### 316. *Kinetics of the Interaction of ·Hydrogen Chloride with Styrene in Presence of Stannic Chloride.*

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At low concentrations of styrene (∼0·1M) and catalyst, the rate of consumption of styrene by hydrogen chloride (to form mainly 1-phenylethyl chloride), in carbon tetrachloride medium, is proportional to the concentration of catalyst and of each reagent. With M-styrene the rate becomes independent of styrene concentration. The facts are consistent with a carbonium ion mechanism, but they do not decide whether initiation is by interaction of catalyst with hydrogen chloride or with styrene.

In carbon tetrachloride solution, in the presence of stannic chloride, styrene reacts with hydrogen chloride to form 1-phenylethyl chloride and short-chain polystyrenes, mainly the dimer to the tetramer (Williams, *J.*, 1938, 1046; Williams and Thomas, *J.*, 1948, 1867). The amounts, and the molecular weights, of the polymers found in the reaction products increase with rising initial concentration of styrene. With 0·08—0·17M-styrene, 75% of the initial material is recovered as 1-phenylethyl chloride. This paper describes experiments on the kinetics 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 some styrene is known to be consumed in short-chain polymerisation as well as in forming the addition product. However, with low reagent concentrations, and with hydrogen chloride present in excess over styrene, some simple kinetic relations are discernible.

In the following, $a$, $b$, and $c$ are the initial concentrations of hydrogen chloride, styrene, and stannic chloride, respectively, in moles per litre. Time is in minutes.

In carbon tetrachloride, there is no reaction in the absence of the catalyst (see Table 5).

*The Influence of Styrene Concentration.*—The effects of changing styrene and stannic chloride concentrations on the rate of reaction between styrene and hydrogen chloride

TABLE 1. *Influence of styrene concentration. Temp.* 25°.

| SnCl$_4$ concn., M. | Expt. no. | HCl concn., M. | Styrene concn., M. | $k_1$ | $k = k_1/ca$ |
|---|---|---|---|---|---|
| 0·0109 | 46 | 0·143 | 0·0335 | 0·0093 | 6·0 |
| | 45 | 0·143 | 0·0365 | 0·0095 | 6·1 |
| | 47 | 0·146 | 0·185 | 0·0097 | 6·1 |
| | 48 | 0·146 | 0·185 | 0·0096 | 6·0 |
| 0·0125 | 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 |
| 0·0126 | 38 | 0·146 | 0·178 | 0·0133 | 7·2 |
| | 42 | 0·151 | 0·395 | 0·0146 | 7·7 |
| 0·0152 | 25 | 0·144 | 0·0386 | 0·0154 | 7·0 |
| | 22 | 0·145 | 0·133 | 0·0157 | 7·1 |
| | 24 | 0·145 | 0·152 | 0·0162 | 7·4 |
| 0·0156 | 19 | 0·144 | 0·0486 | 0·0146 | 6·5 |
| | 18 | 0·145 | 0·102 | 0·0151 | 6·7 |
| | 20 | 0·145 | 0·136 | 0·0151 | 6·7 |
| | 21 | 0·145 | 0·137 | 0·0156 | 7·4 |
| 0·0224 * | 149 | 0·276 | 0·030 | 0·0102 | 1·65 |
| | 152 | 0·276 | 0·101 | 0·0098 | 1·59 |

* At 0°.

have been investigated with solutions containing hydrogen chloride at its constant saturation concentrations in the carbon tetrachloride medium. This condition was ensured by passing a stream of dry hydrogen chloride through the carbon tetrachloride solution of styrene and stannic chloride while the reaction was proceeding, the fall of

styrene concentration with time being measured. In these circumstances, at a fixed concentration of catalyst, the rate of reaction is given by equation (1), for 0·03—0·2M initial styrene concentration :

$$-d[C_8H_8]/dt = k_1[C_8H_8] \qquad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Log $[C_8H_8]$ is linear with time in individual experiments (Fig. 1; the divergent points in expts. 4/5 are for conversions of 90% and more); and the coefficient $k_1$ is independent of the initial styrene concentration (Table 1).

The variations of hydrogen chloride concentration in Table 1 arise from the varying solubility of the gas in solutions of different styrene concentrations (see Table 4). These variations are automatically corrected in the last column of Table 1.

*The Influence of Stannic Chloride Concentration.*—This was also studied, with a flow system, at constant concentration of hydrogen chloride. The results are shown in Table 2.

At 25° the velocity coefficient $k_1$ of equation (1) is approximately proportional to the catalyst concentration over the range 0—0·016M-$SnCl_4$ (see Fig. 2). With higher catalyst concentrations, the rate of reaction increases less than proportionally to the stannic chloride concentration. At 0°, there is little departure from a linear relation up to 0·038M-concentration of stannic chloride.

*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 at other concentrations, because of the extreme volatility of the hydrogen chloride. Table 3 shows the results of experiments made with a closed reaction system (see Experimental section). In this Table, the velocity coefficients, $k_2$, are calculated from the equation :
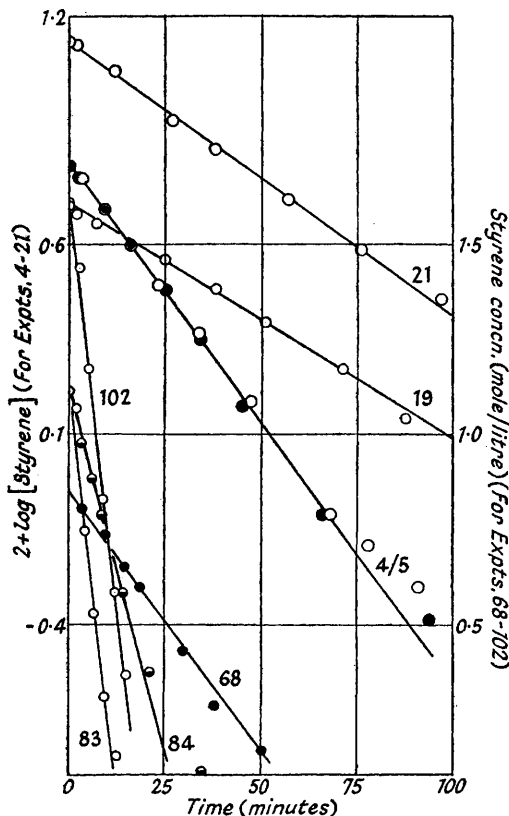
$$-d[C_8H_8]/dt = k_2[C_8H_8][HCl] \quad . \quad (2)$$

Each value for $k_2$ is the mean of several observations, made at different times, upon independently prepared reaction mixtures. The reproducibility is only moderate (see Experimental section).

The results of Table 3 justify the conclusion that equation (2) is valid up to the saturation concentrations of hydrogen chloride at 25° and at 0°. The best demonstration is contained in Fig. 2, which shows that, when plotted against catalyst concentration, the " static " values of $k_2$ (full black circles) from Table 3 fall nearly on the same curves, at the two temperatures, as the values of $k_1/[HCl]$ derived from Tables 1 and 2 for experiments with the flowing stream of hydrogen chloride.

In similar experiments in a closed system, but with the initial concentration of styrene greater than that of hydrogen chloride, $k_2$ rose with time (indicating transition to a lower reaction order) and the styrene concentration fell below the value corresponding to the formation of 1-phenylethyl chloride alone. No doubt some distyrene was formed.



FIG. 1.

*2 + Log [Styrene] (For Expts. 4–21)*

*Styrene concn. (mole/litre) (For Expts. 68–102)*

*Time (minutes)*

The above results may be summarised by the statement that, at 25°, for $[SnCl_4] \ll 0.016M$, $[HCl] \leqslant 0.15M$ (saturation concentration), and for $[HCl] >$ [Styrene], the reaction velocity is given by equation (3) :

$$-d[C_8H_8]/dt = k[SnCl_4][C_8H_8][HCl] \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In equations (1), (2), and (3),

$$k = k_2/c = k_1/ca; \; k_2 = k_1/a \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

the symbols being as defined at the beginning of this paper. From Tables 1 and 2, $k = 6.9$ at 25° and 1.61 at 0°. At 0°, equation (3) is valid over greater concentration ranges, at least up to $[SnCl_4] = 0.038M$ and $[HCl] = 0.28M$.

The variation in $k$ between 0° and 25° corresponds to an overall activation energy of 9.4 kcal. The overall activation energy for the long-chain polymerisation of styrene

TABLE 2. *Influence of stannic chloride concentration.*

| SnCl$_4$ concn., M. | Expt. no. | HCl concn., M. | Styrene concn., M. | $k_1$ | $k_1/[HCl]$ | $k = k_1/ca$ |
|---|---|---|---|---|---|---|
| Temp. 25°. | | | | | | |
| 0.0047 | 33 | 0.145 | 0.0964 | 0.0062 | 0.0430 | 9.2 |
| | 36 | 0.145 | 0.0858 | 0.0042 | 0.0290 | 6.2 |
| 0.0100 | 86 | 0.144 | 0.0442 | 0.0079 | 0.0547 | 5.5 |
| | 85 | 0.144 | 0.0672 | 0.0077 | 0.0535 | 5.4 |
| 0.0109 | | Average from Table 1 | | 0.0095 | 0.066 | 6.1 |
| 0.0116 | 8 | 0.144 | 0.0455 | 0.0124 | 0.0861 | 7.4 |
| 0.0125 | | Average from Table 1 | | 0.0127 | 0.0878 | 7.0 |
| 0.0126 | | Average from Table 1 | | 0.0140 | 0.0964 | 7.5 |
| 0.0132 | 12 | 0.145 | 0.127 | 0.0133 | 0.0917 | 7.0 |
| 0.0152 | | Average from Table 1 | | 0.0158 | 0.109 | 7.2 |
| 0.0154 | 16 | 0.143 | 0.0329 | 0.0139 | 0.0972 | 6.4 |
| | 17 | 0.154 | 0.0574 | 0.0152 | 0.106 | 6.9 |
| 0.0156 | | Average from Table 1 | | 0.0151 | 0.106 | 6.8 |
| 0.0226 | 11 | 0.145 | 0.0994 | 0.0184 | 0.127 | 5.6 |
| 0.0312 | 2 | 0.144 | 0.0604 | 0.0225 | 0.156 | 5.0 |
| | 3 | 0.144 | 0.0604 | 0.0230 | 0.160 | 5.1 |
| 0.0363 | 60 | 0.143 | 0.0328 | 0.0255 | 0.178 | 4.9 |
| 0.0539 | 10 | 0.144 | 0.058 | 0.0271 | 0.188 | 3.5 |
| 0.0887 | 4 | 0.144 | 0.0638 | 0.0317 | 0.220 | 2.5 |
| | 5 | 0.144 | 0.0638 | 0.0306 | 0.212 | 2.5 |
| Temp. 0°. | | | | | | |
| 0.0100 | 150 | 0.276 | 0.0306 | 0.00430 | 0.0156 | 1.57 |
| 0.0122 | 148 | 0.276 | 0.0300 | 0.00569 | 0.0206 | 1.69 |
| 0.0224 | | Average from Table 1 | | 0.0100 | 0.0362 | 1.62 |
| 0.0384 | 151 | 0.276 | 0.0302 | 0.0165 | 0.0598 | 1.56 |

TABLE 3. *Influence of hydrogen chloride concentration.*

| Expt. no. | SnCl$_4$ concn., M. | Styrene concn., M. | HCl concn., M. | $k_2$ | $k_2/c$ |
|---|---|---|---|---|---|
| Temp. 25°. | | | | | |
| 140 | 0.0086 | 0.0301 | 0.0712 | 0.043 | 4.8 |
| 145 | 0.0111 | 0.0284 | 0.0712 | 0.074 | 6.7 |
| 139 | 0.0116 | 0.0301 | 0.0712 | 0.065 | 5.6 |
| 138 | 0.0117 | 0.0301 | 0.0712 | 0.056 | 4.8 |
| 144 | 0.0105 | 0.0284 | 0.0284 | (0.104) | 6.9 |
| From " flow " expts. at 25° | | | | 0.143 | 6.9 |
| Temp. 0°. | | | | | |
| 192 | 0.0179 | 0.0294 | 0.0918 | 0.026 | 1.5 |
| 193 | 0.0179 | 0.0294 | 0.184 | 0.027 | 1.5 |
| From " flow " expts. at 0° | | | | 0.276 | 1.6 |

with stannic chloride in carbon tetrachloride medium is about 3 kcal. (Williams, *J.*, 1940, 775). Both of these activation energies are composite.

*High Styrene Concentrations.*—With the initial styrene concentration $\geqslant 1M$, and with streaming hydrogen chloride, kept at constant (saturation) concentration (*ca.* 0.16M), the process (up to at least 60% consumption of styrene) is better described (except at very low concentrations—0.005M—of $SnCl_4$) by the zero-order equation (5) than by equation (1) (see Fig. 1, expts. 68—102).

$$-d[C_8H_8]/dt = k_0; \; ([HCl] \text{ and } [SnCl_4] \text{ const.}) \quad . \quad . \quad . \quad (5)$$

Since the styrene is largely consumed by the continuous supply of hydrogen chloride, the zero-order behaviour is not to be ascribed purely to the excess of styrene present.

On the assumption that the reaction rate is still proportional to the hydrogen chloride concentration, $k_0/[HCl]$ has been plotted against stannic chloride concentration, in Fig. 3, for experiments with seven different stock preparations of stannic chloride, always with initial concentration in the range 0·85—1·1M. Although the fluctuations are considerable, equation (6) holds approximately for these experimental conditions, up to a much higher concentration of stannic chloride than does equation (3) for low styrene concentrations (cf. Fig. 2).

$$-d[C_8H_8]/dt = k''[SnCl_4][HCl]; \quad \text{(initial } [C_8H_8]\sim1M) \quad . \quad . \quad . \quad (6)$$

In equations (5) and (6), $k'' = k_0/[SnCl_4][HCl]$; and, from Fig. 3, $k''\sim5\cdot2$. This equation probably has a limited validity, for there is some evidence that $k''$ rises with initial concentration of styrene above 1M. For example, in one series, $k'' = 4\cdot8$ and $9\cdot2$

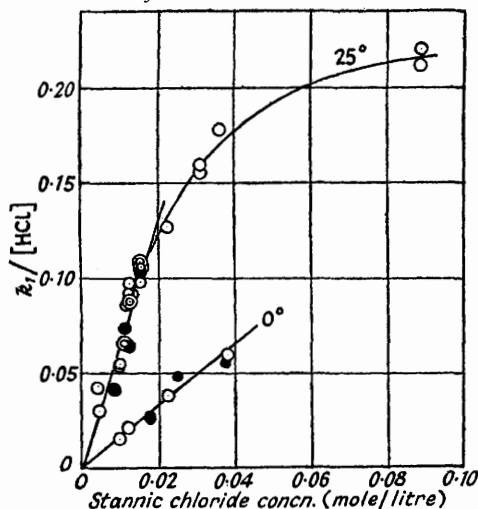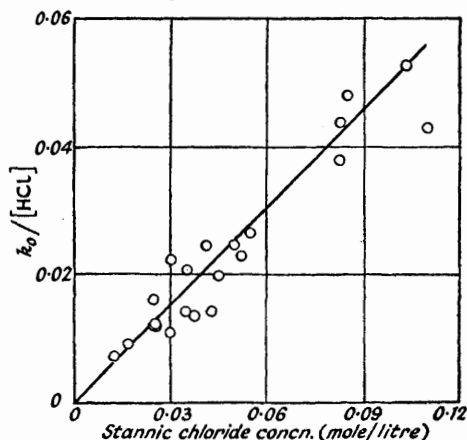FIG. 2.    *Styrene concentration* 0·03—0·1M.



FIG. 3.    *Initial styrene concentration* 0·8—1·1M.



for 1·07M and 1·60M initial styrene, respectively. Analogous behaviour has been observed (Williams, 1940, *loc. cit.*) in the long-chain polymerisation of styrene by stannic chloride in carbon tetrachloride, where a third-order velocity coefficient, valid for given initial conditions, rises with increasing initial styrene concentration in the range 0·4—3·5M. If these reactions have a carbonium ion mechanism, it is conceivable that their speeds are influenced by changes in the dielectric constant of the system (cf. Pepper, *Trans. Faraday Soc.*, 1949, **45**, 397, 404; George and Wechsler, *J. Polymer Sci.*, 1951, **6**, 725) occurring when the proportion of styrene to carbon tetrachloride (having a low dielectric constant) is substantially altered, as it is when initial styrene concentrations above 1M are changed. Velocity coefficients are independent of initial styrene concentrations when these are *low* (Table 1).

Fig. 3 and equation (6) have an empirical use for estimating the kinetic chain-length in the long-chain polymerisation of styrene by experiments on the inhibiting action of small concentrations of hydrogen chloride (unpublished results of Mr. J. S. Coe, M.Sc.).
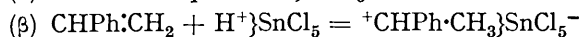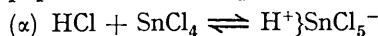
## DISCUSSION

To account for the products of reaction, a carbonium ion mechanism has already been suggested (Williams and Thomas, *loc. cit.*), in accordance with the general opinion about the action of Friedel–Crafts catalysts. This mechanism requires co-operation of the three

reactants in processes which have the result shown in equation (7) (the ion $SnCl_6^=$ might also be formed):

$$CHPh{:}CH_2 + SnCl_4 + HCl \longrightarrow {}^+CHPh{\cdot}CH_3\}SnCl_5^- \qquad . \quad . \quad . \quad . \quad . \quad (7)$$

In the previous paper, the initial steps were formulated:

(α) $HCl + SnCl_4 \rightleftharpoons H^+\}SnCl_5^-$

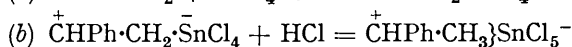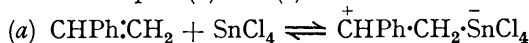(β) $CHPh{:}CH_2 + H^+\}SnCl_5 = {}^+CHPh{\cdot}CH_3\}SnCl_5^-$

Here the hydrogen chloride would act as a co-catalyst to the stannic chloride (cf., *e.g.*, Plesch, *Research*, 1949, **2**, 267). An argument for the interaction (α) was Meerwein's observation (*Annalen*, 1927, **453**, 16) that dilute ethereal solutions of hydrogen chloride and of stannic chloride are, separately, yellow after addition of the indicator *p*-dimethyl-aminoazobenzene; but that an immediate red (acid) colour is formed when the solutions are mixed. We have confirmed this result in ethereal solution, but not in the solvent *carbon tetrachloride*. Meerwein's experiment rested on Hantzsch's observation (*Ber.*, 1925, **58**, 612) that an ethereal solution of hydrogen chloride, coloured red with the indicator, becomes yellow on sufficient dilution with more ether. Hantzsch said that this colour inversion did not occur in the solvent chloroform. It does not occur, either, in carbon tetrachloride. The indicator behaviour in ether may be accounted for by solvation of the proton; and the argument for the occurrence of reaction (α) in carbon tetrachloride, by analogy with Meerwein's result, therefore fails.
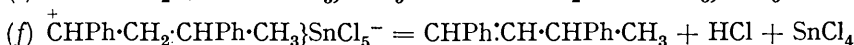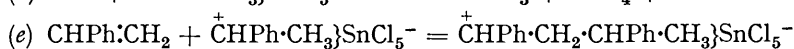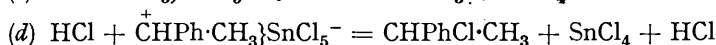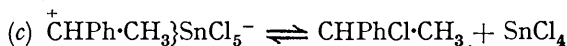
On the other hand, the racemisation of 1-phenylethyl chloride by stannic chloride in benzene solution (Bodendorf and Böhme, *Annalen*, 1935, **516**, 1) is greatly retarded by hydrogen chloride (Böhme, *Ber.*, 1938, **71**, 2372); and immobilisation of the stannic chloride catalyst through complex formation with hydrogen chloride has been proposed as the explanation. The explanation would be more satisfactory if there were independent evidence for the complex (HCl + SnCl₄) in benzene solution. The reaction (*d*) below will not account for the retardation, because it should assist racemisation.

The pairs of compounds (AlCl₃ + HCl) and (AlBr₃ + HBr) catalyse the isomerisation of paraffins, in presence of olefin (*e.g.*, Pines and Wackher, *J. Amer. Chem. Soc.*, 1946, **68**, 595; Fontana and Kidder, *ibid.*, 1948, **70**, 3745); and the complex acids HAlCl₄ and HAlBr₄ have been mentioned as possible intermediates in reactions of this type (Schmerling, *ibid.*, 1944, **66**, 1422; 1945, **67**, 1778; Bloch, Pines, and Schmerling, *ibid.*, 1946, **68**, 153); but physical evidence for their existence in hydrocarbon solvents is lacking (Fontana and Herold, *ibid.*, 1948, **70**, 2881; Schmerling and Ipatieff, *Adv. in Catalysis*, 1950, **2**, 28). Plesch has suggested (*J. Applied Chem.*, 1951, **1**, 269) that interaction of type (α) between hydrogen chloride and stannic chloride is unlikely to occur in a solvent, such as carbon tetrachloride, which cannot readily solvate the proton, and that an alternative is complex formation between stannic chloride and the aromatic ring of styrene.

Another suggestion for the initial step in the reaction of hydrogen chloride with styrene is the reaction pair (*a*) and (*b*):

(*a*) $CHPh{:}CH_2 + SnCl_4 \rightleftharpoons \overset{+}{C}HPh{\cdot}CH_2{\cdot}\overset{-}{S}nCl_4$

(*b*) $\overset{+}{C}HPh{\cdot}CH_2{\cdot}\overset{-}{S}nCl_4 + HCl = \overset{+}{C}HPh{\cdot}CH_3\}SnCl_5^-$

The kinetic results obtained do not distinguish between the pair (α + β) and the pair (*a* + *b*). Among steps which may succeed either pair are:

(*c*) $\overset{+}{C}HPh{\cdot}CH_3\}SnCl_5^- \rightleftharpoons CHPhCl{\cdot}CH_3 + SnCl_4$

(*d*) $HCl + \overset{+}{C}HPh{\cdot}CH_3\}SnCl_5^- = CHPhCl{\cdot}CH_3 + SnCl_4 + HCl$

(*e*) $CHPh{:}CH_2 + \overset{+}{C}HPh{\cdot}CH_3\}SnCl_5^- = \overset{+}{C}HPh{\cdot}CH_2{\cdot}CHPh{\cdot}CH_3\}SnCl_5^-$

(*f*) $\overset{+}{C}HPh{\cdot}CH_2{\cdot}CHPh{\cdot}CH_3\}SnCl_5^- = CHPh{:}CH{\cdot}CHPh{\cdot}CH_3 + HCl + SnCl_4$

Further steps (suggested in the previous paper, *loc. cit.*) may form saturated distyrene and higher polymers. Only di- and tri-styrenes are formed in appreciable amount at low styrene concentrations.

The carbonium-ion mechanism and reversibility for (c) are made very probable for a number of solvents by Bodendorf and Böhme's demonstration (*loc. cit.*) of the racemisation of optically active 1-phenylethyl chloride by stannic chloride. Racemisation in the solvent carbon tetrachloride has since been proved (unpublished experiments by Mrs. K. Heald, M.Sc.). The reversibility of (c) in carbon tetrachloride follows also, first, because 1-phenyl-ethyl chloride reacts with styrene in presence of stannic chloride, to form distyrene (Williams and Thomas, *loc. cit.*), and, secondly, because halogen exchange occurs between $CHPhCl \cdot CH_3$ and $SnBr_4$, and between $CHPhBr \cdot CH_3$ and $SnCl_4$ (experiments by Mrs. K. Heald). A step such as (d) may help to account for a retardation of the halogen exchange by hydrogen halide (but cf. Böhme, *loc. cit.*).

The steps outlined may be combined (with the stationary-state hypothesis) to give a complex kinetic equation which reduces to equation (3) for low reagent concentrations, and contains a term suggesting a qualitative explanation for the transition to equation (6) at high styrene concentrations by increasing intrusion of back-reaction (c) and step (e) as reaction proceeds. Information about the relative rates of individual steps is needed to test this explanation.

## EXPERIMENTAL

*Materials.*—Styrene was made from 2-phenylethyl alcohol and potassium hydroxide (Sabetay, *Bull. Soc. chim.*, 1929, **45**, 69). Pure commercial styrene, washed with alkali, dried, and re-distilled, was also used. The reaction medium was AnalaR carbon tetrachloride, washed with water, dried (KOH), and distilled. Commercial stannic chloride was purified by repeated distillation, under a high vacuum, in a completely closed, all-glass apparatus (cf. Williams, *J.*, 1938, 246), being collected in a series of sealed glass bulbs. For stannic chloride which was to be used in solutions saturated with hydrogen chloride, a simplified method of purification proved satisfactory. With this method, stannic chloride was distilled in an atmosphere of dry hydrogen chloride at 0·1 mm. in an apparatus partly fitted together with ground joints lubricated by " Silicone " grease. It was again collected in sealed bulbs. It was observed that stannic chloride could be preserved for long periods as a clear solution in carbon tetrachloride containing dissolved hydrogen chloride. In the absence of hydrogen chloride, a turbidity develops gradually. The steady current of hydrogen chloride required for kinetic experiments was generated by running concentrated hydrochloric acid (with a head of 3 ft. to ensure sufficient gas pressure) into concentrated sulphuric acid. The gas passed through sulphuric acid, carbon tetrachloride, and a flow-meter before entering the reaction train.

*Analytical Methods.*—Styrene, in carbon tetrachloride solution, was determined by quantitative bromination (bromine in glacial acetic acid) (Williams, 1938, *loc. cit.*). Tests with prepared styrene and with commercial styrene gave : 0·1079, 0·1920M. Calc. : 0·1077, 0·1911M. Hydrogen chloride, in carbon tetrachloride solution, was determined either with standard potassium iodate and sodium thiosulphate solutions, or, if styrene was also present, with standard alkali.

*The Saturation Concentration of Hydrogen Chloride.*—The saturation concentrations of hydrogen chloride in pure carbon tetrachloride and in solutions containing various concentrations of styrene, at 25°, were found to be those given in Table 4. The saturation concen-

TABLE 4. *Saturation concentration of hydrogen chloride.*

| Styrene concn., M : | 0 | 0·1113 | 0·479 | 0·979 | 1·197 | 1·304 | 1·622 |
|---|---|---|---|---|---|---|---|
| HCl concn., M. ...... | 0·1423 | 0·1460 | 0·1516 | 0·1623 | 0·1651 | 0·1693 | 0·1759 |

tration of hydrogen chloride is linear with the styrene concentration over the range investigated.

At 0°, the saturation concentration of hydrogen chloride in pure carbon tetrachloride was found to be 0·276M (cf. Table 5).

*Reaction Velocities with Streaming Hydrogen Chloride.*—A train of glass vessels, *A, B, C, D, E* (each of about 100-c.c. capacity) was mounted in a thermostat. A current of dry hydrogen chloride was led through the train, entering each flask at the bottom and leaving at the top. Each vessel had a stoppered outlet for the removal of samples for analysis. The reaction vessel *C* was protected by sealed-on traps to prevent accidental entry of liquid. Initially, *B* contained a standard solution of styrene in carbon tetrachloride; *A* and *E* contained pure solvent. When all solutions were saturated with hydrogen chloride (requiring about 30 minutes), a weighed

bulb of stannic chloride was smashed under carbon tetrachloride from $E$, to form the standard catalyst solution. A known volume of styrene solution from $B$ was transferred to $C$, and reaction was started in $C$ by addition of a known volume of catalyst solution. Samples were extracted with a pipette at known time intervals, and analysed for styrene. The concentration of stannic chloride was eventually established by filtering and weighing the glass from the smashed bulb in the stock solution.

The result of these operations was to furnish, in the reaction vessel $C$, solutions of styrene and catalyst, both pre-saturated with hydrogen chloride, and to lead through the liquid in $C$ a current of hydrogen chloride pre-saturated with the vapour of the solvent. Without the various precautions taken, there were slow changes of concentration of the reagents in $C$ when no reaction was taking place. With them, concentrations remained constant, in the absence of catalyst as the figures in Table 5 show.

TABLE 5.

*Steady concentration of hydrogen chloride at 25°.*

| Time (min.) | 15 | 40 | 50 | 110 | 120 |
|---|---|---|---|---|---|
| HCl, M ...... | 0·1126 | 0·1420 | 0·1420 | 0·1420 | 0·1420 |

*Steady concentration of styrene at 25° in HCl current.*

| Time (min.) | 4 | 9 | 15 | 30 | 60 | 65 |
|---|---|---|---|---|---|---|
| Styrene, M ... | 0·0971 | 0·0968 | 0·0968 | 0·0972 | 0·0972 | 0·0975 |

*Steady concentration of hydrogen chloride at 0°.*

| Time (min.) | 21 | 42 | 51 | 58 | 66 |
|---|---|---|---|---|---|
| HCl, M ...... | 0·2612 | 0·2755 | 0·2748 | 0·2765 | 0·2755 |

*Steady concentration of styrene at 0° in HCl current.*

| Time (min.) | 4 | 27 | 39 | 45 | 75 | 87 | 99 | 120 |
|---|---|---|---|---|---|---|---|---|
| Styrene, M ... | 0·0391 | 0·0385 | 0·0385 | 0·0385 | 0·0384 | 0·0384 | 0·0384 | 0·0384 |

The bulb $D$ in the train was charged with carbon tetrachloride while reaction was in progress in $C$. Analysis of samples from $D$ for hydrogen chloride served to check the adequacy of the supply of gas passing through $C$. Separate experiments showed that rate of supply of hydrogen chloride to $C$ was $(1—5) \times 10^{-4}$ mole per sec. The maximum consumption of hydrogen chloride did not exceed $3 \times 10^{-5}$ mole per sec.

Experiments at 0° were carried out with an apparatus similar in principle, but simplified so as to allow the essential portions to fit into a large Dewar vessel containing ice-water.

The first-order velocity coefficients were always evaluated graphically (cf. Fig. 1). The reproducibility may be judged from the results given in Tables 1 and 2 (see also Fig. 1, expts. 4/5).

The figures in Table 5 serve to prove that there is no reaction between styrene and hydrogen chloride at 0° and 25°, in carbon tetrachloride in the absence of the catalyst (cf., also, Williams and Thomas, *loc. cit.*).

*Reaction Velocities in Closed System.*—Attempts to construct an apparatus, in which a series of samples for analysis could be withdrawn from a reaction mixture containing hydrogen chloride at less than its saturation concentration, failed, owing to losses of hydrogen chloride gas from the solution. Eventually, independent reaction mixtures were made up in 10-c.c. stoppered tubes; and the styrene concentrations in each tube were measured after different times. Loss of hydrogen chloride at the end of the reaction did not matter, since it was the styrene which was determined; but it was essential to prove that the *initial* hydrogen chloride concentration was correctly known. This was done by running in 5 c.c. of a saturated hydrogen chloride solution, in carbon tetrachloride, under the surface of 5 c.c. of the same solvent in a reaction tube sealed through an internal ground joint (which could be stoppered) to an upper tube (also stoppered). After the mixture had been made up, water was placed in the upper tube. In an analysis for hydrogen chloride, the internal stopper was removed to admit water to the carbon tetrachloride solution, and instantly replaced. After being shaken, the mixture was poured into excess of standard alkali. Results were :

Concn. of hydrogen chloride in tube :

Calc. : 0·0712M. Found : 0·0708, 0·0708, 0·0714, 0·0712M.

Reaction mixtures containing catalyst were made up in a similar way, the known volume of saturated hydrogen chloride solution being added last. Velocity coefficients were calculated from equation (2). Owing to the number of operations involved in making up individual

reaction mixtures for each reading, with the risk of loss of gas, the reproducibility of the results was mediocre (Table 3). Expt. 140 is an example.

*Expt.* 140.    *Initial concn.: styrene,* 0·0301M : *hydrogen chloride,* 0·0712M ;
*stannic chloride,* 0·0086M.

| Time (min.) | 49·5 | 86·3 | 129·8 | 158·0 | 109·0 | 181·3 | 222·5 |
|---|---|---|---|---|---|---|---|
| Conversion, % | 12·3 | 23·2 | 39·0 | 42·0 | 37·5 | 41·5 | 42·8 |
| $k_2$ | 0·038 | 0·045 | 0·037 | 0·049 | 0·039 | 0·053 | 0·039 |

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