydrogen halide acted as a catalyst. Best confirmation of this lay in experiments in which mixtures of hydrogen bromide, hydrogen chloride and propylene in equimolebular proportions were allowed to readt at -78°C. At that temperature hydrogen chloride did not react at any measurable extent in an equimolecular mixture; therefore the hydrogen chloride could be looked upon as a diluent. Nevertheless the reaction rate was far greater than for the hydrogen bromide propylene mixtures in equimolecular proportions and nearly equal to that when hydrogen bromide was in excess. In other words, hydrogen chloride acted as a catalyst in the reaction. (Maas, J.A.C.S., 47 (1925) 2883; 46(1924) 2664).

Kinetic investigations in inert solvents indicated that the reaction was largely of an order higher than second

(Mayo, J.A.C.S., 61, 1454, (1939)). According to Mayo, the mechanism in which the proton of the halogen acid became attached to one of the double bond C-atoms leaving the other as a positive carbonium ion had to be regarded as an over-simplification.

A mechanism considered by Maas and his associates (Can. J. Research, 2, 267, 1930) was that the reaction occurred between halogen acid and halogen acid-alkene complexes (Mayo and Walling, Chem. Revs., 1940, 27, 358). Such a mechanism would explain why the rate depended more on the halogen acid than on the alkene concentrations (Coffin and Maas, Can. J. Research, 3, 526, 1930; Holder and Maas, Can. J. Research, 16B, 453 (1930); Maas and Swerty, J. A. C. S. 47, 2883 (1925)).

Because the complexes would be expected to be less stable at higher temperatures, the negative temperature coefficients sometimes observed could be accounted for.

The effects of metal catalysts were considered consistent with this mechanism (Mayo and Walling loc.cit.) e.g. anhydrous ferric and aluminium chlorides were the most powerful known accelerators for the addition of hydrogen halides. They affected only the rate and not the products of the reaction. Their reaction could be in replacing one molecule of the halogen acid-alkene complex or, by combining with the halogen acid, they might activate the proton so that the latter could more easily form complexes with alkenes.

N.B. Halogen acids and metal halides are all acids in the Lewis sense - see section II.B.

SECTION II.

The Role of the Catalyst

A - The Friedel-Crafts Reaction.

In the catalysed addition of hydrogen chloride to styrene, some light might be thrown on the role of the catalyst by including in the preliminary discussion some account of the Friedel-Crafts reaction - a term which is used, in its widest sense, to cover a variety of different reactions developed by C. Friedel and J. Crafts in 1877 in the alkylation and acylation of benzene.

Since then a great deal of work has been done in attempts to interpret the role of the metal halide in these reactions.

The view that some kind of double compound was formed between the metal halide catalyst and one or other of the reactants as a first step in the reaction has been held for a long time.

Perrier (Comp. Rend. 1893, 116, 1298) and Boesekin (Rec. Trav. Chim. 1900, 19, 19) isolated crystalline compounds of aluminium chloride with a wide variety of acid chlorides

from solutions of carbon disulphide. However, the fact that some Friedel-Crafts reactions could be carried out with less than molecular proportions of aluminium chloride led Boesekin (Rec. Trav. Chim. 1904, 23, 98) to modify this view. Far from being essential in the reaction, in cases where the complex between the alkyl halide and metal catalyst was comparatively stable, there was no reaction. He suggested that it should be replaced by a catalytic hypothesis in which the molecules were activated by the catalyst and reaction took place between these activated molecules. Later, he suggested that the action of aluminium chloride on the molecules was exerted where the molecule was weakest (Rec. Trav. Chim. 1910, 29, 15).

There is now good evidence to show that, in the case of alkylations and acylations using metal halides and organic halides, an initial step in the reaction is the transition of the mainly covalent carbon-halogen bond of the alkyl halide to an ionic bond (Fairbrother, Trans. Far. Soc. 1941, 37, 763).

A new aspect of the intermediate compound theory was given by Meervein (Ann. 1927, 455, 227), who regarded the complexes which were formed as coordination compounds containing the complex anion $[AlCl_4]^-$, thus

$$CH_3COCl + AlCl_3 \longrightarrow (CH_3CO)^+ + [AlCl_4]^-$$

This would, in effect, be a conversion from a covalent carbon-chloride bond into an ionic bond.

Bodendorf and Bohm (Ann. 1935, 516, 1) supposed some form of complex between α-phenylethyl chloride and metal chlorides e.g. $AlCl_3$, $SbCl_3$, $ZnCl_4$, $FeCl_3$ and $SnCl_4$, which caused a loosening of the carbon-halogen bond in the chloride and eventually ionisation, to account for the racemisation of optically active α-phenyl ethyl chloride in the presence of these catalysts. Their explanation could be summarised:

$$R\text{-}Cl + MeCl \rightleftharpoons RCl^{\cdots}MeCl \rightleftharpoons R[MeCl_2^-]$$

$$\rightleftharpoons R^+ + [MeCl_2]^-$$

where R was an alkyl group and Me was the metal.

Further experimental support of the breaking of the C-halogen bond made use of aluminium chloride in which part of the chlorine atoms were unstable isotopes, i.e. radioactive. (Fairbrother, 1937, 503). If an initial step in the reaction involved the formation of a coordination compound between the organic chloride and aluminium chloride in which the organic chlorine atoms left the C-atoms completely to enter a complex anion $[AlCl_4^-]$ then all the chlorine atoms concerned in the reaction would have an equal chance of escaping as hydrogen chloride, and a complete interchange between the active and inactive chlorine atoms would take place. An interchange of this kind was found experimentally (Fairbrother loc. cit.)

He also showed that an interchange of chlorine atoms took place between acetyl chloride and aluminium chloride $CH_3COCl + AlCl_3 \longrightarrow (CH_3CO)^+ + [AlCl_4]^-$ in the absence of any third reactant or the evolution of hydrogen chloride. Further experiments with pairs of organic and inorganic bromides proved that the ease of exchange of radioactive bromine was closely parallel to the reactivity in Friedel-Crafts synthesis (J.C.S. 1941, 293).

It was not necessary that the equilibrium concentration of the carbonium ion-metal complex ion pair should be large for a complete radioactive exchange to take place. In fact, if a large concentration of carbonium ion were formed, there would be decomposition with the liberation of the hydrogen halide and formation of the olefine. This was observed in certain cases, notably with tert-butyl bromide and aluminium bromide and it has long been known that the action of aluminium chloride on aliphatic chlorides gave rise to olefines, e.g. (Kerez, Ann. 1885, 231, 306). From a consideration of the various energy exchanges involved in a reaction such as $2RBr + Al_2Br_6 \rightleftharpoons 2R^+ + 2[AlBr_4]^-$ it appeared that the ionisation of the organic bromide by the inorganic bromide might often be an endothermic process (Fairbrother, J.C.S. 1941, 293). This was borne out by the low conductivities of such solutions (e.g. Wohl and Wertyporoch, Ber. 1931, 64, 1357, 1369) which indicated a small equilibrium concentration of free ions.

However, it was possible that a greater concentration of undissociated ion pairs was present, as indicated by the low dielectric constants of some of the solutions. Fairbrother performed preliminary experiments on the dielectric polarisability of such solutions and the results indicated that, for example, aluminium bromide in cyclohexane solution formed a highly polar complex with ethyl bromide (Fairbrother, J.C.S. 1941, 293).

The question then arose of the role of the hydrocarbon in these alkylations.

Early investigators, among them Friedel and Crafts (Compt. Rend. 100, 692 (1885) supposed the existence of an addition compound between the hydrocarbon and the metal halide as intermediate

$$C_6H_6 + AlCl_3 \longrightarrow C_6H_5AlCl_2 + HCl$$
$$C_6H_5AlCl_2 + RCl \longrightarrow C_6H_5R + AlCl_3$$

Gustavson (J. Prakt. Chem. 2 68, 209, 1903) claimed to have isolated addition compounds of aluminium chloride with aromatic hydrocarbons. However, detailed study of the freezing point diagrams of mixtures of aluminium bromide with benzene, toluene and p-xylene showed that addition compounds of the composition which Gustavson ascribed to them were not formed (Menschutkin, Chem. Abstracts 32, 2516, 1938). However, it seems generally believed that aromatic hydrocarbons do form complexes with aluminium halides, e.g. Norris and Rubinstein claimed to have

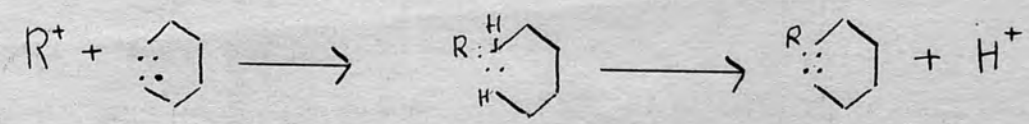
isolated an oily complex the composition of which approximated to $Al_2Br_6C_6H_5CH_3$. They found that these complexes were not found in the absence of hydrogen bromide (J.A.C.S. 1939, 61, 1167) (Nightingale Chem.Revs. 1939, 25, 347).

In an attempt to answer many of the questions which arose Wertyporoch (Ber. 64, 1357 (1931), Ann.500, 287 (1933), Z. Phisik Chem. A.162, 398 (1932)) and his associates used conductivity measurements in an extensive study of the system hydrocarbon-metal halide-alkyl halide and concluded that the Friedel-Crafts reaction was dependent on the formation of an ionised ternary complex between the alkyl halide, metal halide and hydrocarbon.

According to Price (J.A.C.S. 1938, 60, 2499) the R^+, released thus -

$$RXAlCl_3 \longrightarrow R^+ + (XAlCl_3)^- \ ,$$

could coordinate with a pair of electrons in the benzene ring -



$$H + X(AlCl_3)^- \longrightarrow HX + AlCl_3$$

There is, however, no one theory adequately to explain all the different aspects of the alkylations.

B - Olefines and Acid Catalysts.

It seems established that catalysts of the Friedel Crafts type form complexes with unsaturated hydrocarbons.

Confirmation of this was found in its use as basis for an explanation of the observed cis-trans isomerisation of unsymmetrical olefines in the presence of these catalysts, e.g. in the action of boron trifluoride or cis-stilbene (Price and Meister, J.A.C.S. 61, 595 (1939) and for other Friedel Crafts catalysts acting on dimethyl maleate (Gilbert, Tirkevich and Wallis, J.Org. Chem. 3, 616 (1939))

Some reactions of the olefines themselves could be accounted for on the basis of this complex formation. It was assumed by Hunter and Yohe (J.A.C.S. 55, 1248, 1933) to account for the polymerisation of acetylene, ethylene and isobutylene in the presence of aluminium chloride. It could also explain its use in alkylations, e.g. of benzene using aluminium chloride (Bull. Soc. Chim. 2 31,539,(1879); Price and Ciskowski, J.A.C.S. 60, 2499,(1938)).

Evidence has been cited (Luders,Chem.Rev. 27, 547, 1940) to show that Friedel Crafts catalysts were acids (according to Lewis's theory which defines an acid as a substance capable

of accepting a pair of electrons from a base (Lewis J. Frank. Inst. 226, 293, 1938 Luder and Zuffanti: "Electronic theory of acid and bases") also the double bond is characterised by its ability to undergo simple addition (section I); therefore it would be expected that reagents of an 'acidic' type would readily attack the double bond giving an active intermediate. This, in the case of alkylations (e.g. of benzene) would associate with an electron pair from the aromatic nucleus. The final step would be the elimination of the catalyst by an $\alpha-\gamma$ shift of a proton (Price, Chem. Revs. 1941 (29) 37).

Since the activity of the common Friedel-Crafts catalysts was considered to be due to their acidic character, then it might be expected that hydrogen acids could also catalyse such reactions.

Hydrogen fluoride, phosphoric acid and sulphuric acids have in fact been established as catalysts in similar reactions (Simons and Archer, J.A.C.S. 60, 2953, 1938). Also stannic chloride and sulphuric acid have comparable action as dimerisation catalysts (Section III) (cf. also the researches of Maas and his associates - Section I).

SECTION III

A - Polymerisation and Friedel-Crafts Catalysts.

In the presence of catalysts of the Friedel-Crafts type styrene was found to polymerise to form polymers of high molecular weight of the order 1000-3000. (Staudinger, "Die Hochmolekularen Organischen Verbindungen", Berlin, 1932, p.159). Williams studied the kinetics of the polymerisation of styrene in the presence of such catalysts and found the rate approximately proportional to the catalyst concentration (J.C.S. 1938, 246; J.C.S. 1940, 775).

Polymerisation under these conditions might involve a polar chain mechanism initiated by the reaction of the catalyst with the monomer molecule (Williams loc. cit.) The catalysts were, in general, also effective catalysts for the Friedel-Crafts type of reaction which depended on the electron-accepting nature of the catalyst (Price, Chem. Revs. 29, 37, 1941) (See Section II).

In carbon tetrachloride solution, in the presence of stannic chloride, styrene polymerises to form polymers of molecular weight 1500-3000 (Williams, loc. cit.) However, in the presence of a trace of hydrogen chloride, this long chain polymerisation was temporarily but completely inhibited, hydrogen chloride being consumed while it acted as an inhibitor. When a continuous supply of hydrogen chloride was led into a carbon tetrachloride solution of styrene and stannic chloride there

was no long chain polymerisation; instead α phenyl-ethyl chloride, distyrene and short chain polymers were formed. The latter were formedin increasing proportions as the initial styrene concentration was increased (Williams, J.C.S. 1938, 1046). The combined catalytic action of hydrogen chloride and stannic chloride in carbon tetrachloride resembled the catalytic action of aqueous sulphuric or hydrochloric acids in forming small polymers only (Risi and Garvin, Can. J. Research B.14,255,267,1936)

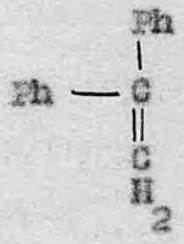
In connection with the structure and mechanism of growth of the low styrene polymers it is of interest to give a brief account of previous work on substances of the same type which form low polymers by similar methods.

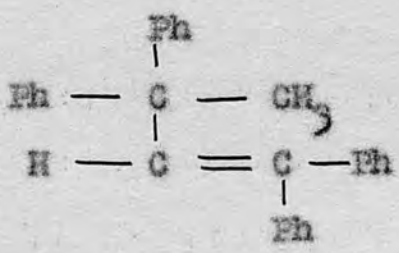
B - Structures and preparation of low polymers of the same type as styrene.

(i) Asymmetrical diphenyl ethylene. $(Ph)_2C = CH_2$

A mixture of two isomeric forms of ↑dic diphenyl ethylene was first prepared by Lebedev (Ber. 56, 2349, 1923) by treating diphenyl ethylene with concentrated sulphuric acid or Fuller's earth.

The unsaturated dimer (m.p. 113°) first prepared by Hildebrand, was shown by Lebedev (loc. cit.) to be 1,1,3,3 tetraphenyl -but-1-ene. This was confirmed by Schlenk and Bergmann (Ann. 463, 239 (1928)).



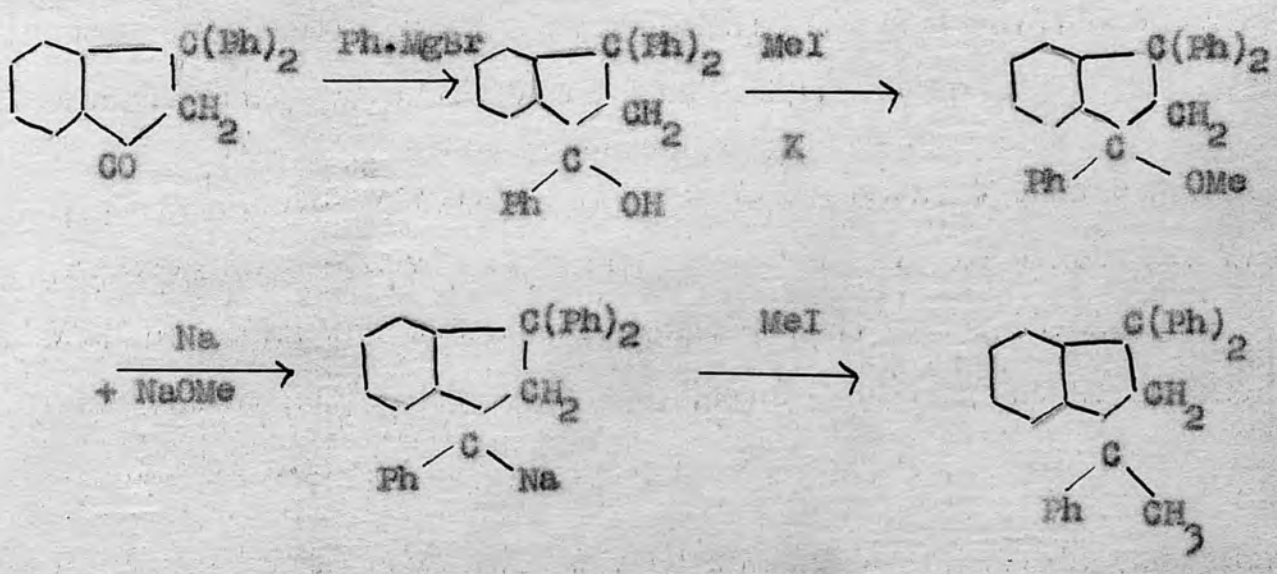


The formation of this could be explained by assuming that two molecules of diphenyl ethylene combined under the influences of such catalysts as sulphuric acid, iodine, stannic chloride to give an unstable intermediate 1,1,44,tetraphenylcyclobutane. This, however, could not be since it appeared from the work of Schlenk and Bergmann (Ann. 463, 7,1928) that this compound (made by the action of mercury on 1:4 disodium 1,1,44 tetraphenylbutane) reverted to diphenylethylene.

A saturated dimer was found among the reaction products in Lebedev's original preparation. He concluded that this compound was tetraphenylcyclobutane, since it did not add bromine nor react with ozone, and gave only benzophenone on oxidation.

The saturated dimer proved very stable to oxidation (Bergmann and Weiss, Ann. 480,49) but by carefully regulating the conditions of oxidation (Schoepfle and Ryan, J.A.C.S. 1930, 4021) a 40% yield of crude oxidation products could be obtained. Among the many oxidation products o-dibenzoyl benzene and benzophenone were isolated. Only the structure 1,1,3,triphenyl-3-methyl hydrindene could give these products on oxidation and could be formed by rearrangement of 1,1,33 tetraphenyl-but-1-ene which had been effected by Lebedev.

Bergmann and Weiss (loc. cit.) synthesised this hydrindene. They treated 1:1 diphenylhydrindene (prepared by intramolecular Friedel Crafts reaction from βββ- triphenyl propionic acid) with phenyl magnesium bromide giving 1,1,3 triphenyl-3-hydroxy hydrindene, the structure of which had been established. This was converted to the methylether with methyl iodide and metallic potassium and the methyl ether group replaced by sodium with sodium and sodium methylate which was then converted to the required compound with methyl iodide.



Schoepfle and Ryan synthesised it independently (loc.cit.) by adding anhydrous stannic chloride to a benzene solution methyl-diphenylchloromethane (obtained by the action of dry hydrogen chloride on the carbinol) and allowing the mixture to stand at room temperature for one week.

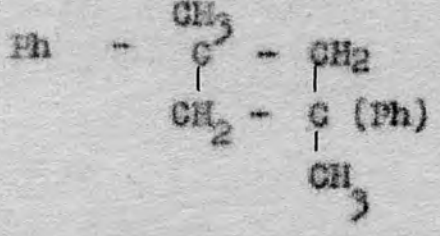
With reference to the fact that tetraphenyl butene could be rearranged to the hydrindene by concentrated sulphuri

acid at room temperature, it was suggested thatnthe former was an intermediate step in the latter. Bergmann and Weiss suggested that the rearrangement of the unsaturated dimer would consist in the addition of sulphuric acid to the double bond and the subsequent removal of the acid to form a stable five-membered ring. The unsaturated dimer could also be rearranged by means of stannic chloride provided that hydrochloric acid was present. Diphenyl ethylene in benzene solution under the influence of stannic chloride polymerised almost exclusively to the saturated dimer, while in the presence of hydrochloric acid, the unsaturated isomer was formed. These results apparently favour an intermediate compound formed by the addition of hydrogen chloride to the unsaturated dimer, but there is some evidence which points to a different mechanism when stannic chloride is used.

(ii) α -methyl styrene ($C_6H_5C(CH_3) = CH_2$)

Tiffeneau (Ann. Chim. Phys. 10, 158, 1906) obtained a saturated dimer (m.p. 52°) by the action of heat on the monomer in the presence of concentrated sulphuric acid or stannic chloride.

This was supposed by Staudinger and Breuch (B.64, 442, 1926) to be a cyclo-butane derivative

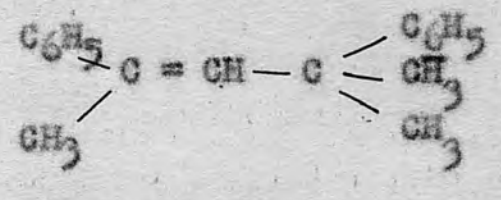


A liquid unsaturated dimer was obtained by polymerising in the presence of phosphoric acid (Klages, B.1902, 35, 2639) or Fuller's earth (Lebedev, B.58,666, 1925). Finally in the presence of stannic chloride or boron trichloride unsaturated together with some saturated dimer and small amounts of trimer were formed. Staudinger and Breuch discussed the possible formulae (B. 64, 442, 1929) and favoured (2).

(1) $C_6H_5C(CH_3) = CH - CH - CH$ (Ph, CH_3)

(2) $C_6H_5CH(CH_3) - CH = CHCH$ (Ph, CB)

However, it was later conclusively proved (Bergmann, Taubadel and Weiss, Ber 1931, 64, 1493) that the structure of the unsaturated dimer prepared by Tiffeneau had the structure



(cf. dimers of diphenyl ethylenes).

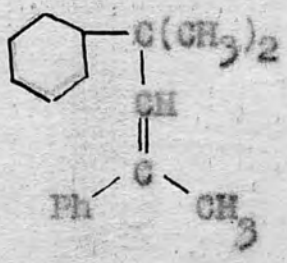
Acetophenone and

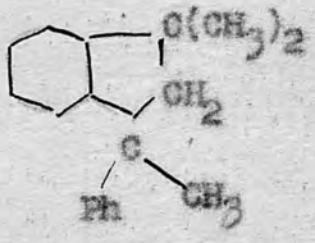
also effected a synthesis.

The first step in the dimerisation, as in the case of diphenyl ethylene was the formation of the unsaturated dimer.

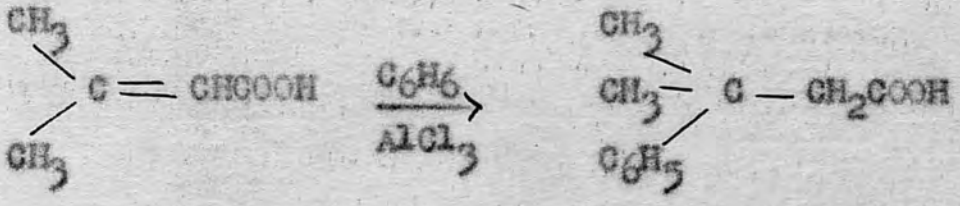
Again the unsaturated polymers underwent cyclization in the presence of such catalysts as stannic chloride, aluminium chloride, zinc chloride and hydrogen chloride.

This, contrary to the opinion of Staudinger (loc.cit.) was proved to have the structure:-



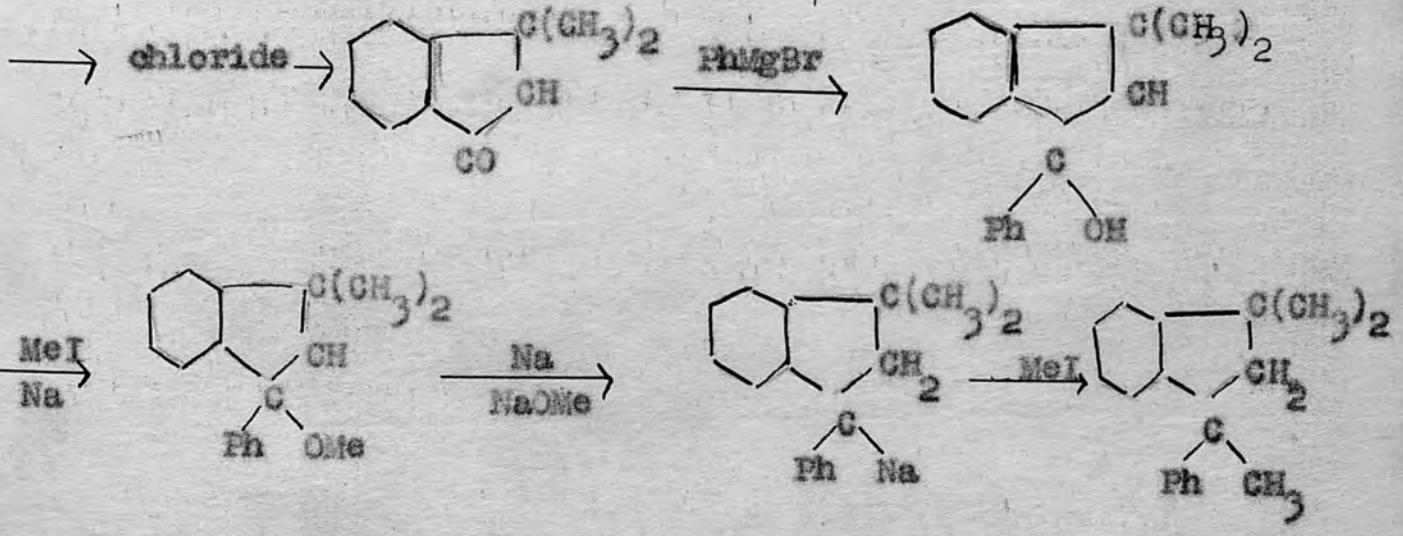


(Bergmann, Taubadel and Weiss - loc.cit.) This they synthesised according to the scheme below:



ββ- dimethylacrylic acid

β-phenyl isovaleric acid



(iv) Distyrene. Liquid distyrene was first prepared by Erlenmeyer (Ann.1865, 135, 122) by the action of heat and concentrated sulphuric acid on styrene at 170°, for several hours. Fittig and Erdmann (Ann. 1883, 216, 179) prepared a similar compound by boiling cinnamic acid with 50% sulphuric acid.

Both these compounds gave dibromides m.p.102° (Stebbe and Posnjak, Ann. 271, 287); also they isolated benzoic acid among oxidation products, and thus ascribed structure (1) to it.

$$C_6H_5 - CH = \underset{\displaystyle C_6H_5 - CH - CH_3}{CH} \qquad (1)$$

They also elucidated the structure of a cyrstalline dibromide originally prepared by Engler and Leist (Ann. 256, 6, 1873) $C_6H_5CH = CH - CH_2CH_2C_6H_5$.

In some cases, during the preparation of dibromides, the unexpected elimination of hydrogen bromide was observed. This suggested the presence of a distyrene of different structure (Stoomer and Kootz, Ber. 1928, 2, 2330). Oxidation, however, still yielded benzoic acid.

They suggested an alternative

$$PhCH_2 - CH = \underset{\displaystyle Ph}{C} - CH_3 \qquad (2)$$

This they synthesised from benzyl acetone and magnesium-bromo-benzene

Distyrene (2) could be prepared from (1) by the prolonged action of heat and dilute sulphuric acid, so its presence in the original specimens of distyrene was attributed to the presence of sulphuric acid in the reagents.

Pure (2) gave no dibromides but strongly evolved hydrogen bromide on bromination. Steomer and Kootz (loc.cit.) claimed to have isolated acetphenone and phenyl acetaldehyde among the products of ozonisation thus confirming their structure.

Staudinger and Steinhoffer (Ann.517,35) isolated another distyrene among the decomposition products of polystyrene in vacuum. Again this was contaminated with a saturated isomer, and indicated by titration with bromine. They could not be separated by distillation, but when the mixture was polymerised, the unsaturated only went to long chain polymers, and the saturated could be isolated by distillation. They suggested the structure 1:3-diphenylpropane and characterised it by a hexanitro derivative.

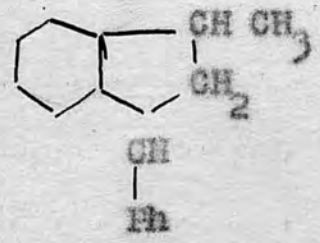
Oxidation of their unsaturated distyrene yielded β-phenyl propiophenone

$$PhCH_2 - CH_2 - \overset{Ph}{\underset{|}{C}}O$$

Thus proving the structures of the hydrocarbon.

The properties and constitution of these distyrenes were later studied by Risi and Gauvin (Can.J.Research 1936, B.14, 255). The distyrene of Fittig and Erdmann contained

30% of a saturated form. The same compound resulted from the action of heat and sulphuric acid on the unsaturated dimer. (Stecmer and Kootz loc.cit) To this they ascribed the formula 3-phenyl hydrindene, by analogy with the known structures of the saturated dimers of methyl styrene.



(iv) Tristyrene. Staudinger and Steinhoffer (Ann.517,35) isolated tristyrene from the products of the composition of polystyrene in vacuum; the yields depended on the temperatures and pressures employed. The product was partly saturated, and they suggested the formulae below for the

(1)

(2)

unsaturated and saturated products respectively. They found it impossible to get pure unsaturated tristyrene though it was formed in large quantities as a constant boiling mixture with the saturated form. Its structure was, however, proved by isolating well defined oxidation products.

The saturated part was, however, obtained pure since the unsaturated could be removed by polymerisation.

Structure (2) was not perfectly confirmed but its molecular weight and boiling point agreed with the synthetic 1,3,5 triphenylpentane.

PART II

EXPERIMENTAL

A - The reaction products

B - Kinetics

PART II

Reaction Products - (Experimental)

Materials. Pure commercial styrene stabilised with quinol was redistilled before use. The stannic chloride was obtained from early fractions taken off during the distillation (in vacuo) of stannic chloride prepared from tin and chlorine (see Part II,B) In later experiments pure commercial styrene (dried with KOH) was used. The reaction medium was AnalaR carbon tetrachloride. Distyrene was made in quantity for determination of conditions of isomerisation by the method used by Bisi and Gauvin (Can. J. Research, 1936, B.14, 225, 267).

90 gm. styrene were refluxed for 8 hours with concentrated sulphuric acid (59 gm.) and water(48 gm.) in the presence of porous pot. The products were extracted with carbon tetrachloride, washed with sodium carbonate and finally with water, dried over anhydrous sodium sulphate and distilled in vacuum. The preparations gave 82% yields of distyrene, 67-79% unsaturated, from which the dibromide was prepared (in acetic acid); a mixture of 16 g. of the dibromide with 6 g. of zinc dust in absolute alcohol was refluxed for 1½ hours. The product was filtered and the bulk of the alcohol distilled off from the filtrate. The residue was poured into water and the distyrene extracted with ether. This gave up to 76% yield of distyrene, 99.5 - 100% unsaturated.

Apparatus. The reaction was carried out in a round bottomed flask fitted with inlet and exit tubes for hydrochloric acid and maintained at 20-25°. Several experiments were carried out at the temperature of boiling carbon tetrachloride. The apparatus then included a reflux condenser.

Procedure. The reactions were carried out by leading a stream of dry hydrogen chloride through solutions of styrene (10 - 30 g., and stannic chloride in carbon tetrachloride. When the styrene concentration had been reduced almost to zero the reaction products were washed three times with water, dried over anhydrous sodium sulphate overnight and finally filtered into a distilling flask. 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. A similar method was employed to determine any further interaction of the reaction products. In this case the reaction was allowed to run for 1 - 2 hours. (See tables 2, 3, 4, part III)

Structure and Physical properties of the Products.

1st Fraction: alleged α-phenylethylchloride - was a colourless mobile liquid - b.p. 80-83°/16 mm., 75-79°/21 mm., 88°/25 mm. (cf. Williams, J.C.S. 1938, 1046). It was purified by washing with potassium carbonate and distilled from a small quantity of anhydrous potassium carbonate. (Found: C, 68.2; H, 64; Cl_2, 25.3. Theoretical: C, 68.3; H, 64; Cl_2, 25.3)

If the first fraction were, in fact, α phenyl ethylchloride, then treatment with sodium would yield 2:3 diphenyl butane. (Ott, Ber. 61, 2142)

$$\begin{matrix} C_6H_5CHCl - CH_3 \\ C_6H_5CHCl - CH_3 \end{matrix} + 2Na \quad \begin{matrix} C_6H_5CH - CH_3 \\ | \\ C_6H_5CH - CH_3 \end{matrix} + 2NaCl$$

7 g. of freshly distilled α-phenyl ethyl chloride, 25 g. sodium wire and 50 ml. sodium dried ether were maintained at about 20° for 5 days. During this time the sodium wire gradually disintegrated, giving place to a bluish black deposit. After the fifth day the ethereal solution was filtered and the solvent removed under vacuum, leaving a white solid: yield 73%. A small quantity of liquid was mixed with the product; this proved to be a liquid isomer. (Ber.61, 2142) This solid was recrystalised from alcohol (m.p. 123-124°; theoretical 124-125°) (Analysis: found - C,91.40; H,8.55; theoretical - C, 91.39; H, 8.61) The liquid isomer was distilled and analayse (found - C, 91.79; H.8.62).

Distyrene.

The distyrene had already been identified (Gwyn Williams, J.C.S. 1938, 1046) as the one prepared by Erlenmeyer (Ann. 1865, 135, 122), by Fittig and Erdmann (ibid, 1883, 316, 179), by Stoemer and Kootz (Ber. 1928, 61, 2330) and by Risi and Gauvin (Can. J. Res. 1936, B.14, 255). Stobbe and Posnjak (Ann. 1909, 371, 287) proved it to be 1:3:diphenyl-but-1-ene.

It was a colourless mobile liquid (b.p.173-174°C/ 16 mm., 135-137°C/ 1 mm.; cryoscopic molecular weight 207.0 - theoretical 208.0. Found C, 92.1; H.7.9; calculated for $C_{16}H_{16}$ C, 92.3; H,7.7%). The distyrene generally contained a detectable trace of halogen, difficult to remove by distillation, or by washing with water or silver nitrate solution.

The dibromide (prepared in acetic acid solution) was recyrstallised from alcohol - m.p. 102°C. Recrystallising from ether - petroleum ether mixture, plates first separated which after twice crystallising gave m.p. 129-130°C. (Found - Br, 43.1., calculated for $C_{16}H_{16}Br_2$ Br, 43.4%). In the second fraction, both plate and needle-shaped crystals were visible, the needles were mechanically separated - m.p.119-120°C. These results corresponded closely with those of Stoomer and Kootz (loc.cit.) They also isolated a third isomeride - m.p. 79°C - from the original mother liquor. A succession of fractions was isolated all of indefinite melting point. The fifth fraction - m.p. 70 - 72°C was probably an impure specimen of the required isomeride, but the yield was too small to allow recrystallisation. Oxidation of distyrene with neutral permanganate gave the unmistakable odour of benzaldehyde, while oxidation with chromic acid yielded benzoic acid which is consistent with the structure.

Saturated Distyrene.

Very unsatisfactory yields in the preparation of dibromides led to a preliminary investigation of the

degree of unsaturation of the distyrene and the factors influencing its variation. When isolated from the reaction mixture distyrene was usually found heavily contaminated with saturated isomer. Table 4 (Part III) shows the extent of unsaturation of the distyrene in a number of experiments, as determined by addition of iodine chloride or bromine to the double bond.

The iodine chloride was prepared by first making an iodine solution of known strength in acetic acid, and passing in dry chlorine until the colour changed from dark red to orange. A known volume of approximately 0.1 solution of distyrene in carbon tetrachloride was added to an excess of the iodine chloride in acetic acid. The residue was destroyed by potassium iodide and the iodine liberated titrated against thiosulphate.

Some typical results with iodine chloride and bromine are quoted:

Conc. $C_{16}H_{16}$ (M):		0.0609	0.0928	0.0923	0.0902
Conc. unsat. $C_{16}H_{16}$ found (M)	After 5 min.	0.0609	0.0803	0.0803	0.0253
	10 min.	0.0610	0.0801	0.0801	0.0251
% of unsat. isomer in $C_{16}H_{16}$.		100	95.6	87.0	27.9

(Times are those for exposure of the solution to the halogen)

In acetic acid solution the amount of substitution is known to be small. In no case did estimations give a

value apparently more than 100% unsaturated. This indicated that the iodine chloride and bromine determinations did in fact give a measure of the unsaturation of the specimen.

Isomerisation of distyrene by hydrogen chloride and stannic chloride.

To determine the effect of the prolonged action of hydrogen chloride or stannic chloride on distyrene, a sample of 100% unsaturated material was necessary. It was prepared on a large scale by the method used by Risi and Gauvin (described earlier); this gave a product which was about 70% unsaturated. 100% unsaturated material was prepared by regenerating the olefine from the dibromide by means of zinc dust and alcohol.

50 ml. of a 0.53 M distyrene solution in carbon tetrachloride was subjected to a current of hydrogen chloride in the presence of stannic chloride (0.047 M). The unsaturation was determined after a known time by the usual method. (Table 5, Part III).

Tristyrene.

Tristyrene was a faintly yellow viscous oil, showing pale blue fluorescence - b.p. 214 - 215°C/ 1 mm.

Physical constants for different samples were tabulated (Table 1). The molecular weights were determined cryoscopically in benzene. The time allowed for the addition of bromine or iodine chloride was specified with the degree of unsaturation because halogen addition was slow and not a

very certain method for the quantitative estimation of the unsaturation in polystyrenes (cf. Staudinger and Steinhoffer, Ann. 1935, 517, 35). In experiments 22, 34, and 33, the unsaturation was measured by the addition of iodine chloride.

Table 1

Sample from expt. No.	b.p./press(mm.)	Mol.wt. (theoretical 312)	% unsaturation/ Time. min.	Analysis %C 92.3	%H 7.77 (Theor)
3	240-45/14	324	-	91.89	7.89
5	240-45/14	290	79/60	-	-
17	225-30/2	291	-	92.10	7.55
collected	215-17/<1	306	59/60	-	-
22	227-28/5	311	68/75	91.7	7.96
34	214-15/<1	308	-	91.98	8.01
33	-	-	74/120	-	-

Attempts to prepare the dibromide gave only a semi-solid mass, which is not surprising in view of the number of possible stereoisomers.

Tristyrene isolated from experiments with high initial styrene concentrations gave benzaldehyde on ozonisation.

Ozonisation. 5 g. tristyrene in glacial acetic acid were submitted to a stream of ozonised oxygen (2 - 3%) overnight. The product was warmed with zinc dust and water to decompose

the ozonide. The aldehydes were then distilled off in steam and extracted with ether. The aldehyde residue (which smelt strongly of benzaldehyde) was divided into two parts. One part was used to prepare the semicarbazone. Repeated recrystallisation, however, failed to produce a pure specimen. (m.p. 213-215°C-mixed with authentic specimen (m.p. 213-214°C) m.p. 201 - 205°).

Similarly the crude 2:4 dinitrophenylhydrazone could not be purified by recrystallisation (m.p. 228-230°C; authentic 234.5 - 235°C)

The experiment was repeated: the crude aldehyde was converted to a 2:4 dinitrophenylhydrazone and purified by chromatography on a column of alumina (2 ft. long, 1 inch diameter).

The benzaldehyde 2:4 dinitrophenyl hydrazone separated: this had the following characteristics (Found: C,54.8; H, 3.8: calculated for $C_{13}H_{10}O_4N_4$: C, 54.5; H,3.5) m.p. 236-237°C; mixed m.p. with the authentic specimens, 233-234°C.

Tetrastyrene.

A very viscous oil. A sample prepared from 4 M styrene and 0.04 M stannic chloride had b.p. 255-258°C/ 1mm. (Found: C,92.2; H, 7.8; Mol. wt. 412: Calculated for $C_{32}H_{32}$: C, 92.3; H, 7.7%; mol. wt. 416).

A solution of tetrastyrene in acetic acid was ozonised in exactly the same way as in the case of tristyrene. The benzaldehyde 2:4 dinitrophenylhydrazone separated by chromatography on a column of alumina had the following characteristics - (found: C, 54.6; H, 3.8%) m.p. 234-235°C; mixed m.p. with authentic specimen, 233.5 - 234.5°C, m.p. of authentic specimen, 234-235°C.

Pentastyrene.

B.p. 280-300°C/ 1 mm., mol. wt. 513 (calc.520) was isolated by distillation of the combined polymers from several reaction mixtures. It was exceedingly viscous.

PART II

B - Kinetics

Calibration of apparatus

The volumes of Grade A pipettes were checked and the results tabulated (Table 2).

Table 2	Cert.vol.	Obs.Vol.	Temp.°C
	25ml.	24.989	20
	20.00	19.989	21
	10.00	10.001	20
	1.995	1.985	20

Observed volumes of graduated flasks were as given in Table 2.

Table 3	Cert.vol. ml.	Obs.vol. ml.	Temp. °C.
	1000	999.64	21
	1000	999.09	19
	100	99.97	16
	250	249.8	19

Preparation and Purification of materials

The styrene used was prepared from freshly distilled β-phenylethyl alcohol (b.p. 119°C/20 mm.) and powdered potassium hydroxide.

A mixture of 68 g.(1 mol.) of alcohol and 42g (1-1.5 mol.) of potassium hydroxide was gently heated in a copper flask. Styrene distilled over between 140-160°C and was collected in a flask containing a small quantity of hydroquinone to prevent polymerisation. The crude product was washed twice with water and dried over caustic potash. Yield 92%, b.p. 48°C/21 mm.

AnalaR carbon tetrachloride was washed twice with water and and dried over caustic potash and distilled through a fractionating column. When Analar carbon tetrachloride was, for some reason, unobtainable, commercial reagent was shaken with 100 cc. of alcoholic potash, then washed with 5 or 6 portions of water, finally dried and distilled as before.

Potassium Iodate

For the preparation of standard solutions AnalaR potassium iodate was recrystallised from water and dried (at 120°C) to constant weight. The strength was checked against standard acid and another iodate solution.

Calculated strength	0.09815N
Observed 1. Standard acid	0.09766N
2. Standard iodate	0.09772N

Thiosulphate solutions were made up to an approximate strength and standardised with iodate.

Styrene was estimated in carbon tetrachloride solution by addition of bromine to the double bond. The addition was carried out in acetic acid solution.

5 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. The excess was destroyed by potassium iodide and the iodine liberated titrated against sodium thiosulphate solution.

Strength of solution	1. Calculated	0.1077M
	2. Found	0.1079M

During the course of the experiments β-phenylethyl alcohol became unobtainable. However, commercial styrene did not require the rigorous purification that was first thought necessary. It was washed with alkali, then water, dried over

anhydrous sodium sulphate and finally distilled before use - b.p. 42°C/14 mm.

Strength of solution 1. Calculated 0.1911M

2. Found 0.1920M

It also gave satisfactory results when used independent experiments on the catalytic polymerisation of styrene by stannic chloride, a reaction known to be very sensitive to traces of impurity.

Preparation and purification of stannic chloride.

In the earlier flow experiments the catalyst, prepared by the action of dry chlorine on tin, was purified by fractional distillation under vacuum.

Preparation. In the apparatus fig. 1, all rubber connections were eliminated beyond A. Bars of tin were granulated by melting and dropping into water from 1 foot above the surface. Chlorine, dried by first bubbling through sulphuric acid and then passing it over phosphorus pentoxide, entered the flask containing the tin and a vigorous reaction followed; flashes of light were seen. After the initial burst, the reaction subsided considerably. The stannic chloride distilled off as it formed and chlorine passed through until all the tin was used.

Purification. Fig.2 represents the apparatus diagrammatically. It had to be built entirely of glass and contain no greased taps or joints beyond the liquid air trap T1 owing to the extremely corrosive nature of stannic chloride. 1, 2, and 3 were

FIG. 1. THE PREPARATION OF STANNIC CHLORIDE

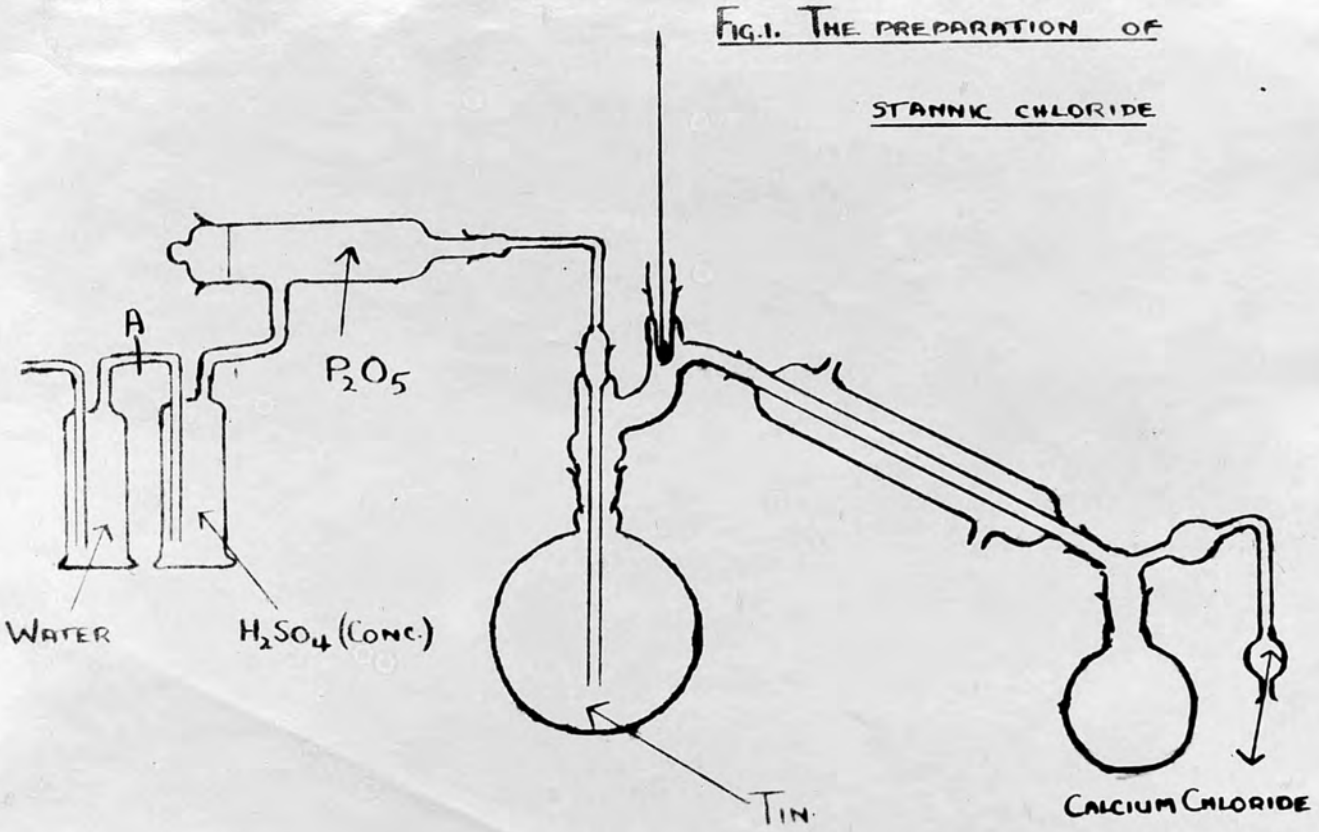
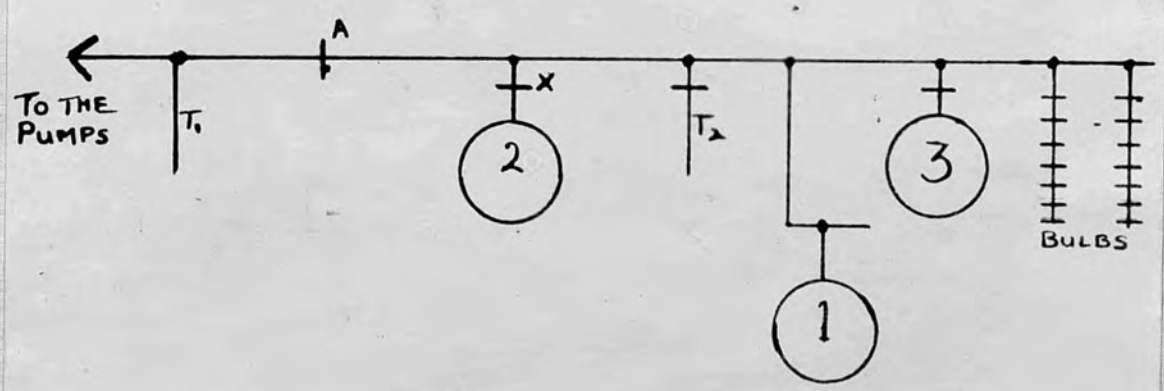


FIG. 2

THE PURIFICATION OF STANNIC CHLORIDE

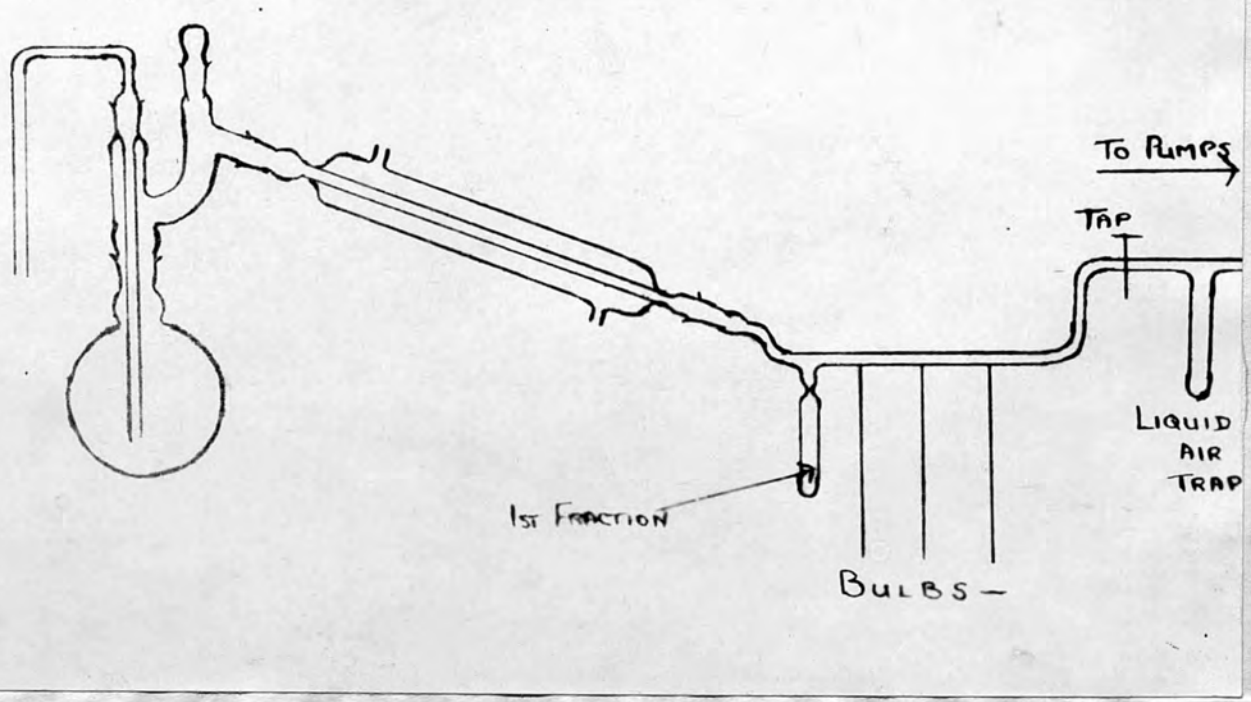


flasks joined to the main line by thick-walled capillaries. T1 was a tube connected in the same way. All small perpendicular lines such as X represented thick-walled capillaries for the purpose of sealing off. The bulbs had fairly thick walls. The diagram shows only two series, but the number of series varied, of course, with the scale of the experiment. The apparatus was connected to a mercury diffusion pump backed by 'Hyvac' pump, also to a McLeod gauge.

The apparatus was first thoroughly dried under vacuum. Flask 1 was surrounded by liquid air, and stannic chloride poured in. The whole apparatus was then sealed and re-evacuated. The liquid air was then transferred from 1 to 2 , and the stannic chloride distilled over into the latter. 1, containing a last fraction, was sealed off. The whole was then sealed off from the pumps at A. By a similar procedure, a first fraction was taken off at T2 (this contained any hydrogen chloride and the more volatile hydrate), the bulk transferred to 3, and 2 removed. By gently warming 3, stannic chloride distilled into the bulbs. These were removed as they filled.

Attempts were made to purify stannic chloride on a smaller and less elaborate scale at a pressure of about .1mm. The apparatus (fig.3) contained ground joints which were smeared with acid resisting silicon grease. The bulbs were similar to those used in the previous purification. The apparatus was thoroughly dried out under vacuum and the air replaced by dry

FIG.3. THE PURIFICATION OF STANNIC CHLORIDE



hydrogen chloride. The stannic chloride (in this case pure commercial material) was introduced into the flask through the syphon arrangement by applying a partial vacuum. The syphon was replaced by a stopper and the flask surrounded by liquid air. The apparatus was then re-evacuated; T1 was closed, then the liquid air replaced gradually by warm water. The stannic chloride, which slowly distilled, was partly condensed by the cold water and finally collected in the bulbs by applying cotton wool soaked in an ice-salt-water mixture to the part of the tube above the bulbs to be filled. The latter were quickly sealed off as they filled..

Hydrogen Chloride supply.

In the first instance, hydrogen chloride was supplied by simply dropping concentrated sulphuric acid from a funnel into concentrated hydrochloric acid and drying the gas by bubbling through concentrated sulphuric acid. This stood the test of preliminary experiments, but as the reaction apparatus increased in complexity a greater pressure and a more easily regulated supply of gas became necessary. Also the occurrence at intervals of unexpectedly low values for velocity constants could only be attributed to an insufficient supply of hydrogen chloride.

The apparatus (fig.4) proved a satisfactory answer to these demands. The hydrogen chloride container was well

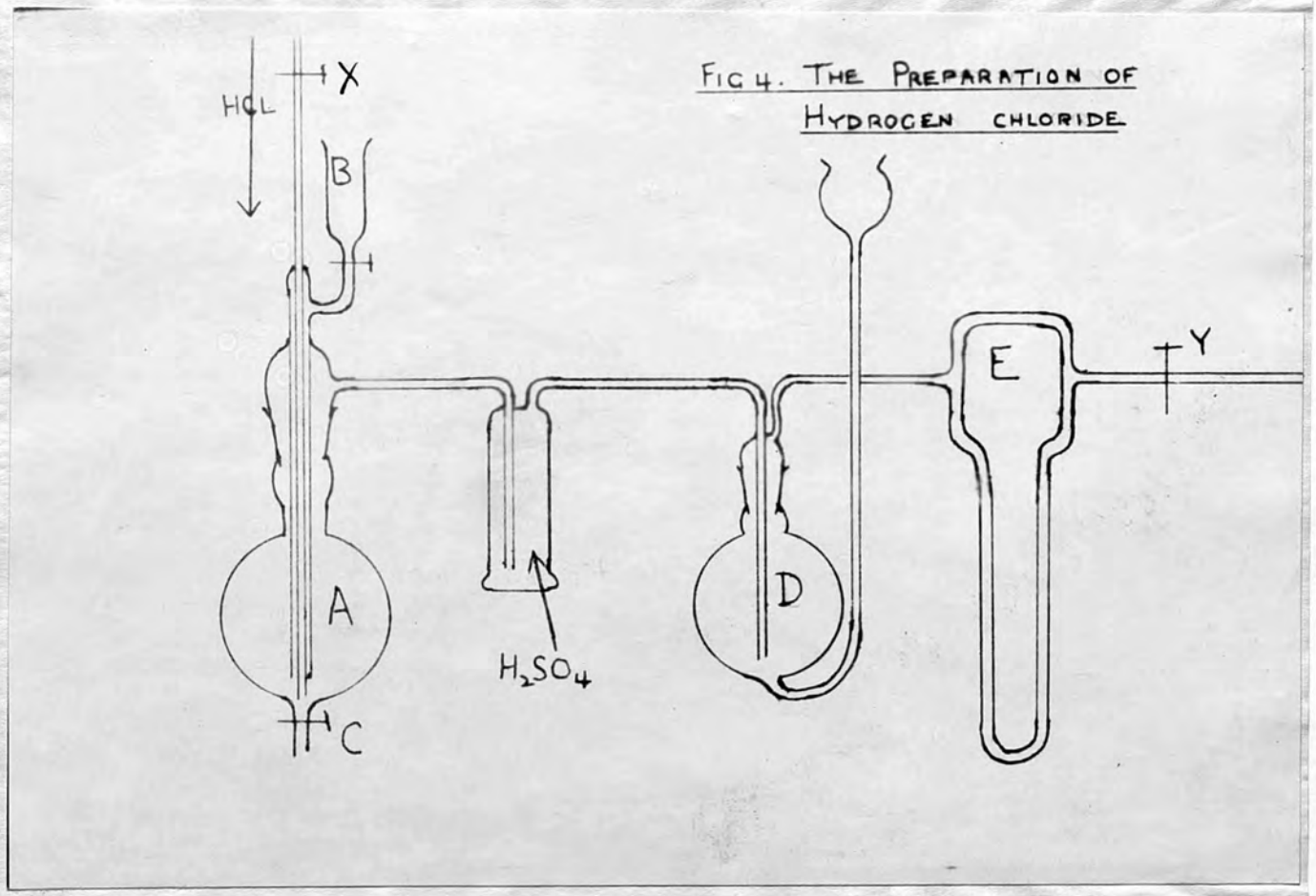


FIG 4. THE PREPARATION OF HYDROGEN CHLORIDE

above the level of the flask A, giving increased pressure. Concentrated sulphuric acid was supplied through B. Hydrogen chloride flowed into the flask through a capillary below the surface of the sulphuric acid. The used acids were run out through C. The gas generated was dried by bubbling through concentrated sulphuric acid, and a steady flow maintained by further passing it through the trap D, which contained carbon tetrachloride. E was a flow meter containing the liquid butyl phthalate. The taps X and Y regulated the supply of gas-Y giving the fine adjustments. With this arrangement a steady flow was maintained over a period of two hours.

Control Experiments.

Experiments in which hydrogen chloride was one of the variables proved unsatisfactory owing to the continual loss of hydrogen chloride during the reaction.

The "Flow" method. A constant stream of hydrogen chloride had to flow through the solution during the course of the experiments thus maintaining the hydrogen chloride concentration at its saturated value. An arrangement such as that illustrated proved a suitable reaction vessel. The gas entered through B and escaped at C, titres were withdrawn at A. The stoppers and joints were of ground glass. (fig.6 flask A)

In all subsequent work, unless otherwise stated, hydrogen chloride was estimated with iodate and thiosulphate and

the styrene as before, by addition of bromine.

1. Hydrogen chloride bubbled through carbon tetrachloride in the flask and the concentration of acid determined at intervals; it reached a constant value in between 15 and 40 minutes. (Table 4).

Table 4	Time (mins.)	HCl conc.	Temp.
	15	0.1126N	25°C
	40	0.1420N	
	50	0.1420N	
	110	0.1420N	
	120	0.1420N	

2. The carbon tetrachloride was replaced by a dilute solution of styrene and the concentration measured at intervals during the passage of a current of hydrogen chloride. It rose gradually from 0.0658 to 1.03M in 90 minutes (Table 5).

Table 5	Time (mins.)	Styrene (M)	Temp.
	10	0.0658	25°C
	30	0.0874	
	35	0.0882	
	75	0.0900	
	90	1.03	

This indicated that carbon tetrachloride vapour was being swept away in a stream of hydrogen chloride gas. To counteract this loss the hydrogen chloride entering the flask was first bubbled through a guard tube containing carbon tetrachloride.

2 was repeated with this precaution.

3. The concentration remained constant at 0.0903 for 5 minutes. Then after 5 and 15 minutes, it fell to 0.0893 and remained at this value for 120 minutes (Table 6).

Table 6

Time (mins.)	Styrene(M)
0	0.0903
5	0.0903
15	0.0895
20	0.0892
32	0.0891
42	0.0895
80	0.0893
100	0.0894
135	0.0895

4. 3 was repeated using two (fig.6) flasks connected in series; the first contained carbon tetrachloride and the second styrene solution. Again the concentration remained constant at 0.0923 for 10 minutes and in between 10 and 15 minutes fell to 0.0915M and remained constant for 65 minutes (Table 7).

Table 7

Time (Mins.)	Styrene (M)
5	0.0919
10	0.0923
15	0.0915
30	0.0915
45	0.0915
65	0.0915

Thus the styrene concentration appeared to remain constant after approximately the time taken for the solutions to become saturated with hydrogen chloride.

5. In the next experiment the styrene solution was made up in carbon tetrachloride that had been presaturated with hydrogen chloride. The concentration remained constant for 65 minutes. (Table 8).

Table 8	Time (mins.)	Styrene (M)
	4	0.0971
	9	0.0968
	15	0.0968
	30	0.0972
	60	0.0972
	65	0.0975

Rate of supply of hydrogen chloride

Simple experiments were attempted to obtain a rough estimate of the rate of supply of hydrogen chloride.

The estimation was effected by passing hydrogen chloride at a known pressure (measured in centimetres of butyl phthalate) through a sodium carbonate solution of known strength (CA·IN) for a definite time and titrating the residual alkali against normal hydrochloric acid. Values for the pressure were as nearly an average as could be attained with the meniscus in a continuous state of fluctuation within the range of 0.5 cm

also the readings were taken while the two-way tap Y (fig.4) was open to the atmosphere. The alternative would clearly depend on the volume of sodium carbonate used. It was calculated that, even at the highest styrene concentrations the quantity of hydrogen chloride consumed did not exceed 40 ml./min. So the results at least sufficed to show that the supply of hydrogen chloride was adequate to meet the needs of the ensuing reactions. (Table 9).

Table 9	Pressure cm.	Time(secs.)	ml.HCl (N.T.P.)	Rate ml./mn.
	42	10	27	162
	48	60	350	350
	48	90	640	426
	40	30	115	230
	3.4	60	207	207
	9.5	30	154	307
	9.5	60	286	286

Variation in the concentration of hydrogen chloride in styrene solutions of different strengths.

Though negligible at low concentrations this effect became appreciable as the concentration increased. In the first experiments, hydrogen chloride was estimated in the usual way, but the influence of styrene on the end point in iodine titrations proved disastrous. Iodine was absorbed by styrene, presumably forming some loose addition compound which subsequently decomposed, causing the end point to be indistinct. Therefore,

as in the preceding section, the strength of the acid was determined with standard alkali (Table 10). The results were plotted on a graph (fig.1).

Table 10	Styrene (M)	HCl (N)
	0.00	0.1423
	0.1113	0.1460
	0.4787	0.1516
	0.9785	0.1623
	1.197	0.1651
	1.304	0.1693
	1.622	0.1759

Reaction Velocities

Knowledge of the possible mechanical errors gained in the preliminary experiments was made use of in the apparatus which finally took the form (in fig.6), described below.

A, B, C, D and E were similar flasks fitted with ground glass stoppers and having a capacity of about 100 ml. Flasks B, D and E are not shown in the diagram. Because rubber connections were attacked by hydrogen chloride they were avoided where possible, and, if used, as at R and S, were frequently renewed.

C was the reaction vessel and the traps X and Y prevented any actual shifting of the liquid into C from B and D. The whole was clamped in a thermostat at 25°C; the water level is indicated by the dotted line.

CONCENTRATION OF HYDROGEN CHLORIDE IN STYRENE SOLUTIONS OF VARYING STRENGTHS. FIG. 1.

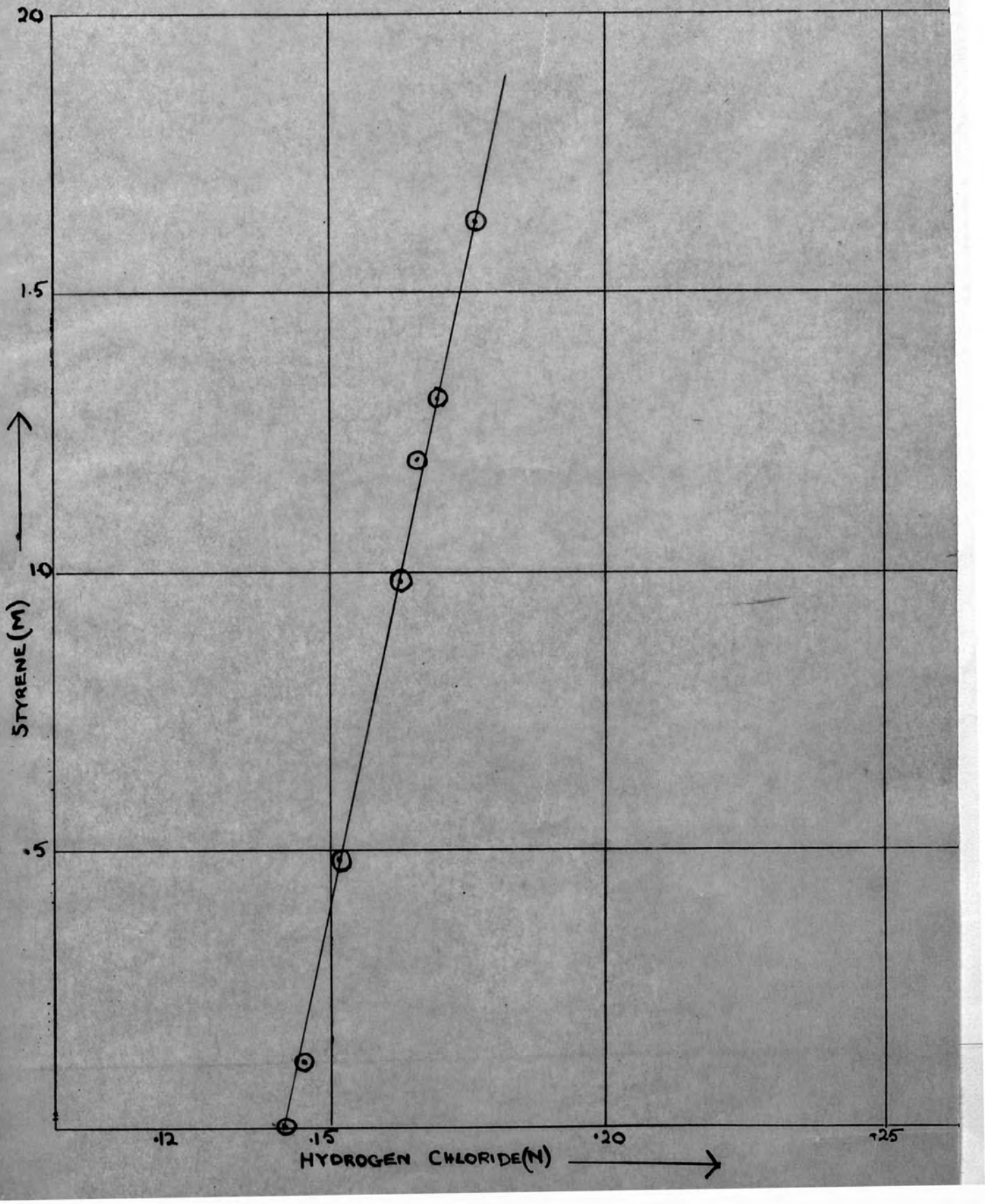
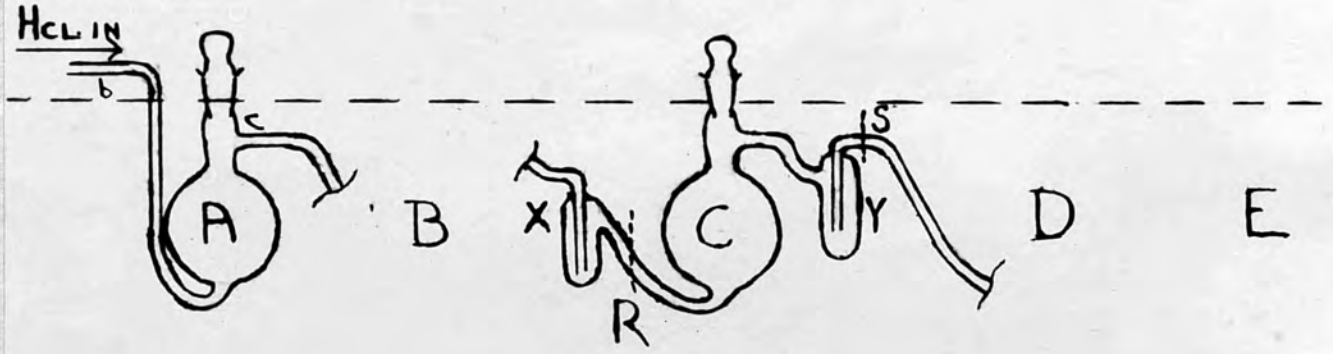


FIG.6 THE REACTION APPARATUS.



Method of procedure.

Initially A and E contained carbon tetrachloride and B the stock styrene solution. These were saturated with hydrogen chloride. A weighed stannic chloride bulb, contained in a reagent bottle, was smashed under 50 ml. of carbon tetrachloride from E. Again a known volume of styrene solution from B was transferred to the reaction vessel C, and the reaction initiated by the addition of a known volume of catalyst. The rate of reaction was followed by determining the styrene concentration at intervals over a period of 1 to 2 hours. In some experiments when suspicion had been cast on the gas supply, a little carbon tetrachloride was poured into D at the start of the reaction and the acid concentration determined after about the time required to reach saturation.

"Flow" experiments at 0°C.

Velocity measurements were carried out at 0°C in a similar manner to those at 25°C. The apparatus had to be considerably simplified to fit into a Dewar flask of ice water. However, the same principles applied in its construction. Traps similar to X (fig.6) replaced A and B; styrene solutions were made up independently with carbon tetrachloride that had been presaturated with hydrogen chloride. Control experiment 5 was carried out with this arrangement (Table 11).

Table 11.	Time (mins.)	Styrene (M)
	4	0.0391
	27.0	0.0385
	39.0	0.0385
	45.0	0.0385
	75.0	0.0384
	87.0	0.0384
	69.0	0.0384
	120.0	0.0384

The saturation concentration of hydrogen chloride in carbon tetrachloride at 0°C.

Constant values were eventually attained by saturating the solutions at atmospheric pressure for between 40 and 50 minutes. Because the saturation concentration at 0°C was considerably greater than at room temperature some difficulty was experienced in pipetting the solutions. This was largely overcome by cooling the pipette several times with the solution (table 12).

Table 12.	Time (mins).	Conc.(M).
	21	0.2612
	42	0.2755
	51	0.2748
	58	0.2765
	66	0.2755
		223
		0.2756

Variation in initial hydrogen chloride concentration.

Owing to the volatility of hydrogen chloride in carbon tetrachloride solution, reaction rates could not be followed by the usual method of removing the stopper of the reaction vessel and withdrawing titres at intervals during the course of the reaction.

The apparatus (fig.7) was used in an attempt to overcome this difficulty. It consisted of two bulbs of about 75 ml. capacity joined by an internal ground joint. A capillary inlet for hydrogen chloride was led into the top bulb and titres were withdrawn from the lower bulb by sucking into a graduated pipette of 2 ml. capacity with a two-way tap attached.

Procedure. The lower bulb contained a volume of styrene solution of known strength in carbon tetrachloride, and the upper a volume of carbon tetrachloride, presaturated with hydrogen chloride. A stream of hydrogen chloride was maintained through the latter while a known volume of stannic chloride solution (in carbon tetrachloride) was added. The internal stopper was removed to start the reaction, then rapidly replaced. In some experiments the stopper was hollow and connected during the reaction to another flask containing hydrogen chloride over a solution of about the same strength as in the reaction mixture.

FIG. 7

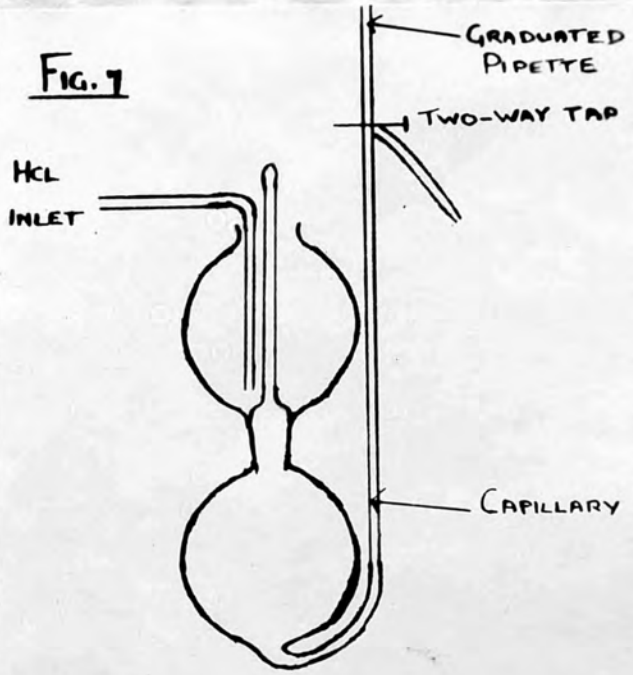


FIG. 8.

Control experiments.

The concentration of hydrogen chloride was determined by an iodine titration as before.

1. The stopper was solid (Table 13).

Table 13

Time (mins.)	Conc.(M).
5	0.1005
5	0.1078
10	0.0904
10	0.0909
20	0.0832
20	0.0813

2. The stopper was covered by a layer of mercury to prevent possible loss of gas through the ground joint. The concentration fell from 0.1318 to 0.1057 in 30 minutes.(Table 14)

Table 14

Time (Mins.)	Conc.(M)
4	0.1318
6	0.1245
11	0.1145
14	0.1160
27	0.1073
30	0.1057

3. The stopper was replaced by a hollow one which was connected to an atmosphere of hydrogen chloride above a saturated solution. The concentration rose from 0.1353 to 0.1460 M in 34 minutes (Table 15).

Table 15.	Time (mins.)	Conc.(M)
	4	0.1353
	5	0.1356
	18	0.1380
	22	0.1400
	34	0.1460

4. The stopper was connected to an atmosphere of hydrogen chloride above a solution of the same concentration as in the lower bulb. There was still a slight fall from 0.0726 to 0.0678 M in 59 minutes. (Table 16).

Table 16.	Time (mins.)	Conc.(M)
	5	0.0726
	8	0.0721
	18	0.0707
	21	0.0683
	30	0.0678
	33	0.0687
	45	0.0683
	48	0.0697
	54	0.0673
	59	0.0678

However, the state of affairs which would exist when there was a continual fall of hydrogen chloride in the reaction mixture could not be predicted in these preliminary experiments. The only test could be in the consistency of velocity

experiments.

Plots of $\log \frac{a - x}{b - x}/t$ (or(using the equation for second order reaction, see Part III) in some particular cases gave approximate straight lines, but random variations between different experiments were frequent and violent an extent that rendered the method almost valueless. These were more than could be accounted for by the regular rise or fall that would be expected from a gradual change in acid concentration in the reaction mixture due to the change in volume above the solution and the relative vapour pressures of hydrogen chloride above the reaction mixture and guard solution. It had been assumed in the preliminary experiments that carbon tetrachloride would reach its saturation value with hydrogen chloride in the required time irrespective of the vessel containing the solution and of the method of leading the gas into this vessel. This however proved a fallacy. Numerous experiments led to the conclusion that the most convenient method of attaining constant saturation was that used in the "flow" experiments.

However, the above arrangement did yield one purely qualitative contribution towards knowledge of the course of the reaction when hydrogen chloride concentration was equal to or less than the original styrene concentration (see Part III p78.)

"Closed Tube" experiments.

An attempt was then made to follow reaction rates by using separate tubes for each reading in one particular velocity experiment.

Each tube was of a little more than 10 ml. capacity and closed with a well-fitting B14 standard joint. Known volumes of styrene and stannic chloride were put into each of the bulbs. A further known volume of carbon tetrachloride saturated with hydrogen chloride was withdrawn from a vessel such as one of those in fig.6, and run into the tube under the surface of the liquid. This reduced loss of hydrogen chloride. The stopper was rapidly replaced, the tube inverted three times to ensure good mixing, then replaced in the thermostat at 25C (or in ice water). The volumes were adjusted in such a way as to make the total volume 10 ml. The styrene concentration in each tube was determined after different times. Loss of hydrogen chloride in this final pipetting did not matter, since it was the styrene concentration that was always measured.

Hydrogen chloride concentration in the tubes.

Owing to the extreme volatility of the gas, it was impossible to determine its concentration by withdrawing the stopper and withdrawing a known volume. An estimation was effected thus:

A tube of 10 ml. capacity was attached to a slightly wider tube by means of an internal ground joint. The upper tube was fitted with a B24 standard cap stopper (fig.8).

The tube contained 5 ml. of carbon tetrachloride; then 5 ml. of saturated hydrogen chloride solution (in carbon tetrachloride) were added under the level of the liquid as described above. The tube was quickly stoppered (A). About 10 ml. of distilled water were placed in the upper tube above A. A was then removed, and B quickly inserted. The whole was well shaken so that the hydrogen chloride all dissolved in the aqueous layer. The mixture was poured into excess of standard sodium carbonate and titrated against standard hydrochlorine acid. (Table 17).

Table 17.

Saturation concentration of hydrogen chloride - carbon tetrachloride at 25°
(estimated by acid alkali titration)

Time for saturation - 40-45 mins.

Concentration (M) - 0.1427, 0.1427, 0.1423

Concentration of hydrogen chloride in tubes -

Calculated - 0.0712 M

Found - 0.0708 M

0.0714 M

0.0712 M

In some experiments, in order to get a wider variation in the intial hydrogen chloride concentration, similar but larger tubes were used (15 ml.) When the reaction was of long duration, loss of hydrogen chloride through the stopper was suspected, the latter was then smeared with acid resisting c silicone grease. Owing to the number of pipettings involved in every reading, in addition to the risk of loss of hydrogen chloride in transferring the saturated solution to the tube, the degree of accuracy attained was not very high. (See Part III).

PART III

SUMMARY AND DISCUSSION OF RESULTS

A. THE REACTION PRODUCTS.

B. KINETICS.

PART III

Summary and Discussion of Results

A - The Reaction Products

(i) Results. To support the kinetic study of the catalysed addition of hydrogen chloride to the styrene double bond, the reaction products have been examined.

Table 1 summarises the varying proportions of the different products with increasing initial styrene concentration. (For identification of the reaction products, see experimental section, Part IIA).

At the lowest styrene concentrations, a maximum of 75% of styrene is recovered as α - phenyl-ethyl-chloride. The proportion of the latter falls with the initial concentration of styrene, and the yield of distyrene appears to reach a maximum of 40% at about 2.5M(Expts. 13,20,24, Table 1). The yields of products classified in Table 1 as "short chain polystyrenes" increase at still higher styrene concentrations (e.g. expts. 37, and 38, Table 1). The short chain polystyrene consists of tritetra and pentastyrene, all of which could be distilled at pressures of 1 mm. : it also contains a certain proportion of polymer of higher molecular weight which could not be distilled under the conditions employed. Experiment 38 (Table 1), carried out with 30 grammes of styrene at 5.3M concentration shows that the amount of non-distillable polymer does not exceed 8% of the initial styrene: presumably non-

distillable polymer would be formed in smaller proportions at lower styrene concentrations. In experiments performed with smaller initial quantities of styrene, the attempted quantitative separation of distillable from non-distillable polymer tended to exaggerate the latter (e.g. in expt. 37). Only at the highest initial styrene concentrations does the non-distillable polymer residue contain polystyrene of high enough molecular weight to be capable of precipitation by methyl alcohol. The mean (cryoscopic) molecular weight (see Part IIA) of non-distillable residue from 4M initial styrene was 633. The non-distillable residue from 5.3M initial styrene contained 3.8% as polymer, with mean molecular weight 881, which was precipitated by methyl alcohol. In experiments of long duration (e.g. expts. 24 and 20 in table 1), the yields of individual products may have been affected by interaction between α-phenyl-ethyl-chloride and distyrene (cf. table 2) after the initial styrene had been used up.

Table 1

Interaction of styrene with hydrogen chloride and stannic chloride.

Solvent - Carbon tetrachloride

Temperature - 20 - 25°C

Dry hydrogen chloride led through the solutions.

Expt.No.	Styrene (M)	$SnCl_4$ (M)	Time (mins.)	% styrene recovered as: C_8H_9Cl	$C_{16}H_{16}$	short chain polymers	Total yield
10	0.08	0.044	180	73.9	11.0		84.9
11*	0.08	0.044	187	74.0	20.1		94.1
9	0.17	0.026	172	75.0	15.0	3.9	93.9
6	0.17	0.035	210	64.0	7.3	9.9	81.2
7	0.17	0.044	186	69.0	7.1	5.5	81.6
1	1.11	0.022	183	58.0	7.9	14.0	79.9
4	1.73	0.044	(150)	38.0	54.0		92.0
14	1.73	0.088	(182)	50.5	31.7	16.1	98.3
13.	2.5	0.088	(180)	22.1	40.2	33.9	96.2
5	3.4	0.088	(175)	8.5	12.0	66.0	86.5
12	3.4	0.088	(180)	2.4	29.1	57.2	88.7
37	4.0	0.088	10	11.1	31.3	54.5*	96.9
38	5.3	0.088	12	7.4	27.4	59.2†	94.0
3	5.3	0.088	(180)	2.0	9.0	59.0#	70.0
#31	1.73	0.044	(90)	21.1	37.4	23.0	81.5
#30	2.5	0.088	(105)	6.2	9.0	50.4	65.6

* Containing at least 23.5% of the initial styrene as tri and tetra styrenes.

(continued over)

† Short chain polystyrene composed of 24.0% of initial styrene as fraction b.p. 185-300°/12 mm. (mainly tristyrene), 27.3% as fraction with b.p. 300-360°/12 mm. (mainly tetra and pentastyrenes): and 7.9% as the distillation residue.

ǂ 3.8% of the initial styrene recovered as polymer insoluble in methyl alcohol.

at 76°C.

Further Interaction of the Products

Distyrene solution was not appreciably affected under the combined action of hydrogen chloride and stannic chloride, except for the slow conversion to its saturated isomer (expts. 15, 35 and 36, Table 3). α-phenyl-ethyl-chloride reacted with styrene (expt. 32, table 2), and more slowly, with distyrene (expt. 33, table 2) to form polymers. The number of moles of starting materials and end products wes given in parenthesis for the relevant experiments in table 2.

Table 2

Further Interaction of Products

Current of hydrogen chloride passed only in Expts.15, 35 and 36

Expt. No.	Starting materials (M)	$SnCl_4$ (M)	Time (mins.)	% styrene recovered as:- C_8H_9Cl	$C_{16}H_{16}$	$(C_8H_8)_{3-4}$	non distillable polymer	Yield %
15	$C_{16}H_{16}$* :0.89M	0.088	18	0	92	0	4	96.2
35	$C_{16}H_{16}$†:0.53M	0.047	75	0	91.0‡			91.0
36	$C_{16}H_{16}$‡:2.06M	0.047	75	0	90.0#			90.0
32	C_8H_8: 1.81M (0.079)							
	C_8H_9Cl: 0.92M (0.040	0.080	92	2.1 (0.0026)	41.6 (0.050)	30.7 (0.037)	17.3 (0.024)	91.7
33	$C_{16}H_{16}$:0.877 (0.073)							
	C_8H_9Cl: 0.757 (0.030)	0.080	38.5	16.4 (0.017)	53.0 (0.055)	19.8 (0.020)	2.5 (0.0026,	91.7

* Partly saturated
† 100% unsaturated
‡ 95.5% unsaturated
\# 87% unsaturated

In nos. 32 and 33, the moles of starting material were corrected for the amounts of solution extracted for analysis. The yield was calculated on the total styrene in the starting materials. Moles of polystyrene are always given as moles of styrene in a given weight of polymer.

Saturated distyrene

When isolated from the reaction mixture, distyrene

was usually heavily contaminated with a saturated isomer. Table 3 shows the extent of unsaturation of the distyrene in a number of experiments, as determined by the addition of iodine chloride or bromine to the styrene double bond.

Formation of distyrene dibromide from the partially saturated material followed by regeneration of the olefine (described earlier) gave distyrene 99.5 - 100% unsaturated, as estimated by the same procedure (always assuming one $>C=C<$ per molecule). The formation of the saturated distyrene is not surprising because stannic chloride is known to catalyse the conversion of the unsaturated dimer into a saturated isomer (Risi and Gauvin, Can. J. Research 1936, B.14, 255). The structure of the saturated isomer has not been proved. By analogy with the known structures of the saturated dimers of α-methyl-styrene and 1:1 diphenyl ethylene (Schoepfle and Ryan, J.A.C.S. 1930, 52, 4021: Bergmann and Weiss, Ann.1930, 480, 49: Bergmann, Taubadel and Weiss, Ber. 1931, 64, 1493) the saturated dimer has been supposed (Risi and Gauvin,(loc.cit): Stanley, Chem. and Ind. 1939, 58, 1080) to be 1-phenyl-3-methyl hydrindene contrary to the opinion of Stecmer and Kootz (Ber. 1928, 61, 2330) who thought the isomer was unsaturated. (cf. Part I, Section III).

Table 4

The Extent of Unsaturation of Distyrene

Expt.No.	Styrene (M)	$SnCl_4$ (M)	Time (mins.)	% styrene recovered as: C_8H_9Cl	$C_{16}H_{16}$	% unsaturation of $C_{16}H_{16}$
28	1.73	0.085	28	31	30	27.7
25	1.89	0.048	45	45.1	12	47
27	1.89	0.048	33	30.5	26.4	38
29	2.02	0.021	71	29.0	19.1	36
26	2.31	0.044	46	39.5	28	31
23	2.5	0.04	25	24	31	20
24	2.5	0.04	15	33	37	20
20	2.5	0.04	120	13	37	76
22	2.5	0.04	120	14	36	23

Isomerisation of distyrene by hydrogen chloride and stannic chloride.

cf. Part II.

The unsaturation fell to 95.5% in 1½ hours. Using the distyrene recovered from this experiment (95.5% unsaturated) a more concentrated distyrene solution was subjected to the same treatment for 75 minutes; the unsaturation fell to 87% (table 5).

Table 5

The effect of hydrogen chloride and stannic chloride on distyrene

Expt.No.	$(C_8H_8)_2$ (M)	$SnCl_4$ (M)	Time (mins.)	% styrene recovered as $(C_8H_8)_2$	Initial unsaturation	Final unsaturation
35	0.53	0.047	75	91	100	95.5
36	2.06	0.047	75	90	95.5	87

(ii) Discussion. Hydrogen chloride inhibits the long chain polymerisation of styrene, catalysed by stannic chloride. Styrene reacts with hydrogen chloride, in the presence of stannic chloride, in carbon tetrachloride medium, to form α-phenyl-ethyl-chloride, and di-, tri-, tetra- and pentastyrenes, all of which have been isolated. The polymers are formed in increasing proportion as the initial concentration of styrene is raised (Table 1). Ozonisation shows them to have the structure $CHPh{:}CH.(CHPhCH_2)_n.CHPhCH_3$.

Some of these products can react further among themselves (Table 2). Previous experiments (G.Williams, J.C.S. 1938, 1046) have already proved:

1. that styrene and hydrogen chloride do not react together in the absence of a catalyst.
2. that racemic α-phenyl-ethyl-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 medium.

The results in Table 2 show:

3. that distyrene does not change appreciably under the combined action of hydrogen chloride and stannic chloride, except for a slow conversion to its saturated isomer (expts. 15,35,36)

4. but that α-phenyl-ethyl-chloride reacts with styrene (expt.32), and more slowly, with distyrene to form polymers. This is particularly evident from the number of moles of starting materials and end products, given in parenthesis for the relevant experiments in Table 2. In the long experiment quoted below (VIII) taken from the work of G. Williams (J.C.S.1938, 1046), the α-phenyl-ethyl-chloride is completely consumed.

No.	Starting materials	Stannic chloride	Time (mins.)	C_8H_9Cl	$C_{16}H_{16}$	low polymer	Yield
VIII	C_8H_8 : 1.7M (0.14) C_8H_9Cl : 0.75M (0.060	0.086	1500	0	20 (0.050)	66 (0.16)	86

The following suggested interpretation of the reaction is based upon evidence which exists that an alkyl halide and metal halide catalyst form a complex which is ionised though not necessarily much dissociated into free ions in a solvent of low dielectric constant (see Part I).

"Normal" Polymerisation

$$CHPh = CH_2 + SnCl_4 \rightleftharpoons \overset{+}{C}HPh.CH_2.\overline{S}nCl_4 \quad \text{.....(1)}$$

$$CHPh:CH_2 + \overset{+}{C}HPh.CH_2.\overline{S}nCl_4 = \overset{+}{C}HPh.CH_2.CHPh.CH_2\overline{S}nCl_4 \quad \text{.....(2) (etc.)}$$

In the presence of hydrogen chloride

$$HCl + SnCl_4 \rightleftharpoons H^+ + SnCl_5^- \quad \text{.....(3)}$$

$$CHPh{:}CH_2 + H^+ = \overset{+}{C}HPh.CH_3 \quad \text{.....(4)}$$

$$\overset{+}{C}HPhCH_2.SnCl_4 + H^+ = \overset{+}{C}HPh.CH_3 + SnCl_4 \quad \text{.....(5)}$$

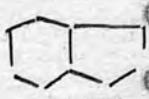
$$\overset{+}{C}HPh.CH_3 + HCl = CHPhCl.CH_3 + H^+ \quad \text{.....(6)}$$

$$\overset{+}{C}HPh.CH_3 + SnCl_5^- \rightleftharpoons CHPhCl.CH_3 + SnCl_4 \quad \text{.....(7)}$$

$\overset{+}{C}HPh.CH_3 + CH.Ph{:}CH_2$

$$CHPh.CH_2.\overset{+}{C}HPh.CH_3 + SnCl_5^- = CHPh{:}CH.CHPh.CH_3 + HCl + SnCl_4 \quad \text{..(8)}$$

(I)



$$+ HCl + SnCl_4 \quad \text{.....(9)}$$

(II)

$\overset{+}{C}HPh.CH_2.CHPh.CH_3 + CHPh{:}CH_2$

$$\overset{+}{C}HPh.(CH_2.CHPh)_2\,CH_3 + SnCl_5^- = CHPh.CH.CHPhCH_2.CHPh.CH_3 + HCl + SnCl_4$$

(III)

$\overset{+}{C}HPh(CH_2.CHPh)_2\,CH_3 + CHPh{:}CH_2$

$$\overset{+}{C}HPh(CH_2.CHPh)_3\,CH_3 + SnCl_5^- = CHPh{:}CH(CHPh.CH_2)_2CHPhCH_3 + HCl + SnCl_4.$$

(IV)

In the absence of hydrogen chloride, stannic chloride catalyses the polymerisation of styrene to relatively long-chain products, e.g. with 1.7 M initial styrene, to molecules of the order $(C_8H_8)_{23}$

If catalysts of the "Friedel-Crafts" type 4 initiate polymerisation by polarising the olefinic double bond (see Part I, Section II) the "normal" polymerisation may be propagated

by processes of the type shown in equations (1) and (2). The presence of hydrogen chloride prevents the "normal" polymerisation: with 1.7 M styrene in the presence of stannic chloride and 0.147 hydrogen chloride, none of the material formed can be precipitated in methyl alcohol, and the largest polymer isolated is $(C_8H_8)_{3-4}$, in about 16% yield (Table 1, expt.14). The reaction in the presence of hydrogen chloride is also faster than the normal polymerisation in its absence. This is shown in table 6 which compares results on normal polymerisation (G. Williams, J.C.S. 1940, 775) with figures from Tables 1 and 4.

Table 6

Stannic chloride: 0.04 - 0.05 M.

Conc. C_8H_8 (M):	0.17	0.35	0.86	1.7	1.9	2.5	3.5	4.0
"Normal" polymerisation in absence of HCl.								
% consumption of C_8H_8	-	46	50	61	-	-	84	-
Time (mins.)	-	5400	1600	190	-	-	162	-
Reaction with 0.14 M HCl: complete consumption of styrene in								
Time (mins.)	186	-	-	-	33	15	-	10

It follows that the formation of the products cannot be due to the interruption of "normal" polymerisation chains, since the latter are initiated too slowly to account for the formation of these products within the times observed. Hydrogen chloride and stannic chloride in combination must act in two ways: (a) in stopping the"normal" polymerisation chains, and (b) in propagating much shorter chains by a different mechanism. The

polymerisation complex of equation (1) must either be decomposed into styrene by hydrogen chloride, or it must be diverted by hydrogen chloride into an alternative path (equation 5).

The combined catalytic action of hydrogen chloride + $SnCl_4$ in carbon tetrachloride resembles the catalytic action of aqueous sulphuric or hydrochloric acid upon styrene (Risi and Gauvin, Can. J. Res., 1936, B.14, 225) in producing small polymers only. In the presence of stannic chloride, therefore, the catalytic behaviour of hydrogen chloride is similar to that of a strong acid. By analogy with the influence exerted by Friedel-Crafts catalysts upon alkyl halides, it seems probable that hydrogen chloride and stannic chloride will react, in carbon tetrachloride, as shown in equation (3). (Alternatively $SnCl_6^{--}$ may be formed). Evidence for some such interaction may be seen in Meerwein's observation (Ann. 1927, 453, 16) that dilute ethereal solutions of hydrogen chloride and of stannic chloride are, separately, yellow after the addition of the indicator p-dimethylaminoazobenzene; but that an immediate red colour is formed as soon as the two yellow solutions are mixed. The virtually free proton from (3) may react with styrene, as in (4), or may decompose the "normal" polymerisation complex, as in (5), forming in either event a carbonium ion, which can be converted into α phenyl-ethyl-chloride by (7), and perhaps also by (6). The reaction (7) must be supposed reversible to account for Bodendorf and Bohm's discovery (Ann. 1935, 516, 1) that optically active α-phenyl-ethyl chloride is racemised by

the action of stannic chloride (interpreted by these authors by equations equivalent to 7); and also to account for the reactions of α-phenyl ethylchloride with styrene and distyrene (Table 2). (cf. also, the elimination equilbrium discussed by Hughes, Ingold and Scott, J.C.S. 1937, 1271). The formation of polystyrenes, (I), (III) and (IV) is represented by the addition of monomeric styrene to a carbonium ion of increasing chain length, coupled with the stabilisation process, typified by (8), which is evidently more efficient than the chain termination processes occurring in the normal polymerisation in the absence of hydrogen chloride. The stabilisation reactions are not reversible, because distyrene does not polymerise further in the presence of hydrogen chloride and stannic chloride (Table 2), though it does undergo slow isomerisation into its saturated isomer (II). In view of the slowness of this isomerisation (Table 5, expts. 35 and 36), it seems doubtful whether substantial amounts of saturated distyrene in the reaction products can be formed by direct isomerisation within the times observed (Table 4, expts. 23 - 29). It is more probable that the saturated distyrene (II) is produced by cyclisation of the carbonium ion, through attack by the positive end of the ion upon the benzene ring with elimination of a proton (equation 9).

Whether styrene <u>must</u> be in the form of a complex in order to take up a proton, as in (5), cannot be certain; but equation (4) seems to represent a likely reaction.

The general question - whether the hydrocarbon component in a Friedel-Crafts alkylation needs to be activated by association with the catalyst,- has been raised by Ingold (Trans. Far. Soc., 1941, 37, 769). See Part I, Section II.

B - Kinetics.

(i) Results.

"Flow" Experiments.

"Flow" experiments were carried out by the method outlined in Part IIB.

Hydrogen chloride does not add to the styrene double bond in carbon tetrachloride solution in the absence of a catalyst. Tables 7 and 8 show this for initial styrene concentrations 0.039 to 0.1 M.

Table 7

Initial styrene - 0.0971 M.

Hydrogen Chloride - 0.143 M.

Temerature - 25°C.

Time (mins.)	Styrene (M)
4	0.0971
9	0.0968
15	0.0968
30	0.0972
60	0.0972
65	0.0975

Table 8

Initial Styrene - 0.0391 M.

Hydrogen Chloride - 0.143 M.

Temperature - 25°C.

Time (mins.)	Styrene (M)
4	0.0391
27	0.0385
39	0.0385
45	0.0385
75	0.0384
87	0.0384
69	0.0384
120	0.0384

There is a slow addition in chloroform solution (Table 9).

Table 9.

Initial styrene - 1.251 M.

Hydrogen chloride - 0.205 M.

Temperature - 25°C.

Time (mins.)	Styrene (M)
0	1.251
6	1.251
12	1.222
19.5	1.191
26.75	1.158
44.25	1.099
62.25	1.043
91.5	.9654

However, no kinetic measurements have been made in chloroform solution.

Course of the Reaction

The rate of the reaction is measured by following the fall of styrene concentration with time. This has to be done because of the difficulty of estimating hydrogen chloride in the presence of stannic chloride; but it has the drawback that styrene is known to be consumed in polymerisation as well as in the formation of the addition product. However, with 0.14 M initial hydrogen chloride concentration and with initial styrene concentration up to 0.08 M α-phenyl-ethyl-chloride forms 75% of the final reaction products (Table 2, Part IIIA), and so long as hydrogen chloride is initially present in excess over styrene, the kinetic evidence is in favour of the view that the rate of consumption of styrene is approximately the same as the hydrogen chloride addition reaction. On the other

hand, when the initial styrene concentration is greater than the initial hydrogen chloride concentration, the amount of styrene consumed becomes greater than that calculated for the addition reaction alone, even at relatively low styrene concentrations. Qualitative confirmation of this is found using the apparatus described in Part IIB in attempts to determine reaction rates at different initial hydrogen chloride concentrations, (Tables 10 and 11).

Table 10

Experiment No.136 Temperature 25°C

Stannic chloride - 0.0263 M

Initial styrene - 0.1002 M

Initial hydrogen chloride - 0.059*

Time (mins.)	Styrene (M)
6	0.0901
15	0.0810
23	0.0727
39	0.0598
48	0.0551
59	0.0508
75	0.0428
91	0.0374
106	0.0321

For pure addition reaction the theoretical final styrene concentration is 0.0412 M.

Table 11

Experiment No.135 Temperature 25°C

Stannic chloride - 0.0203 M.

Initial styrene - 0.182 M

Initial hydrogen chloride 0.130*

Table 11 (contd.)

Time (mins.)	Styrene (M)
4	0.170
14	0.152
30	0.136
45	0.123
64	0.106
76	0.101
92	0.091
122	0.079
149	0.071
236	0.052
331	0.039

For pure addition theoretical final styrene concentration is 0.052 M.

* the actual hydrogen chloride concentration might be lower than this. (see Part IIB).

Kinetics of the Reaction

The kinetic experiments were nearly all made with hydrogen chloride initially in excess over styrene. Under these conditions some simple kinetic relations are discernible. The effects of varying the styrene and stannic chloride concentrations were investigated by "flow" experiments in which hydrogen chloride was kept at a constant concentration (its saturation value in carbon tetrachloride) throughout each experiment. This procedure avoids the very considerable experimental difficulties caused by the volatility of hydrogen chloride from its solutions in carbon tetrachloride.

It appears that under the conditions described the addition was first order with respect to styrene. Experiment numbers 4 and 5 are quoted in full to show the reproduceability of individual velocity measurements. The average value of

the velocity constant was determined graphically using the first order reaction equation:-

$$k_1 = \frac{2.303}{t} \log \frac{b}{b-x} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where b and b - x are, respectively, the concentrations of styrene at time o and t. (Tables 12 and 13, figs. 2 and 3).

Table 12, fig.2

Experiment No.4 Temperature 25°C

Initial styrene - 0.0638 M.
Initial hydrogen chloride - 0.143 M.
Stannic chloride - 0.0887 M

Time (mins.)	log 100(a-x)	Styrene (M)	% decomposition
	0.805		
2.5	778	0.0600	6.0
9.0	694	0.0494	22.6
16.0	599	0.0297	37.8
25.0	479	0.0301	51.3
34.0	348	0.0223	65.1
45.0	0.173	0.0149	76.7
60.0	-0.108	0.0078	87.8
94.0	-0587	0.0041	90.5
111.0		0.0028	95.7

T. 892
T. 613

k_1 (from graph) = 0.0310

Table 13, fig.3

Experiment No. 5 Temperature 25°C

Initial styrene - 0.0638 M.

Initial hydrogen chloride - 0.143 M.

Stannic chloride - 0.0887 M k_1 (from graph) =0.0306

Time (mins.)		Styrene (M)	% decomposition
0	0.805		
3.0	772	0.0592	7.2
9.0	690	0.0490	23.2
16.0	596	0.0334	38.2
25.0	490	0.0309	51.6
33.5	364	0.0231	63.8
47.0	185	0.0153	76.0
68.0	-0.108	0.0078	80.0
76.0	-0.187	0.0065	88.0
91.0	-0301	0.0050	92.1
101.5		0.0042	93.4

T. 813
T 699

k_1 (from graph) = 0.026

FIG. 2. EXPT. 4

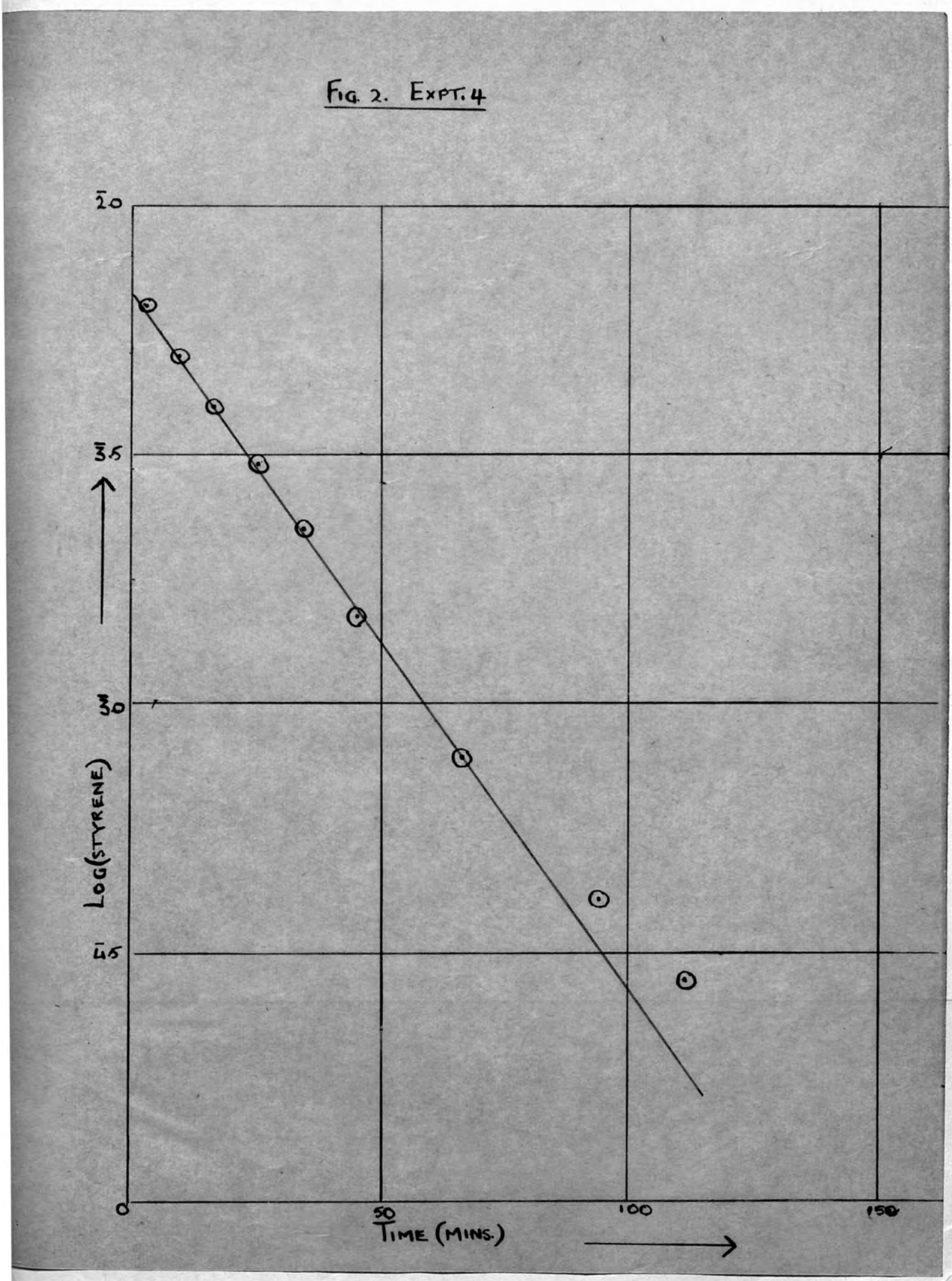
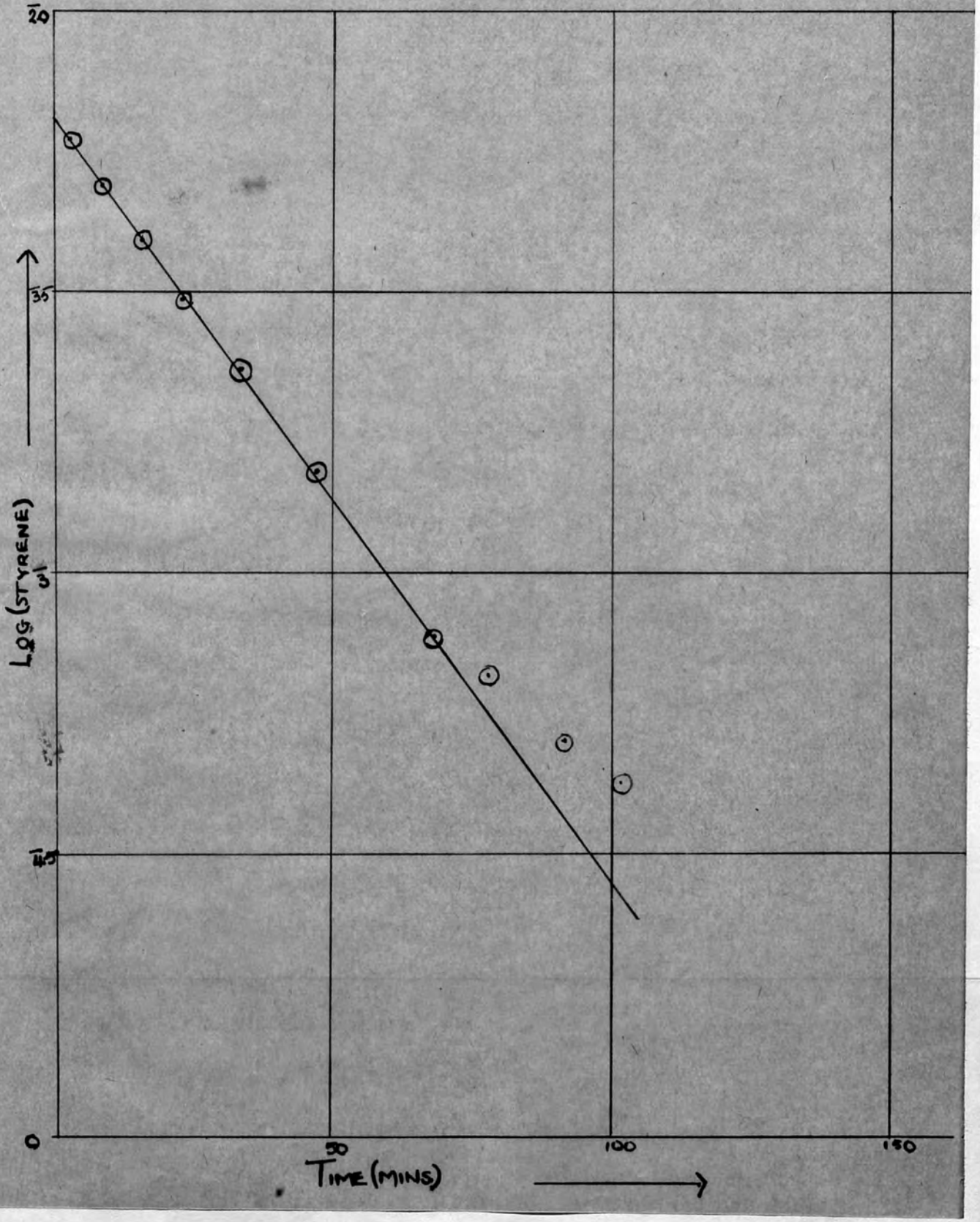


FIG. 3. EXPT. 5.



The Influence of styrene concentration.

Maintaining the hydrogen chloride at its saturated value and keeping the stannic chloride constant within a series, velocity measurements were carried out at different initial styrene concentrations.

There is good evidence to show that over the range of styrene concentration 0.03 - 0.2 M the rate of consumption of styrene is proportional to the concentration of styrene. (The term series is used to include those velocity measurements carried out with stannic chloride solution prepared from the same bulb.)

Experiment numbers 18, 19, 20 and 21 are a typical series showing the constancy of K_1 over a range of styrene concentration from 0.04 to 0.18 M and are quoted in full. (Tables 14,15,16,17, fig.4).

Table 18 summarises the evidence which led to the above conclusion. Individual velocity experiments are not described in full but each value of k_1 was determined graphically, using equation (1), as in the typical series.

Table 14

Experiment No. 18 Temperature 25°C.

Initial styrene - 0.106 M.

Initial hydrogen chloride - 0.145 M.

Stannic chloride - 0.0157 M.

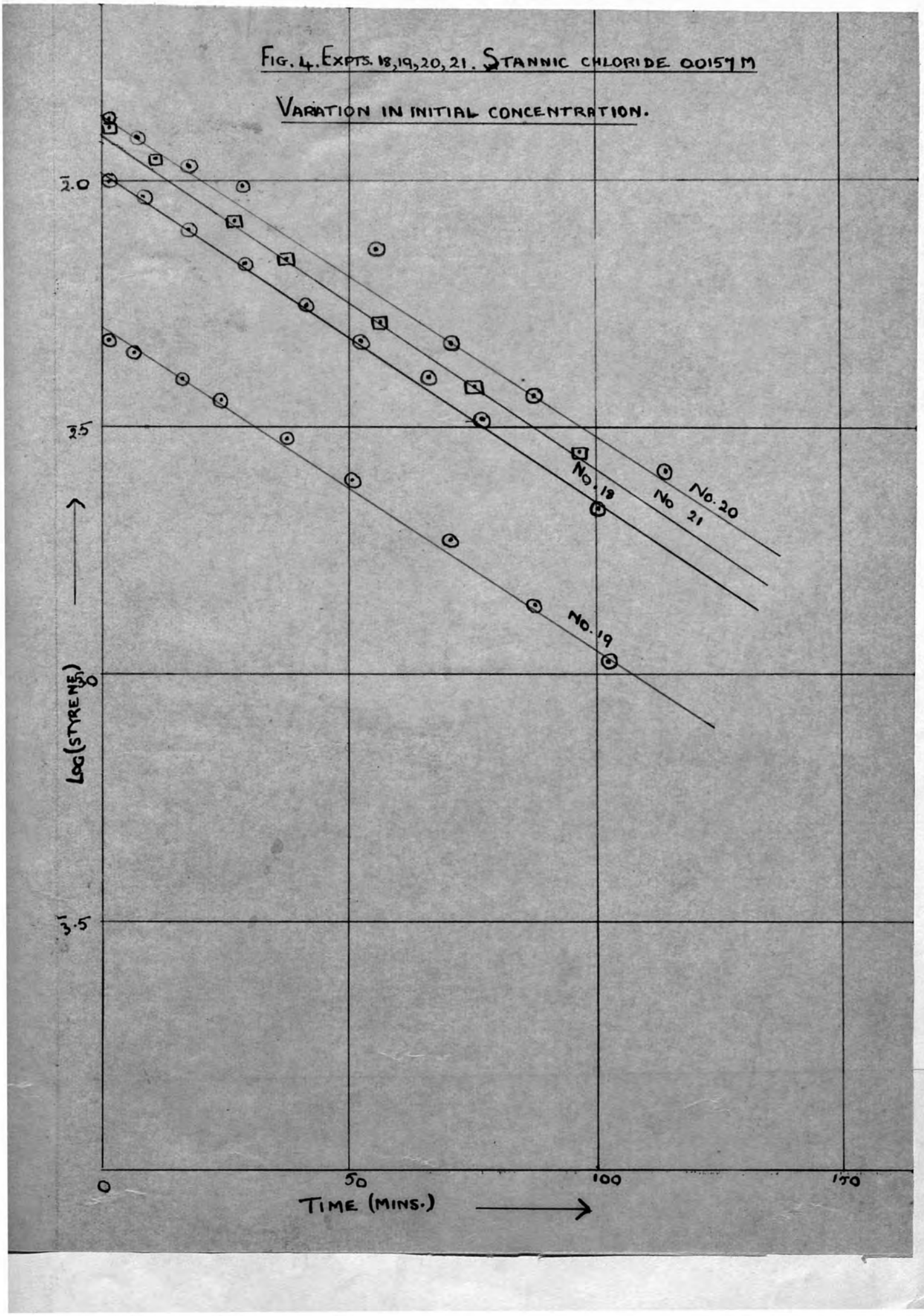


FIG. 4. EXPTS. 18,19,20,21. STANNIC CHLORIDE 00159 M
VARIATION IN INITIAL CONCENTRATION.
2.0
2.5
3.0
3.5
LOG (STYRENE)
No. 18
No 21
No. 20
No. 19
0
50
100
150
TIME (MINS.)

Table 14 (contd.)

Time (mins.)	Styrene (M)	% decomposition
2.5	0.102	3.8
9.0	0.0935	11.8
18.0	0.0810	23.6
20.75	0.0678	36.0
42.0	0.0559	47.2
53.0	0.0476	55.1
66.75	0.0399	62.3
77.25	0.0330	68.8
101.0	0.0211	80.1

k_1 (from graph) = 0.0151

Table 15

Experiment No. 19 Temperature 25°C

Initial Styrene - 0.0519 M

Initial Hydrogen chloride - 0.143 M

Stannic chloride - 0.015 M

log(a-x)100	Time (mins.)	Styrene (M)	% decomposition
0.715	0		
682	2.0	0.0481	7.3
654	7.0	0.0451	12.9
599	17.0	0.0397	23.5
559	24.75	0.0362	30.2
483	38.0	0.0304	41.4
396	51.0	0.0249	52.0
272	71.0	0.0187	64.0
140	87.5	0.0138	73.4
025	103.0	0.0106	79.5

k_1 (from graph) = 0.0146

Table 16

Experiment No. 20 Temperature 25°C

Initial Styrene - 0.139 M

Initial hydrogen chloride - 0.145 M

Stannic chloride - 0.0157 M

Time (mins.)	Styrene (M)	% decomposition
2.0	0.135	3.2
8.0	0.125	10.5
18.0	0.109	22.3
29.0	0.0939	32.7
56.0	0.0733	47.4
71.0	0.0473	66.1
88.0	0.0367	73.7
114.5	0.0263	81.2

k_1 (from graph) = 0.0151

Table 17

Experiment No. 21 Temperature 25°C

Initial styrene - 0.137 M.

Initial hydrogen chloride -0.145 M.

Stannic chloride - 0.0157 M.

$\log \frac{a}{a-x}$	Time (mins.)	Styrene (M)	% decomposition
1.137	0		
1.127	2.0	0.134	1.9
1.057	11.75	0.114	16.8
0.926	27.0	0.0843	38.4
0.848	38.0	0.0704	48.6
0.714	56.75	0.0518	62.1
0.584	76.0	0.0384	72.0
0.455	97.0	0.0285	79.1

k_1 (from graph) = 0.0156

Numbers 20 and 21 are duplicates. They were designed to test the stability of a stannic chloride solution in carbon tetrachloride saturated with hydrogen chloride. Expt.21 was carried out three days after Expt. 20.

Table 18 Variation with styrene ("flow" experiments)

Temperature 25°C

Expt.No.	Hydrogen chloride (M)	Styrene (M)	k_1	k_1/ca ✓
Stannic chloride - 0.0109 M				
45	0.143	0.0365	0.0095	6.1
46	0.143	0.0335	0.0093	6.0
47	0.146	0.185	0.0097	6.1
48	0.146	0.185	0.0096	6.0
Stannic chloride - 0.0125 M				
28	0.143	0.0324	0.0130	7.3
29	0.145	0.136	0.0125	6.9
32	0.145	0.146	0.0125	6.9
Stannic chloride - 0.0126 M				
38	0.146	0.178	0.0133	7.2
42	0.151	0.395	0.0146	7.7
Stannic chloride - 0.0152 M				
22	0.145	0.133	0.0157	7.1
24	0.145	0.152	0.0162	7.4
25	0.144	0.0386	0.0154	7.0
Stannic chloride - 0.0156 M				
18	0.145	0.102	0.0151	6.7
19	0.144	0.0486	0.0146	6.5
20	0.145	0.136	0.0151	6.7
21	0.145	0.137	0.0156	7.4

Table 18 also shows the reproduceability of series.

"Flow" experiments at 0°C.

Similar velocity measurements were carried out at 0°C using a slightly simplified apparatus (see Part IIB).

The Influence of Styrene Concentration

As at 25°C the rate of consumption of styrene is proportional to the styrene concentration. Table 19 shows the constancy of k_1 over the range of initial styrene. Concentration 0.03 - .1 M.

Table 19.

Temperature - 0°C

Stannic chloride - 0.0224 M.

Hydrogen chloride - 0.275 M.

Expt.No.	Initial styrene	k_1	$k_1/ca.$
149	0.030	0.0102	1.66
152	0.101	0.0098	1.59

Increase in Styrene Concentration

At higher styrene concentrations the reaction rates are increased more than could be accounted for by the increase in the saturation concentration of hydrogen chloride in carbon tetrachloride (cf. expts. 67-70, Tables 21 and 18), also directly in Table 20.) Since the addition is followed by styrene consumption an apparent increase in rate would be reasonable if appreciable amounts of polymer were formed during a reaction. However, even at 1.7 M initial styrene (see Part III A, Table 1, expt. 14) there was up to 50% formation of α-phenylethyl chloride. In the series 67 - 70 (Table 21) individual velocity measurements are first order with respect to styrene and k_1 is proportional to the square of the catalyst concentration (fig. 5A) In the series 71 - 75 immediately following, for

no easily apparent reason, the rate seemed independent of catalyst concentration though individual measurements remained first order. (A typical example from each series is quoted in full. Tables 22, 23, fig.5a).

In later experiments, and, as far as could be judged with no change in the initial conditions, two successive series, (expts. 81 - 84 and 98 - 101, Table 21) the rate was further increased and the reaction became zero order with respect to styrene up to between 70 and 80% consumption of styrene: again, a typical example from each series is quoted in full (Tables 24 and 25, fig.6).

Also, k_o is approximately proportional to stannic chloride (fig.7). The significance of these anomalous results is discussed in the next section.

Table 20.

Temperature - 25°C k_1 is the first order velocity constant

Expt.No.	HCl (M)	Initial styrene	k_1 (from graph)	k_1 / ca.
Stannic chloride = 0.0046 M				
36	0.145	0.096	0.0044	6.6
X 34	0.157	0.663 x/	0.0064	8.9
35	0.170	(1.380) ?	0.0109	13.9 ?
Stannic chloride = 0.010 M				
85	0.144	0.0672 x	0.0077	5.3
86	0.143	0.0440	0.0079	5.5
87	0.161	0.862	0.0177	11.0
89	0.170	1.399	0.0282	16.6

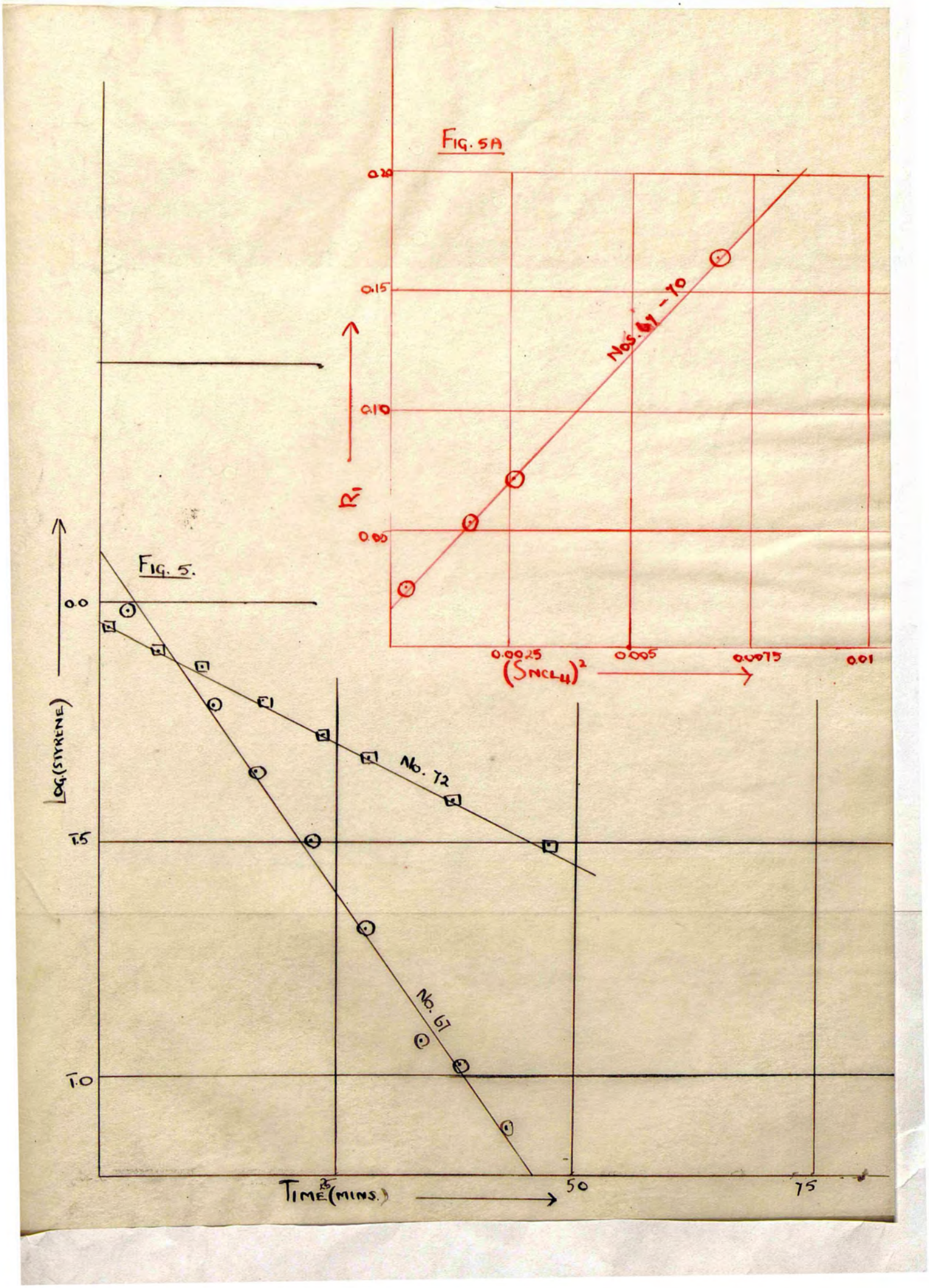


FIG. 5A
0.20
0.15
0.10
0.05
R_i
Nos. 67 - 70
0.00
0.0025
0.005
0.0075
0.01
$(SnCl_4)^2$
FIG. 5.
0.0
LOG (STYRENE)
1.5
1.0
No. 72
No. 67
25
50
75
TIME (MINS.)

FIG. 7

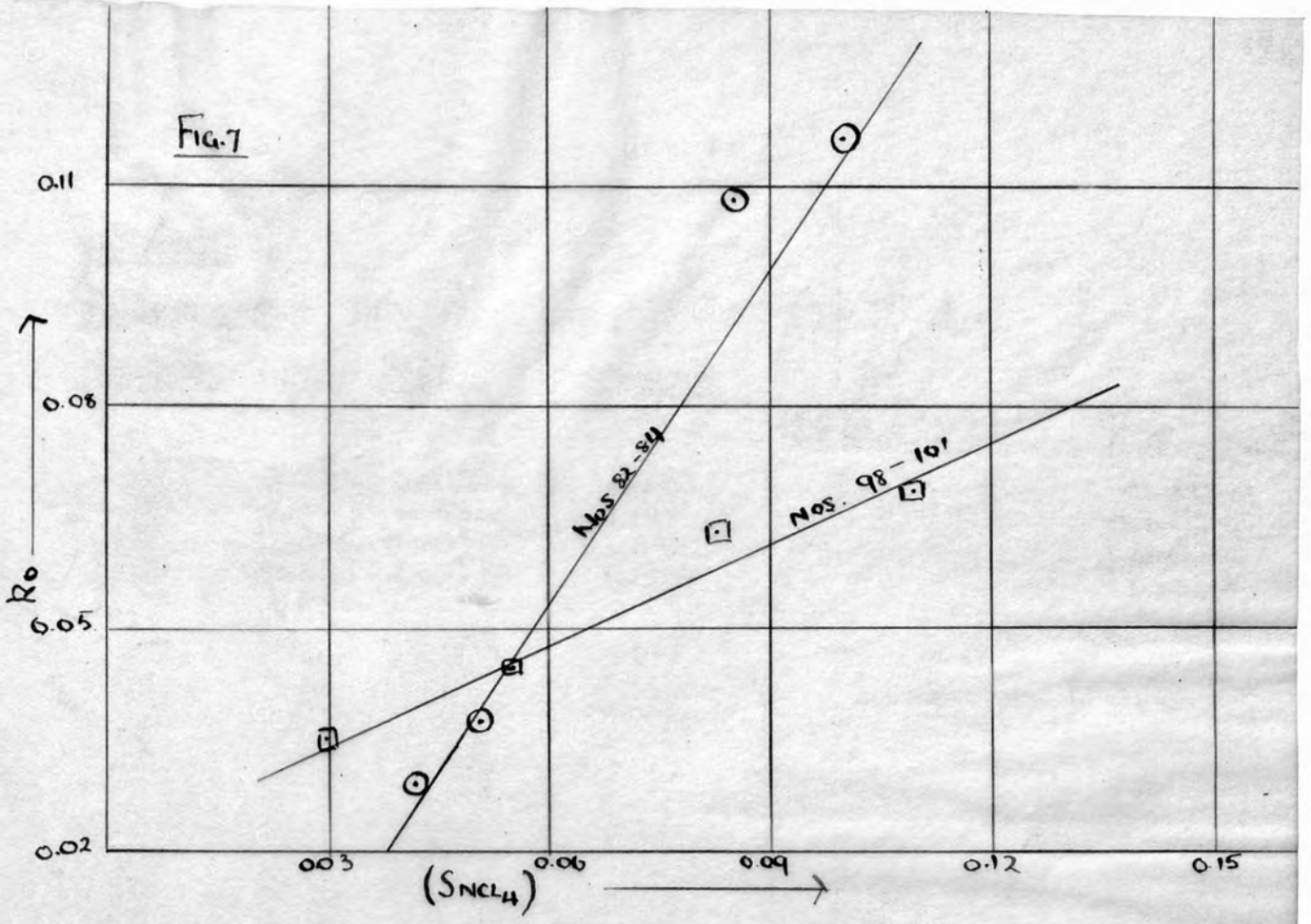

0.11
0.08
Ro
0.05
0.02
003
0.06
0.09
0.12
0.15
(SNCL4)
NOS 82-84
NOS. 98-101

FIG. 6

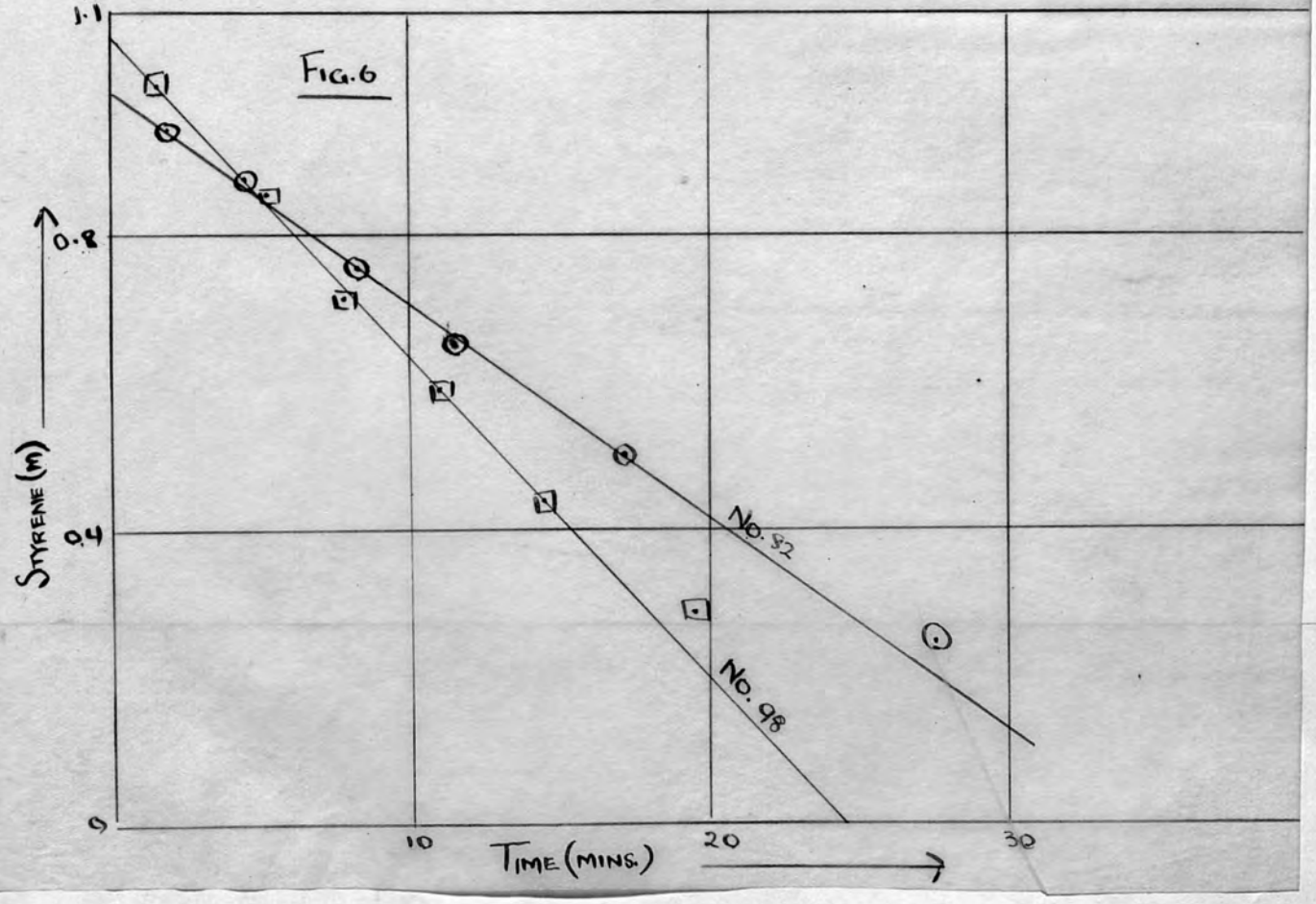

1.1
0.8
0.4
0
STYRENE (M)
10
20
30
TIME (MINS.)
No. 82
No. 98

Table 21

Temperature - 25°C

Expt.No.	HCl (M)	$SnCl_4$ (M)	Styrene (M)	k_o (from graph)		k_1 (from graph)
					k/ca.	
68	0.166	0.0184	1.141		8.05	0.0246
67	0.165	0.0412	1.096		7.71	0.0524
70	0.165	~~0.0508~~ 0.046	1.022		8.52	0.0714
69	0.163	0.0826	0.957		12.18	0.164
71	0.165	0.0249	1.070		5.9	0.0241
75	0.165	0.0249	1.070			0.0308
73	0.165	0.0375	1.047			0.0248
74	0.162	0.0428	0.933			0.0266
72	0.162	~~0.0529~~ 0.049	0.933		2.5	0.0239
82	0.163	0.0424	1.016	0.0289	4.1	
84	0.167	0.0508	1.116	0.0374		
81	0.163	0.0848	1.016	0.108	6.6.1	
83	0.167	0.1017	1.116	0.116		
101	0.165	0.0300	1.042	0.0348		
98	0.163	0.0551	0.973	0.442		
99	0.163	0.0826	0.973	0.0625		
100	0.163	0.1102	0.961	0.0677		
57	0.162	0.0363	0.923	-	6.02	0.0354

k_o - zero order velocity constant

k_1 - first order velocity constant

Table 22

Expt. No. 67 Temperature - 25°C

Initial styrene (M) - 1.096

Hydrogen chloride (M) - 0.165

Stannic chloride (M) - 0.0412

Time (mins.)	Styrene (M)	% decomposition
3.5	0.9614	12.3
12.0	0.6100	44.3
16.25	0.4396	59.7
22.0	0.3197	70.9
27.75	0.2050	81.3
33.5	0.1196	89.1
37.5	0.1074	90.2
42.5	0.0781	93.0

k_1 (from graph) = 0.0524

Table 23

Expt.No. 72 Temperature - 25°C

Initial styrene (M) - 0.933

Hydrogen chloride (M) - 0.162

Stannic chloride (M) - 0.0599

Time (mins)	Styrene (M)	% decomposition
1.25	0.8956	3.97
6.25	0.8003	14.3
10.75	0.7350	21.2
17.25	0.6173	34.0
23.0	0.5295	43.2
28.0	0.4710	49.5
37.0	0.3855	58.7
47.0	0.3075	77.7

k_1 (from graph) = 0.0239

Table 24

Expt. No. 82 Temperature - 25°C

Initial styrene (M) - 1.016

Hydrogen chloride (M) - 0.163

Stannic chloride (M) - 0.0424

Time (mins.)	styrene (M)	% decomposition
2.0	0.9442	7.1
4.5	0.8714	12.3
8.25	0.7496	26.2
11.5	0.6499	36.1
17.25	0.4964	51.2
27.5	0.2410	76.3

k_o (from graph) = 0.0289

Table 25

Expt. No. 98 Temperature - 25°C

Initial Styrene (M) - 1.070

Hydrogen chloride (M) - 0.163

Stannic chloride (M) - 0.0551

Time (mins.)	Styrene (M)	% decomposition
1.5	1.004	6.2
5.25	0.8505	20.4
7.75	0.7136	33.3
11.0	0.5890	45.0
14.5	0.4375	59.0
19.5	0.2800	73.4
27.0	0.1173	89.1

k_o (from graph) = 0.0442

The Influence of Hydrogen Chloride Concentration

In order to vary the initial concentration of hydrogen chloride, the use of saturated hydrogen chloride solutions must necessarily be abandoned. It has proved to be very difficult to prepare reliable hydrogen chloride solutions in carbon tetrachloride & other concentrations, owing to the extreme volatility of the hydrogen chloride. This difficulty has already been illustrated in the experimental section (Part II). It has not been possible to vary the initial concentration in the same systematic way as the styrene concentration, but some direct variation experiments have been made at 0°C. At this temperature, the saturation concentration of hydrogen chloride is 0.275 M, compared with 0.143 M at 25°C.

The following evidence indicates that the rate of consumption of styrene is proportional to the concentration of hydrogen chloride.

1. "Closed Tube" Experiments at 25°C.

In the following experiments, carried out by the "closed tube" method (described in Part II), the individual readings were each obtained from an independent reaction mixtures (Tables 26, 27, 28, 29).

Table 26

Expt. No. 138 Temperature - 25°C.

Initial styrene - 0.0301 M

Initial hydrogen chloride - 0.0712 M

Stannic chloride - 0.0117 M

Time (mins.)	% conversion	k_2
33.5	10.0	0.047
50.25	11.2	0.053
50.75	16.0	0.050
51.25	19.0	0.062
72.5	26.0	0.058
76.25	27.4	0.065

Average k_2 = .056

Table 27

Expt. No. 139 Temperature - 25°C

Initial Styrene - 0.0301 M

Initial hydrogen chloride - 0.0712 M

Stannic chloride - 0.0117 M.

Time (mins.)	% conversion	k_2
59	21.3	0.060
63	26.9	0.074
80.25	29.3	0.065
86.5	29.3	0.060

Average k_2 = 0.065

Tables 26 and 27 also show that series are reproduceable.

Table 28

Expt. No. 140 Temperature - 25°C

Initial styrene - 0.0301 M

Initial hydrogen chloride - 0.0712 M

Stannic chloride - 0.0086 M.

Time (mins.)	% conversion	k_2
49.5	12.3	0.038
80.25	23.2	0.045
129.75	39	0.037
158.0	42	0.049
109.0	37.5	0.039
181.25	41.5	0.053
222.5	42.8	0.039

Average k_2 = 0.043

Table 29

Expt. No. 145 Temperature - 25°C

Initial Styrene - 0.0284 M

Initial Hydrogen chloride - 0.072 M

Stannic chloride - 0.0111 M

Time (mins.)	% conversion	k_2
23	9.2	0.062
42.25	19.0	0.072
89.25	31.0	0.062
145.75	55.3	0.088

Average k_2 = 0.071

In these experiments, the constants k_2 are calculated from the equation

$$k = \frac{2.3}{t(a-b)} \log \frac{b}{a} \frac{a-x}{b-x}$$

where a = initial hydrogen chloride concentration

b = initial styrene concentration

x = concentration of styrene consumed in time t.

Within rather wide limits of error, the velocity coefficent k_2 remains constant up to about 50% conversion for given initial conditions.

If it is permissible to write

$$-d\left[C_8H_8\right]/dt = k\left[SnCl_4\right]\left[HCl\right]\left[Styrene\right] \quad \ldots\ldots(2)$$

together with $$-d\left[C_8H_8\right]/dt = k_1\left[Styrene\right] \quad \ldots\ldots\ldots\ldots(3)$$

for constant $\left[SnCl_4\right]$ and $\left[HCl\right]$

and $$-d\left[C_8H_8\right]/dt = k_2\left[Styrene\right]\left[HCl\right] \quad \ldots\ldots\ldots\ldots(4)$$

for constant $\left[SnCl_4\right]$

Then $$k_1/\left[HCl\right] = k_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

and $$k_2/\left[SnCl_4\right] = k \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

From experiments 138 to 145 (Tables 26 - 29), equation (4) holds for given initial conditions. The validity of (6) is examined in a later section by plotting values of $k_1/\left[HCl\right]$ $(= k_2)$ against $\left[SnCl_4\right]$ for a series of "flow" experiments, all at approximately 0.14 M hydrogen chloride concentration, it is also tested at 0°C where the hydrogen chloride concentration is 0.275 M. (the hydrogen chloride being held constant during a velocity measurement by saturation.)

The mean values of k_2 from experiments 138-140, all with initial hydrogen chloride 0.0712 M fall very nearly on the same curve (see fig.9, red points), which indicates that

equation (4) is valid for changes of initial hydrogen chloride concentration from 0.14 M to 0.07 M.

2. In experiments 138 - 145, quoted above, the hydrogen chloride (0.0712 M) is initially in excess over stannic chloride (0.0086 - 0.0117 M). When hydrogen chloride is in only small excess over stannic chloride (Expt. 143, Table 30), the velocity coefficient k_2 rises with increasing consumption of styrene and the rise becomes marked when stannic chloride is in excess over the initial hydrogen chloride (expts. 142 and 146, Tables 31 and 32), indicating that the reaction order is now less than 2.

Table 30

Expt. No. 143 Temperature - 25°C

Initial styrene - 0.0284 M

Initial hydrogen chloride - 0.0284 M

Stannic chloride - 0.0193 M

Time (mins.)	% conversion	k_2
14.75	3.1	0.0746
29.25	4.9	0.0635
56.5	11.4	0.0802
89.75	18.8	0.0906
120	23.8	0.0910
176	32.4	0.0955

Table 31

Expt. No. 142 Temperature - 25°C

Initial styrene - 0.0285 M

Initial hydrogen chloride - 0.0284 M

stannic chloride - 0.0414 M

Table 31 (contd.)

Time (mins.)	% conversion	k_2
53.5	16.9	0.133
82.75	25.0	0.141
108.0	34.8	0.175
137.5	58.7	0.365

Expt. No.142(a)

Initial styrene - 0.0285 M

Initial hydrogen chloride - 0.0712 M

Stannic chloride - 0.0414 M

Time (mins.)	% conversion	k_2
40.25	25.7	0.11
89.25	63.4	0.18

Incidentally, Experiment nos. 142 and 142(a) give some direct indication of the validity of equation (4). k_2 is at least of the same order over the range of initial hydrogen chloride from 0.0285 M to 0.0712 M.

Table 32

Expt. No. 146 Temperature - 25°C

Initial styrene - 0.0284 M

Initial hydrogen chloride - 0.0284 M

Stannic chloride - 0.044

Time (mins.)	% conversion	k_2
16.25	4.6	0.106
44.25	17.9	0.174
60.0	26.8	0.208
85.75	34.2	0.211
124.5	50.3	0.287

The significance of this behaviour is discussed later, but it may be noted that the reaction is approximately first order with respect to styrene. The slope of the plot of log(a - x) against time for No.146 gives

$$k_1 = 0.00523$$

whence $k_2 = k_1/HCl = k_1/0.0284 = 0.184$

This value falls on the general plot of k_1/HCl at 0.14 M hydrogen chloride against stannic chloride. This implies that, with stannic chloride concentration 0.0444 M, equation (4) is valid for change of initial hydrogen chloride concentration from 0.0284 M to 0.14 M. This relationship may, however, be coincidental.

3. "Closed tube" experiments at 0°C.

"Closed tube" experiments were made at 0°C for different hydrogen chloride concentrations (Tables 33 and 34).

Table 33

Expt. No. 192 Temperature - 0°C

Initial styrene - 0.0294 M

Initial hydrogen chloride - 0.0918 M

Stannic chloride - 0.0179 M

Time (mins.)	% conversion	k_2
78	17.0	0.0269
98	27.0	0.0263
148.5	26.0	0.0245
227	30.9	0.0188

Average k_2 - 0.0259 (0.0241)

(The figure in parenthesis includes the value of k_2 at 227 minutes

the latter was omitted because a leakage of hydrogen chloride was suspected.)

Table 34

Expt. No. 193 Temperature - 0°C.

Initial styrene - 0.0294 M

Initial hydrogen chloride - 0.1837 M

Stannic chloride - 0.0179 M

Time (mins.)	% conversion	k_2
68.75	31.9	0.0312
94	38.1	0.0282
173	51.7	0.0240
215	56.8	0.0243

Average k_2 = 0.0269

Within the errors of experiment, equation (4) is justified for each of these experiments, and the mean velocity coefficient k_2 is the same for the two experiments. The values of k_2 are also consistent with the results of other "flow" experiments designed to test the influence of stannic chloride at 0 C. (Table 39). From Fig.10 it is seen that equation (2) is valid from a change in stannic chloride concentration from 0.01 to 0.04 M.

Consequently the relation $k_2/[SnCl_4] = k$ holds, within a limited range.

Table 35

Expt. No.	192	193	148-151
Initial hydrogen chloride	0.0918	0.0184	0.275
k_2	0.026 (0.024)	0.027	-
$k_2/[SnCl_4]$	1.45	1.52	1.63

Nos. 148 to 151 were "flow experiments."

From this table it appears that the rate of consumption of styrene is proportional to hydrogen chloride concentration for a change in initial hydrogen chloride from 0.0918 to 0.275 M.

Another pair of "closed tube" experiments (156 to 157) (Tables 36 and 37) confirms the conclusion that equation (4) is valid for change of initial hydrogen chloride from 0.0612 M to 0.153 M, but the corresponding values of $k_2 / [SnCl_4]$ are, for some reason, inconsistent with the results of Table 35.

Table 36

Expt. No. 156 Temperature - 0°C.

Initial styrene - 0.0306 M

Initial hydrogen chloride - 0.153 M

Stannic chloride - 0.0141 M

Time (mins.)	% conversion	k_2
21.75	10.1	0.0348
65.0	30.9	0.0416
95.25	41.9	0.0428
120.75	46.5	0.0394
141.5	48.0	0.0355
183.25	57.8	0.0381

Average k_2 - 0.0387

$k_2 / [SnCl_4]$ - 2.74

Table 37

Expt. No.157 Temperature - 0°C

Initial styrene - 0.0306 M

Initial hydrogen chloride - 0.0612 M

Stannic chloride - 0.0141 M

Table 37 (contd.)

Time (mins.)	% conversion	k_2
32.5	6.9	0.0406
63.25	11.7	0.0373
145.0	22.0	0.0337
198.0	27.4	0.0437

Average k_2 - 0.388

$k_2/[SnCl_4]$ - 2.68

Variation with stannic chloride

In "flow" experiments at 25°C with the initial styrene concentration kept below 0.15 M the catalyst concentration was varied. The results are summarised in Table 38. The experiments between the horizontal lines in Table 38 are velocity measurements in a series, i.e. making use of the same stannic chloride bulb. k_1, the first order reaction constant, was obtained graphically as described earlier. The different values of k_2 are plotted against catalyst concentration in fig.9. Doubly ringed points indicate where velocities within a series have been averaged (cf. Table 38) and treble rings were series have been averaged. Red points were average values of k_2 from "closed tube" experiments described earlier (Tables 26, 27, 28, 29).

Up to 0.015 M stannic chloride, equation (6) was valid, i.e. k_2 is directly proportional to catalyst concentration. However, above 0.015 M, this simple relationship does not hold. (fig.9).

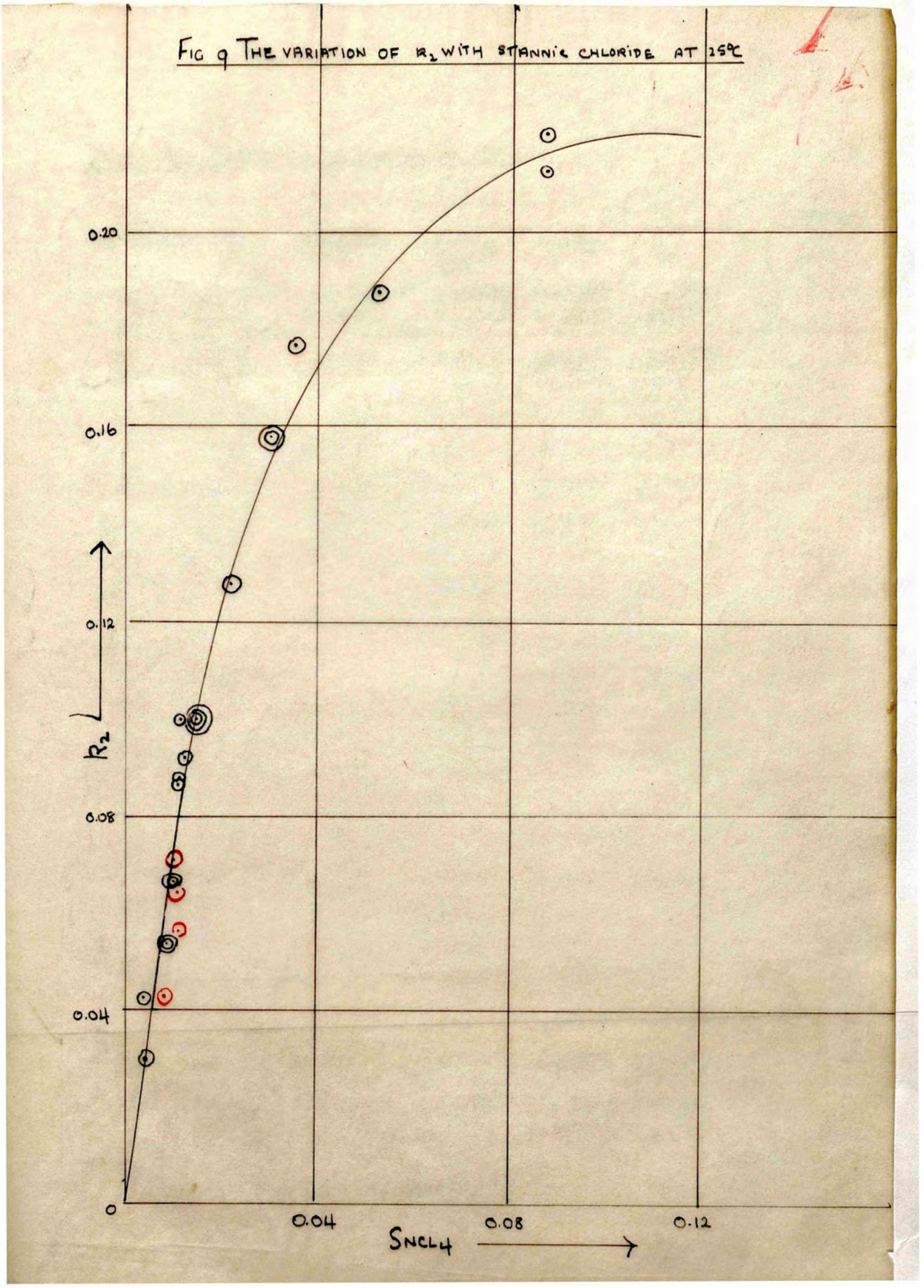


FIG 9 THE VARIATION OF R_2 WITH STANNIC CHLORIDE AT 25°C
0.20
0.16
0.12
0.08
0.04
0
R_2
0.04
0.08
0.12
$SnCl_4$

Table 38 "Flow" experiments at 25°C.

Expt. No.	HCl (M)	Styrene (M)	$SnCl_4$ (M)	k_1	$\frac{k_1}{HCl} = k_2^*$	Average k_2
- 33	0.144	0.0964	0.0046	0.0062	0.0430	
- 36	0.144	0.0964	0.0046	0.0043	0.0300	
- 85	0.144	0.0672	0.0998	0.0771	0.0535	
- 86	0.143	0.0442		0.0787	0.0550	0.0543
I 45	0.143	0.0365	0.0109	0.00950	0.0664	0.0666
I 47	0.143	0.0335		0.00957	0.0669	
- 8	0.143	0.0455	0.0116	0.0124	0.0867	
28	0.143	0.0324	0.0125	0.0153	0.107	
29	0.146	0.136		0.0125	0.0874	
126 → - 12	0.144	0.127	0.0132	0.0133	0.0924	
I 22	0.146	0.133	0.0152	0.0157	0.108	
I 24	0.146	0.152		0.0162	0.111	0.108
I 25	0.144	0.0386		0.0154	0.105	
- 16	0.143	0.0329	0.0154	0.0139	0.0972	
- 17	0.143	0.0574		0.0152	0.106	0.102
I 18	0.145	0.102	0.0156	0.0151	0.105	
I 19	0.143	0.0488		0.0146	0.101	
I 20	0.145	0.130		0.0151	0.105	0.105
I 21	0.145	0.137		0.0156	0.108	
- 11	0.144	0.0994	0.0226	0.0184	0.128	
- 2	0.144	0.0604	0.0312	0.0225	0.156	0.158
- 3	0.144	0.0604		0.0230	0.160	
- 60	0.144	0.0328	0.0363	0.0255	0.177	
- 1	0.144	0.0604	0.0402	0.0201	0.136	
- 10	0.144	0.058	0.0539	0.0271	0.188	
- 4	0.144	0.0638	0.0887	0.0317	0.220	
- 5	0.144	0.0638		0.0306	0.212	

* Compare equation (5)

Similar experiments were carried out at 0°C where the saturation concentration of hydrogen chloride in carbon tetrachloride is 0.275 M. (Table 39, fig.11). Red points (nos. 181 and 183) were "closed tube" experiments at 0.0918 M initial hydrogen chloride (Table 40) and nos. 192-193 were average values of the constant in "closed tube" experiments described earlier (Table 35). Here it is difficult to judge where the simple k_2/stannic chloride relationship breaks down, but it tends to hold over a wider range of catalyst concentration (fig.11).

Table 39 "Flow experiments.

Temperature - 0°C

Hydrogen chloride (M) - 0.275

Expt.No.	Styrene (M)	$SnCl_4$ (M)	k_1 ($min.^{-1}$)	$\frac{k_1}{HCl} = k_2$ ($min.^{-1}$)
150	0.0306	0.010	0.0043	0.0156
148	0.0300	0.0122	0.0057	0.0207
149	0.0300	0.0224	0.0105	0.0382
151	0.0302	0.0384	0.0165	0.0600

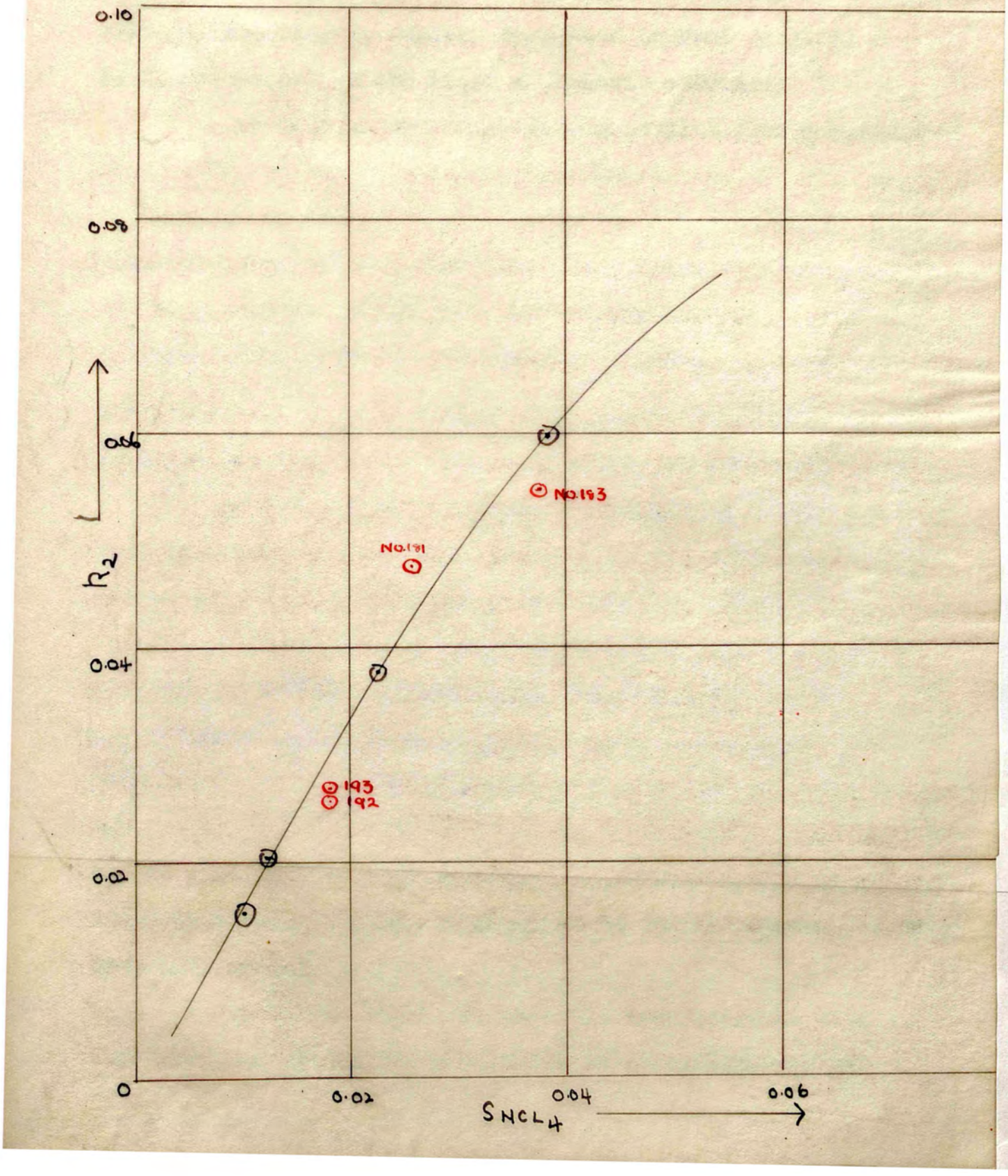
Table 40 "Closed tube" experiments

Temperature - 0°C

Hydrogen chloride (M) - 0.0918

Expt. No.	Styrene (M)	$SnCl_4$ (M)	k_2 ($min.^{-1}$)	k_2/C
181	0.0303	0.0251	0.048	1.91
183	0.0302	0.0377	0.055	1.46

FIG 10. THE VARIATION OF R_2 WITH STANNIC CHLORIDE AT 0°C



Part III B (ii)

The mechanism for the catalytic addition of hydrogen chloride to styrene suggested in Part II A(ii) is now discussed in the light of kinetic evidence.

Stannic chloride may form a complex with a hydrogen chloride b styrene. Complex formation between stannic chloride and hydrogen chloride has been assumed in the scheme of reactions proposed to account for the products of the reaction. But since styrene polymerises in the presence of stannic chloride (in the absence of hydrogen chloride) styrene must be capable of some interaction with stannic chloride. Kinetic evidence does not decide clearly between the alternatives.

However, a seems probable for the reasons given when discussing the reaction products. A further indication in favour of a is provided by the 'flow' results at 0°C (Fig.10). With hydrogen chloride concentration constant at 0.275 M and initial styrene 0.03M, the constant, k_1, is proportional to the stannic chloride over the range 0.01 to above 0.038. If a complex between styrene and stannic chloride were involved in the rate determining step it would, perhaps, be odd that this proportionality should persist throughout the range in which the ratio of catalyst to initial styrene changes from 0.33 to 1.3.

If in the first instance the assumption is made, that provided the hydrogen chloride is in excess over the

initial styrene , the rate determining step involves only the complex (a) and styrene, then the mechanism would be represented by

$$HCl + SnCl_4 \rightleftharpoons H^+SnCl_5^- \qquad 1$$

$$CHPh = CH_2 + H^+SnCl_5^- = C^+HPh-CH_3 + SnCl_5^- \qquad 2$$

and 2 is the rate determining step.

Let a = initial hydrogen chloride concentration

b = initial styrene concentration

c = stannic chloride

and denote $[H^+SnCl_5^-]$ by [complex.]

Let the fraction λ of stannic chloride be present at complex.

Then for the equilibrium 1

$$K = \frac{\lambda c}{(a - \lambda c)(c - \lambda c)}$$

and for the reaction rate

$$-d[\text{styrene}]/dt = k\,[\text{styrene}]\,[\text{complex}]$$
$$= k\,[\text{styrene}]\,\lambda c$$

k = the theoretical velocity constant. Experimentally, for a given value of C:-

$$-d[\text{styrene}]/dt = k_2\,[\text{styrene}][HCl]$$

(Part III B(i) equation 4)

Equating the theoretical and experimental rates

$$k_2\,[\text{styrene}][HCl] = k\,[\text{styrene}]\,\lambda c$$

and $$k_2 = \frac{k}{[HCl]}\,\lambda c \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3$$

The experimental order of the reaction with respect to styrene follows directly from the above discussion.

The Variation of k_2 with hydrogen chloride.

The experimental observations are:-

a) When hydrogen chloride concentration is greater than the stannic chloride, k_2 is independent of hydrogen chloride over the range a = 0.07 to 0.14M.

b) When hydrogen chloride falls below the catalyst concentration or is equal to it, then the reaction order falls from 2 towards the value 1.

Considering first the situation a

Let $c = y$, and let a_n and y_n be corresponding values for initial hydrogen chloride and for the concentration of complex respectively at a fixed value of stannic chloride.

Now if k_2 is to be independent of a, then from - 3

$$k_2 = \frac{ky_1}{a_1} = \frac{ky_2}{a_2}$$

so

$$\frac{y_1}{a_1} = \frac{y_2}{a_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

$$y_2 = y_1 \frac{a_2}{a_1}$$

Also from 1 :-

$$K = \frac{y_1}{(a_1 - y_1)(c - y_1)} = \frac{y_2}{(a_2 - y_2)(c - y_2)}$$

$$= \frac{y_1 \frac{a_2}{a_1}}{(a_2 - \frac{a_2}{a_1} y_1)(c - \frac{a_2}{a_1} y_1)}$$

Let $\frac{a_2}{a_1} = p$

then $p(a_1 - y_1)(c - y_1) = (a_2 - py_1)(c - py_1)$

$$p(a_1c - a_1y_1 - cy_1 + y_1^2) = (a_2c - pa_2y_1 - pcy_1 + p^2y_1^2)$$

$$pa_1c - pa_1y - pcy_1 + py_1^2 = a_2c - pa_2y_1 - pcy_1 + p^2y^2$$

$$pa_1 = a_2$$

$$a_2c - a_2y - pcy_1 + py_1^2 = a_2c - pa_2y_1 - pcy_1 + p^2y_1^2$$

$$p^2y_1^2 - py_1^2 = pa_2y_1 - a_2y_1$$

$$y_1^2p(p-1) = y_1a_2(p-1)$$

$$y_1^2 = \frac{a_2y_1}{p}$$

$$y_1^2 = a_1y_1$$

(i) $y_1 = 0$ and $y_2 = p_1y_1$ $\quad y_2 = 0$

or $y_1 = a_1$ $\quad y_2 = a_2$ $\Big\}$ — 6

For $a_2 > a_1 > c$ only the solution $y_1 = 0$ is admissable.

Thus, when hydrogen chloride is present in excess over stannic chloride, the experimental observations described by 2 can only be true if λ is small, that is, if very little of the stannic chloride is converted into complex with hydrogen chloride. On the other hand, if stannic chloride is in excess over hydrogen chloride, the same result is obtained if hydrogen chloride is almost completely converted to complex. However, under these conditions equation 2 is observed experimentally not to hold.

These conclusions are confirmed by arithmetic tests using arbitrary values of the equilibrium constant, K, from equation 1 . Two extreme values, i.e., K = 1 and K = 100, are taken in an attempt to test whether the experimental results can be reproduced taking very small or large values of K. λ is calculated from equation 1 for different values

of hydrogen chloride and is substituted in 3 giving theoretical k_2 in terms of k. This is done at stannic chloride concentrations that satisfy conditions a and b respectively. The results are summarised in table 1.

Table 1

a	c	λ	λc	k_2	Ratio
K = 1					
0.143	0.0100	0.125	0.00125	0.0091k)	1.08
0.0715	0.0100	0.07	0.0007	0.0098k)	
0.0284	0.0444	0.125	0.0056	0.195k)	0.88
0.0142	0.0444	0.055	0.0024	0.172k)	
K = 1					
0.143	0.0100	0.92	0.0092	0.0643)	1.90
0.0715	0.0100	0.87	0.0087	0.122)	
0.0284	0.0444	0.452	0.0199	0.706)	1.09
0.0142	0.0444	0.246	0.0109	0.769)	

It is evident that the second order reaction for $a > c$ and $a = 0.07 - 0.14M$ is reproduced only by using a small value of K.

Neither a small nor a large value of K will reproduce the reduction of order observed for the condition $a < c$, but it is to be noted that styrene and hydrogen chloride were present in equal concentrations in these experiments: and it has already been pointed out that reactions other than simple addition of hydrogen chloride to the styrene may become

prominent if hydrogen chloride is not present in excess over styrene.

The Variation of k_2 with stannic chloride

Experimentally, the variation of k_2 with catalyst concentration is shown in figs. 9 and 10. Fig.9 consists of an initial approximately linear portion for the range c = 0 - 0.01M followed by a portion in which k_2 rises less than linearly with rise in c.

In the 'flow' experiments hydrogen chloride is maintained throughout at its saturated value. So equations 1 and 3 become

$$K = \frac{\lambda c}{(a-\lambda c)(c-\lambda c)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 7$$

$$\text{and } k_2 = \frac{k}{a}\lambda c \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 8$$

in which a = constant = 0.14M at 25°. In the range c = 0 - 0.01M k_2 is approximately proportional to c. This result may be reconciled with the simple theory in more than one way.

The result clearly follows if λ tends to 1 at low catalyst concentrations.

$$k_2 \text{ tends to } \frac{k}{a}\, c$$

Also qualitatively it would seem reasonable that the curve should depart from linearity as the catalyst concentration increased. The argument below makes this point clear for

large values of K.

Put $\lambda c = \frac{k_2 a}{k}$ into 7

$$K\left(a - \frac{k_2 a}{k}\right)\left(c - \frac{k_2 a}{k}\right) = \frac{k_2 a}{k}$$

$$= Kack^2 - Kak_2 ka - Kak_2 kc + Ka^2 k_2^2 - ak_2 k = 0$$

Differentiating with respect to c and simplifying, it follows that

$$\frac{dk_2}{dc} = \frac{Kakk_2 - Kk^2 a}{aKa^2 k_2 - Ka^2 k - ak - Kkac} \quad \ldots\ldots\ldots\ldots 10$$

Again, put $k_2 = \frac{k\lambda c}{a}$

$$\frac{dk_2}{dc} = \frac{k^2(a - \lambda c)}{ack(1-2\lambda) + a^2 k + \frac{ak}{K}} \quad \ldots\ldots\ldots\ldots 11$$

If K is very large this approximates to:-

$$\frac{dk_2}{dc} = \frac{k^2(a - \lambda c)}{ack(1-2\lambda) + a^2 k}$$

This simplifies to

$$\frac{dk_2}{dc} = \frac{k}{a}\left[\frac{1}{\frac{1-\lambda}{\frac{a}{c}-\lambda} + 1}\right] \quad \ldots\ldots\ldots\ldots 12$$

Now when $\lambda \rightarrow 1$

$$\frac{dk_2}{dc} = \frac{k}{a} \text{ as before} \quad \ldots\ldots\ldots\ldots 13$$

as stannic chloride increases, consider the effect on

$$\frac{1-\lambda}{\frac{a}{c}-\lambda} + 1$$

Now decreases with increasing stannic chloride

Also $\frac{a}{c}$ always greater than 1.

As λ decreases both $(1 - \lambda)$ and $(\frac{a}{c} - \lambda)$ increase but the effect on $(1 - \lambda)$ is greater than on $(\frac{a}{c} - \lambda)$ with the result that there is an overall increase in $\frac{(1 - \lambda)}{(\frac{a}{c} - \lambda)}$

It follows that $\frac{dk_2}{dc}$ decreases with increasing catalyst concentration. Clearly, from 10 and 13 it should be possible to obtain values of k and K from the slope of the graph. Actual calculations showed that K was nothing like constant over the range of the experimental curve.

Moreover, it has already been shown that a small value of K is required to account for the influence of hydrogen chloride on the reaction rate, and the discussion following supports this idea - also approximate numerical calculations firmly indicate that the term $\frac{ak}{K}$ cannot be neglected in comparison with the other terms in the denominator of equation 11 .

The assumption that K is large may be examined by a rough numerical test, thus -

Suppose that $\lambda = 0.9$ when $c = 0.005$, then from

7 $K = 65$

Using this value of K we can calculate λ for other values of c

also $k_2 = \frac{k}{a} \lambda c$

Take $k_2 = 003$ for $c = 0.005$ (from graph)

Then $k = \frac{ak_2}{\lambda c} = \frac{0.143 \times 0.03}{0.9 \times 0.005}$

$= 0.95$

Then applying this value of k to the non linear part of the curve k_2 should be predicted.

Thus for $c = 0.09M$ and $\lambda = 0.82$

$k_2 = 0.49$

The experimental value for k_2 is 0.22

It is evident therefore that the assumption that $\lambda \rightarrow 1$ for low catalyst concentrations gives too small a curviture to the relation between k_2 and c. An approximate proportionality should be preserved over a wider range than is observed experimentally.

However, since a = 0.143, a is at least ten times the catalyst concentration throughout the linear portion so either a small of a large value of K would reproduce the experimental results.

This follows clearly below;-

For very small values of c relative to a 7 reduces to:-

$$K = \frac{\lambda c}{a(c - \lambda c)}$$

so $$\lambda c = \frac{Kac}{1 + Ka}$$

but $$k_2 = \frac{k \lambda c}{a}$$

so $$k_2 = \frac{k K a c}{a(1 + Ka)}$$

Therefore since k, K and a are constants, k_2 is proportional to c for any value of K.

Experiments with varying hydrogen chloride concentration favour a small value of K. But this again

is not consistent with the departure from linearity in the region where c is greater tha 0.015 M. In fact it is found by trial that the combination of equations 1 and 7 cannot be fitted to the whole range of the experimental curve for any values of k andK. This is illustrated below by taking a arbitrary values of K. It has already been shown that a large K does not do.

Take K = 1

Then for a = 0.143 and c = 0.01

$\lambda = 0.125$

Putting $k_2 = 0.065$ for c = 0.01

The following results are derived from equations 7 and 8

k_2' = The theoretical k_2

c	λ	λc	k_2'	$\frac{k_2'}{c}$	k_2	$\frac{k_2}{c}$
0.01	0.125	0.00125	0.065	0.00065	0.065	0.00065
0.02	0.124	0.00248	0.129	0.00064	0.122	0.00061
0.05	0.120	0.00600	0.312	0.00062	0.187	0.00037
0.08	0.107	0.00856	0.445	0.00056	0.212	0.00026

Then take an intermediate value of K = 16

For a = 0.143 c = 0.005

$\lambda = 0.694$

putting $k_2 = 0.274$ for c = 0.005

k = 1.24

The following results are then derived as before.

c	λ	λc	k_2'	$\frac{k_2'}{c}$	k_2	k/c
0.005	0.694	0.00327	0.0274	0.00055	0.0274	0.00055
0.04	0.651	0.0260	0.218	0.00054	0.172	0.00043
0.06	0.627	0.0376	0.312	0.00052	0.198	0.00033
0.09	0.591	0.0532	0.446	0.00049	0.216	0.00024

In both cases there is a slow departure from linearity above c = 0.02 M ,but this is very much less than the experimental curvature. It is possible,of course,to fit the theoretical curve more closely to the experimental curve at higher values of c by taking different values of k, but then there are marked deviations at low catalyst concentrations.

If the simple mechanism considered hitherto applies at all it is more natural for it to apply at the lowest stannic chloride concentrations and to seek for causes of divergence at the higher concentrations.

Many attempts have been made to determine absolute values of the constants k and K.

Now,from 7 and8,it follows that

$$K = \frac{\frac{k_2 a}{k}}{\left(a - \frac{k_2 a}{k}\right)\left(c - \frac{k_2 a}{k}\right)} = \frac{\frac{k_2' a}{k}}{\left(a - \frac{k_2' a}{k}\right)\left(c' - \frac{k_2' a}{k}\right)}$$

Here k_2 and c and k_2' and c' represent pairs of values taken from different parts of the experimental curve. If the variation of k_2 with stannic chloride can be represented by the simple combination of equations 7 and8 it should be p possible to derive values for the constants from the experimental curve. This was tested using many different pairs of values of k and c and substituting in 13. In all cases this gave imaginary solutions for k.-another indication that the simple theory does not hold over the whole range of catalyst concentration.

Even if it is assumed that within narrow limits the simple theory is applicable it leaves many of the experimental features unexplained.

1 The substantial departure from linearity of the curve plotting k_2 against catalyst concentration in the 'flow' experiments-Table 38, figs.9 and 10.

2 The lowering of the reaction order in the 'closed tube' experiments when stannic chloride becomes equal to or rises above the hydrogen chloride. It is to be noted that simultaneously the hydrogen chloride is equal to the styrene. Tables 30-32, pages 93-95.

3 The increase in the rate of the reaction and anomalous dependence of the rate upon catalyst concentration at much higher styrene concentrations. pp 84-86, figs.5-7.

However it is reasonable that it is only when the hydrogen chloride is in considerable excess over the other reagents that the other possible reactions suggested in part III A may be neglected. Also under the conditions involved in features 1-3 complications are known to occur. For example, the observation (tables 10 and 11, pp 78-79) that for stannic chloride 0.02-0.03 M and styrene in excess over hydrogen chloride the consumption of styrene is greater than would correspond to the simple addition of hydrogen chloride to the double bond suggests that short chain polymerisation is coming into prominence under these conditions. It is shown also (part III A) that the proportion of polymer formed during the reaction increases with initial styrene concentration. A likely scheme is drawn out below;-

$$HCl + SnCl_4 \rightleftharpoons H^+SnCl_5^- \quad (i)$$

$$PhCH{:}CH_2 + SnCl_4 \rightleftharpoons Ph\overset{+}{C}H\text{-}CH^-SnCl_4 \quad (ii)$$

$$PhCH{:}CH_2 + H^+SnCl_5^- \xrightarrow{k_3} Ph\overset{+}{C}H.CH_3 \,|\, SnCl_5^- \quad (iii)$$

$$Ph\overset{+}{C}H\text{-}CH_2^-SnCl_4 + H^+SnCl_5^- \xrightarrow{k_4} Ph\overset{+}{C}H.CH_3 \,|\, SnCl_5^- + SnCl_4 \quad (iv)$$

$$Ph\overset{+}{C}H - CH_3 \,|\, SnCl_5^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} PhCHCl.CH_3 + SnCl_4 \quad (v)$$

$$Ph\overset{+}{C}H.CH_3 \,|\, SnCl_5^- + PhCH = CH_2 \xrightarrow{k_6} Ph\overset{+}{C}H_1CH_2.CHPhCH_3 \,|\, SnCl_5^- \quad (vi)$$

$$Ph\overset{+}{C}H.CH_2.CH.PhCH_3 \,|\, SnCl_5^- \xrightarrow{k_7} PhCH{:}CH.CHPhCH_2CHPhCH_3 + HCl + SnCl_4 \quad (vii)$$

Also possibly

$$Ph\overset{+}{C}H - CH_2^-SnCl_4 + HCl \xrightarrow{k_8} Ph\overset{+}{C}H.CH_3 \,|\, SnCl_5^- \quad (viii)$$

$$Ph\overset{+}{C}H.CH_3 \,|\, SnCl_5^- + HCl \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} PhCHCl.CH_3 + H^+SnCl_5^- \quad (ix)$$

In a non polar solvent such as carbon tetrachloride the free ions are perhaps more properly visualised as ion pairs. The large number of possible mechanisms involved in the above scheme makes even the following qualitative discussion of the observed features of the reaction little more than speculation. A more detailed kinetic study of the reaction is needed in the regions where the styrene and acid concentration are nearly equal for it is know that here the reaction is complicated by polymerisation. It is probable also that the rate of consumption of styrene does not equal the rate of consumption of hydrogen chloride, so following the fall in styrene concentration may not give a true measure or the rate of the addition reaction. It would be useful to evolve a method for measuring the rate by the fall in acid concentration. If the entity $Ph\overset{+}{C}H\text{-}CH_3 \,|\, SnCl_5^-$ is denoted by X- Then the total rate of consumption of styrene will be given

by the sum of the rates of reactions (iii), (iv), (viii) and (vi) and further terms if polymers higher than the dimer are taken into account.

$$-d[\text{styrene}]/dt = k_3[PhCH{:}CH_2][H^+SnCl_5^-] + k_4[PhCH^+.CH_2.SnCl_4][H^+SnCl_5^-] + k_8[PhCH^+.CH_2SnCl_4^-][HCl] + k_6[PhCH{:}CH_2][X] \quad \text{— A}$$

It may be supposed that the styrene and hydrogen chloride compete for stannic chloride in (i) and (ii). It is also supposed that reaction (iii) proceeds more readily than (iv). Excess of hydrogen chloride over styrene will favour (i) and (iii). (It will also favour (ix), if this is a possible reaction, over (vi). In any event the formation of dimer by (vi) and (vii) will be discouraged at low styrene concentrations. In these circumstances the rate of reaction will be dominated by the first term in (A) which reduces to the simple theory described earlier.

The Influence of Stannic chloride in 'Flow' experiments

Fig. 9

As the stannic chloride concentration increases relative to hydrogen chloride it seems likely that (ii) and consequently (iv) and (viii) will intrude but again (vi) will not be emphasised. If k_4 and k_8 are less than k_3 a rising proportion of stannic chloride would lead to a less than proportional rise in the observed rate: although (v) may be intrinsically easier than reaction (viii) the relative concentrations of HCl and $H^+SnCL_5^-$ favour (viii) against (iv).

The reasoning may be false unless (viii) predominates over (iv) because the rate of (iv) would be proportional to the square of the catalyst concentration.

2 - Reduction in order in 'closed' tube experiments

Either excess of catalyst over hydrogen chloride or excess of styrene over hydrogen chloride will favour (ii) and consequently (iv) and (viii). Excess of stannic chloride will favour the back reaction (v). In equation A the third second and even the fourth terms may come into play under these conditions. If the second and third terms principally determine the rate, a reduction of reaction order below 2 will result if the proportion of $Ph\overset{+}{C}H\text{-}CH_2.\overset{-}{S}nCl_4$ is not negligibly small in comparison with the concentration of styrene and stannic chloride in the equilibrium (ii) i.e. if $Ph\overset{+}{C}H\text{-}CH_2.\overset{-}{S}nCl_4$ is not proportional to styrene.

3 - At high styrene concentration

Under these conditions all the terms in equation A are probably significant.

From a consideration of the stationary concentration of $Ph\overset{+}{C}H\text{-}CH_3\ \overset{-}{S}nCl_5$ = X it follows that

$$X = \frac{\left[\begin{array}{l} k_3\left[PhCH{:}CH_2\right]\left[H^+SnCl_5^-\right] + k_4\left[Ph\overset{+}{C}H\ .CH_2SnCl_4\right]\left[H^+SnCl_5^-\right] \\ + k_8\left[Ph\overset{+}{C}H.CH_2\overset{-}{S}nCl_4\right]\left[HCl\right] + k_5\left[PhCHCl.CH_3\right]\left[SnCl_4\right] + k_8\left[PhCHCl.CH_3\right]\left[H^+SnCl_5^-\right] \end{array}\right]}{k_5 + k_6\left[PhCH{:}CH_2\right] + k_9\left[HCl\right]}$$

A full expression of the reaction rate is then given by substituting this value of X in A. Now if it is assumed that α phenylethylchloride is always present in its equilibrium concentration the full equation is somewhat simplified. Further, if a series of approximations are made it is possible to derive a simple expression which would predict the first order velocity measurements and the proportionality of k_2 to the square of the catalyst concentration (Experiments 67-70, p.84). The zero order reactions (Experiments 81-84, p.85) may also be predicted

but the argument is based on different and contradictory assumptions concerning the relative magnitudes of the equilibrium and velocity constants. In general, however, mixed behaviour might be expected. If α-phenylethylchloride is not assumed to be present in equilibrium concentration there are further possibilities. Further complexities must also arise from the formation of higher polymers and of saturated distyrene.

It is difficult to account for the series (Expts. 72-75, p.84) in which k_2 is independent of catalyst concentration except by experimental error. Possibly there was an insufficient supply of hydrogen chloride.

As has been suggested earlier further detailed kinetic studies are needed before a more comprehensive discussion is possible.