

199. *Kinetics of the Catalysed Polymerisation of Styrene. Part II.
Inhibition of Stannic Chloride Catalysis by Hydrogen Chloride.*

By GWYN WILLIAMS.

Hydrogen chloride is a temporary complete inhibitor for the long-chain polymerisation of styrene in carbon tetrachloride, catalysed by stannic chloride at 25°. Styrene and hydrogen chloride combine, under these conditions, to form α -phenylethyl chloride, distyrene, and short-chain polystyrene in proportions depending on the reagent concentrations. The formation of all three products is considered to be dependent on the addition of hydrogen chloride to the styrene double bond. Inhibition of polymerisation is ascribed to the removal of those styrene molecules which are in a condition to start polymerisation chains; and a method is proposed for estimating the rate of chain-initiation. Initial inhibition periods, observed in polymerisations with unpurified catalyst, are thought to be due to contamination with hydrogen chloride.

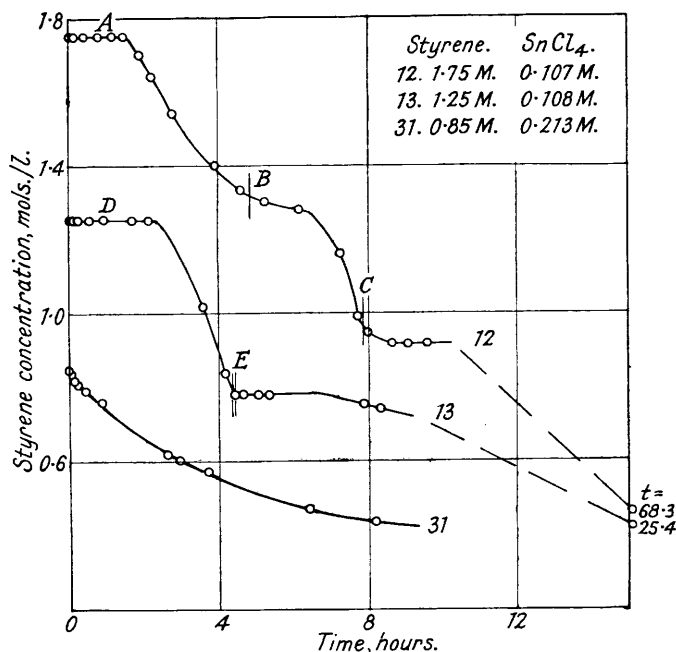
IN the presence of stannic chloride, styrene polymerises in carbon tetrachloride solution to hemi-colloidal products; and the rate of reaction can be measured at 25° by titration of the residual monomer with bromine (Part I, this vol., p. 246). Although a period of induction * is commonly observed in the early stages of the reaction, the concentration

* The term "induction period" is used to describe a stage in which reaction velocity increases as the reaction proceeds.

of monomeric styrene begins to fall immediately after addition of the stannic chloride catalyst to the styrene solution, provided that both reactants have been carefully purified; and, so far as can be detected, polystyrene of high molecular weight (of the order 2500) is formed from the start. On the other hand, when high-grade commercial specimens of anhydrous stannic chloride are used as catalysts without further purification, the polymerisation of styrene may be preceded by a period of total *inhibition*,* which can be as long as 4 hours (Williams, *Nature*, 1937, **140**, 363), after which polymerisation proceeds smoothly to completion. In the course of experiments on this effect, hydrogen chloride was found to be an inhibitor for the polymerisation of styrene in the presence of stannic chloride.

The influence of hydrogen chloride is shown in Fig. 1. In Expts. 12 and 13, redistilled styrene and unpurified commercial "c.p." stannic chloride were employed, polymerisation

FIG. 1.



Polymerisation of styrene in carbon tetrachloride at 25°.

being started, as usual, by crushing a glass bulb containing the catalyst under the surface of the styrene solution. For Expt. 13, the styrene was specially dried. During the polymerisation phase, which followed the initial inhibition shown at A and D, the reaction mixtures were further treated: at the time marked B on curve 12, moist air was bubbled through the solution, and at time C, air which had passed through concentrated hydrochloric acid was used. Over the time interval of 3 minutes shown at E (curve 13), a current of air carrying *dry* hydrogen chloride passed through the solution. In each case, the current of gas, flowing through the reaction mixture for *only a few minutes*, influenced the rate of polymerisation for a period of 1 or 2 hours. It is evident that the addition of hydrogen chloride arrests polymerisation temporarily, and it is plausible to suppose that the inflexion at B is due to hydrogen chloride produced by hydrolysis of stannic chloride (Pfeiffer, *Z. anorg. Chem.*, 1914, **87**, 235).

Chain theories of polymerisation processes recognise distinct stages of chain initiation, chain growth, and chain termination in the formation of a long polymer molecule (*e.g.*, Gee and Rideal, *Trans. Faraday Soc.*, 1936, **32**, 5, 656, 666; Staudinger, *ibid.*, p. 97;

* The term "inhibition period" implies total arrest of a particular reaction (in this paper, long-chain polymerisation) within the errors of measurement.

Mark, *Naturwiss.*, 1937, **25**, 753). Hydrogen chloride may inhibit the catalytic polymerisation either by preventing the initiation of polymerisation chains or by interrupting chain growth. Objections to the second alternative are stated below, and the very completeness of the inhibition favours the first, which implies that practically all of the styrene molecules which are suitably activated for the initiation of polymerisation chains are removed by some alternative reaction. Since inhibition of long-chain polymerisation by small amounts of hydrogen chloride is temporary, hydrogen chloride must be used up in the inhibition process; and it is more likely that inhibition is due to interaction of hydrogen chloride with styrene than with stannic chloride.

The Interaction of Hydrogen Chloride and Styrene.—Hydrogen chloride adds on to the styrene double bond to form α -phenylethyl chloride (Schramm, *Ber.*, 1893, **26**, 1709; Hughes, Ingold, and Scott, *J.*, 1937, 1271). Stannic chloride seemed a likely catalyst for this reaction, which was investigated by experiments at room temperature, included in Table I.

EXPERIMENTAL.

Materials.—Unless otherwise stated, the materials used for the kinetic experiments and for the experiments in Table I were redistilled commercial styrenes and high-grade commercial

TABLE I.

Interaction of Styrene and Hydrogen Chloride.

Solvent: carbon tetrachloride. Temp. 20–24°. Dry hydrogen chloride passed through solutions, except in I, VIII, IX, X. In polystyrene formulæ, $m = ca. 3-4$; $n = ca. 20-30$.

Expt. No.	Initial solution.	SnCl ₄ , m.	Duration, mins.	Per cent. of starting material recovered as				Total recovered, %.
				C ₈ H ₈ Cl.	(C ₈ H ₈) ₂ .	(C ₈ H ₈) _m .	(C ₈ H ₈) _n .	
I, A	C ₈ H ₈ , 1.7M	0.086	3600	0	0	0	95	95
*I, B	C ₈ H ₈ , 1.7M	0.2	329	0	0	0	86	86
II	C ₈ H ₈ , 1.7M	0	160	0	0	0	0	94 §
III	C ₈ H ₈ , 1.7M	0.086	65	35	35	12	0	82
IV	C ₈ H ₈ , 1.7M	0.086	50	28	49	20	0	97
V	C ₈ H ₈ , 0.43M	0.021	150	70	22	2	0	94
VI	C ₈ H ₈ , 0.43M	0.086	98	59	25	7	0	91
†VII	C ₈ H ₈ , 0.43M; C ₈ H ₉ Cl, 0.19M	0.021	165	58	24	13	0	95
†VIII	C ₈ H ₈ , 1.7M; C ₈ H ₉ Cl, 0.75M	0.086	1500	0	20	66	0	86
IX	C ₈ H ₉ Cl, 1.6M	0.09	140	89	<--- <3 --->		0	92
X	C ₈ H ₉ Cl, 1.7M	0.086	130	90	<--- <5 --->		0	95
‡XI	C ₈ H ₈ , 1.7M	0.086	180	26	29	3	30	88

* Yield collected after double reprecipitation in methyl alcohol. Some polymer dissolved in the methyl alcohol and was not collected.

† Percentage of products calculated on total C₈H₈ in combined (C₈H₈ + C₈H₉Cl) in initial solution.

‡ Long-chain polymerisation started, and interrupted by a current of hydrogen chloride when one-third complete. § Unchanged C₈H₈.

anhydrous stannic chloride, which was not given the rigorous purification applied in Part I (*loc. cit.*). Chloroform was washed, dried, distilled, protected against oxidation by addition of 0.1% of dimethylaminoazobenzene (Weissberger and Fasold, *Z. physikal. Chem.*, 1931, **157**, 79), and freshly redistilled when required as a reaction medium.

Experiments recorded in Table I.—A stream of dry hydrogen chloride was passed through a solution containing styrene and stannic chloride until the styrene concentration was reduced almost to zero,* as indicated by bromine titration. The solution was then washed thoroughly with water to remove hydrogen chloride and stannic chloride, dried with anhydrous sodium sulphate, and distilled under reduced pressure, the reaction products being collected after removal of the solvent.

In the first experiment (III in Table I), the reaction products distilled in three fractions, A, B, and C, all colourless oils. No long-chain polystyrene was formed, precipitation by methyl alcohol [in which polystyrenes higher than (C₈H₈)₁₀ are insoluble] being used as a criterion (cf. Staudinger, "Die Hochmolekularen Organischen Verbindungen," Berlin, 1932, p. 161).

* Addition of bromine to distyrene is much slower than to styrene, but the method described previously for the bromine titration of styrene is only approximate in the presence of distyrene.

Fraction A (yield, 35% of theory; b. p., 75°/16 mm.) was identified as α -phenylethyl chloride (Found * : C, 68.2; H, 6.0; Cl, 25.7. Calc. for C_8H_9Cl : C, 68.3; H, 6.4; Cl, 25.3%).

Fraction B [yield, 35% of theory; b. p., 178—181°/14 mm. Found † C, 91.2; H, 7.2. Calc. for $(C_8H_8)_x$: C, 92.3; H, 7.7%] gave, on treatment with bromine, a crystalline dibromide (Found : Br, 43.0. Calc. for $C_{16}H_{16}Br_2$: Br, 43.4%) having m. p. 102° after recrystallisation from alcohol. On further recrystallisation from light petroleum, large crystals, m. p. 129°, were obtained, as well as the substance of m. p. 102°. These results, corresponding closely to data given by Stoermer and Kootz (*Ber.*, 1928, 61, 2330), suffice to identify fraction B as distyrene. The amount of dibromide used was too small to permit isolation of two further stereoisomeric distyrene dibromides found by Stoermer and Kootz, who showed that the substance of m. p. 102° was a mixed crystal. Three *structurally* distinct distyrenes are known (cf. Risi and Gauvin, *Canadian J. Res.*, 1936, B, 14, 255); fraction B is the one prepared by Erlenmeyer (*Annalen*, 1865, 135, 122) and by Fittig and Erdmann (*ibid.*, 1883, 216, 179). Its structure was determined by Stobbe and Posnjak (*ibid.*, 1909, 371, 287) to be $CHPh \cdot CH \cdot CHPh \cdot CH_3$.

Fraction C (b. p. ca. 250°/16 mm. Found : C, 91.8; H, 7.7. Calc. : C, 92.3; H, 7.7%) was very viscous at room temperature and consisted of polystyrenes of short chain-length. Since it can be distilled, it is unlikely to contain any polymer higher than tri- or tetra-styrene (Staudinger, *op. cit.*, p. 161; Staudinger and Steinhof, *Annalen*, 1935, 517, 35). Fraction C, together with a very small viscous residue, amounted to 12% of the theoretical.

The results of this experiment are confirmed by others (Table I), one of which (IV) gave an even larger proportion of distyrene. Reaction products from different starting materials (Table I, col. 2) were isolated by the same procedure as above. As a test of the materials employed, two straightforward polymerisations, without added hydrogen chloride, are included in the table (Found for polystyrene from I, B : C, 91.6; H, 7.8; *M*, estimated by viscosity measurement, ca. 3000). In a third experiment, after 230 mins., the extent of polymerisation as shown by bromine titration was 66.6, and by precipitation of polymer, 67.6%. The precipitated polystyrene was not quite pure (Found : C, 90.1; H, 7.8%). No distyrene could be detected in these experiments.

DISCUSSION.

It is thus established that, in carbon tetrachloride solution at room temperature, stannic chloride catalyses the interaction of styrene and hydrogen chloride, producing α -phenylethyl chloride, distyrene, and short-chain polystyrene, but none of the long-chain polystyrene which is the sole product when hydrogen chloride is absent. The following arguments (in which Roman numerals in parentheses refer to the experiments in Table I) may be applied to the reactions which occur.

(1) Hydrochloric acid is itself a catalyst for a slow polymerisation of styrene to distyrene at the boiling point (cf. Risi and Gauvin, *loc. cit.*). Direct catalysis by hydrogen chloride is excluded in our experiments at room temperature, since styrene is recovered unchanged after treatment with hydrogen chloride in the absence of stannic chloride (II).

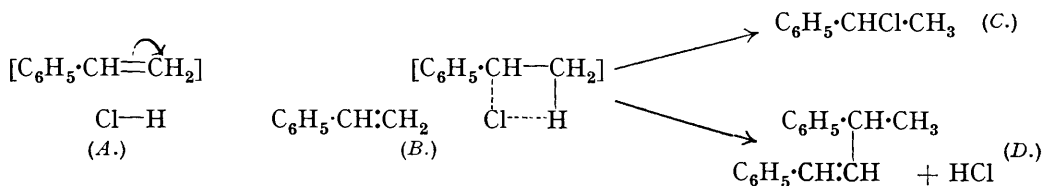
(2) The incomplete formation of α -phenylethyl chloride is not due to the equilibrium $C_6H_5 \cdot CHCl \cdot CH_3 \rightleftharpoons C_6H_5 \cdot CH : CH_2 + HCl$, observed by Hughes, Ingold, and Scott (*loc. cit.*) in sulphur dioxide and formic acid solutions, because, in carbon tetrachloride solution, α -phenylethyl chloride is very little affected by stannic chloride alone (IX, X) over a period of time greater than that required for complete consumption of styrene by hydrogen chloride. This result is in agreement with the experiments of Bodendorf and Böhme (*Annalen*, 1935, 516, 1), according to which the only action of stannic chloride upon optically active α -phenylethyl chloride in some non-hydroxylic solvents is to bring about racemisation. The experiments (IX, X) also exclude the possibility that the di- and poly-styrene fractions were formed during the isolation of the reaction products and not in the original interaction of styrene and hydrogen chloride (cf. Taylor, J., 1937, 345, on the formation of distyrene in the interaction of styrene and hydrogen bromide).

(3) It seems, therefore, that distyrene formation requires the participation of all three reactants, hydrogen chloride, styrene, and stannic chloride. Styrene probably reacts in

* Microanalyses by Dr. G. Weiler and Dr. F. B. Strauss, Oxford.

† The specimen used for analysis contained Cl, 0.4%, suggesting contamination from fraction A. No indications were observed of addition of hydrogen chloride to the double bond of distyrene.

the form of a complex with stannic chloride (see below). If we suppose that the determining factor in the addition of hydrogen chloride to the styrene double bond is the attraction of hydrogen to the β -carbon atom, assisted by polarisation as shown at (A) (Ingold, *Ann. Reports*, 1928, 25, 147), then the intermediate complex at (B) may be stabilised to form α -phenylethyl chloride (C); but if, before stabilisation, it collides with a free styrene molecule (B), distyrene of the required constitution (D) can be formed.



Compounds in square brackets are imagined to be in complex formation with stannic chloride. Such a mechanism, closely allied to that proposed by Whitmore (*Ind. Eng. Chem.*, 1934, 26, 94; cf. Bergmann, J., 1935, 1359) for acid-catalysed polymerisation, and formally equivalent to reaction by a three-body collision, is in accord with the observed fact that the ratio $\text{C}_8\text{H}_9\text{Cl}/\text{C}_{16}\text{H}_{16}$ in the reaction products is greatly increased by reducing the initial styrene concentration (V, III, IV), and somewhat decreased by reducing the concentration of stannic chloride (V, VI).

(4) A complication to be considered is that α -phenylethyl chloride, formed from styrene and hydrogen chloride, may react further with styrene. When introduced initially into a solution of styrene and stannic chloride, and treated with hydrogen chloride (VII), α -phenylethyl chloride is partly consumed; and, in the absence of hydrogen chloride, it is entirely consumed (VIII) with elimination of long-chain polymerisation. [In VII, if the added α -phenylethyl chloride is assumed to have remained intact throughout the reaction, then the styrene must have given $\text{C}_8\text{H}_9\text{Cl}$, 40; $\text{C}_{16}\text{H}_{16}$, 34; $(\text{C}_8\text{H}_8)_m$, 19%, proportions quite different from those obtained in V.] Extra distyrene is formed, but the notable feature in VII and VIII is an increase in the formation of short-chain polystyrene. It is tempting to suppose that distyrene is formed mainly by the mechanism of paragraph (3) whilst interaction of α -phenylethyl chloride with styrene accounts for the appearance of short-chain polystyrene in many of the experiments in Table I.

The alternative explanation, already referred to, *viz.*, that the formation of short-chain polystyrenes is due to interruption of chain growth, *i.e.*, that normal polymerisation chains started by the catalyst are cut short at an intermediate stage by hydrogen chloride or by α -phenylethyl chloride, is met, as regards Expts. V, VI, VII (with 0.43M-styrene), by the quantitative objection that long-chain polymerisation in the absence of hydrogen chloride is too slow to account for the observed amounts of polystyrene within the times given in Table I. From the kinetic results of the previous paper, with 0.433M-styrene and 0.0507M-stannic chloride, 10 hours were required for 13% consumption of styrene to form polystyrene of mean molecular weight 1200. In Expts. V, VI, VII, at least, short-chain polystyrenes must have been formed as a result of the interaction of styrene and hydrogen chloride and it seems probable that the same is true of the other experiments in Table I, with the possible exception of VIII, in which no hydrogen chloride was added.

In any given solution, the products formed will depend on the concentration conditions, and a detailed kinetic study is needed; but the experiments in Table I serve to show that the various reactions which may occur in the combination of styrene with hydrogen chloride all depend essentially on the primary interaction of styrene and hydrogen chloride molecules. It is therefore a plausible assumption that the inhibition of long-chain polymerisation is due to the capture by hydrogen chloride of those styrene molecules which would otherwise start polymerisation chains. Expt. XI shows that when polymerisation in full progress is interrupted by a *continued* supply of hydrogen chloride, the reaction products are the same as those obtained in Expts. III—VI. Under these conditions, long-chain polymerisation and hydrogen chloride addition (with its dependent distyrene formation) are alternative side reactions. If hydrogen chloride is present in *limited* amount, as in

the experiments of Fig. 1, it can be gradually consumed, and inhibition of polymerisation is temporary. In the experiments of Fig. 1, appreciable consumption of styrene continued for a few minutes after addition of the inhibitor. The horizontal portions on the curves probably represent the consumption of inhibitor concentrations below the limit of analysis (0.02M-styrene). Inhibition of polymerisation is thus apparently completely effective when the concentration of hydrogen chloride is only a small fraction of that of styrene; so the styrene-stannic chloride complex is probably a relatively long-lived species, which ordinarily survives several abortive collisions before making one which is successful in starting a polymerisation chain.

The Initiation of Polymerisation Chains.—It cannot be stated, at present, whether the formation of the styrene complex is fast or slow compared with the other stages occurring in long-chain polymerisation. Skraup and Freundlich (*Annalen*, 1923, **431**, 243) have made colorimetric measurements of dissociation constants in benzene solution for complexes of stannic chloride with a number of aromatic hydrocarbons having unsaturated side chains (*e.g.*, *as.*-diphenylethylene), and they do not record that measurable time was required for the establishment of equilibrium. There is abundant evidence that chain initiation is the slowest stage in vinyl polymerisations; with styrene, if complex formation is assumed to be rapid, the slow stage will be the union of a styrene-complex molecule with another styrene molecule. The individual rates of the various polymerisation stages cannot be measured directly; but, if the explanation given above for hydrogen chloride inhibition is correct, it should be possible to estimate the rate of initiation of polymerisation chains in styrene-stannic chloride systems by measuring the rate of hydrogen chloride addition to styrene which just fails to arrest polymerisation. Some preliminary measurements of the rate of interaction of hydrogen chloride and styrene in carbon tetrachloride and chloroform at 25° are shown in Table II.

TABLE II.*

Rate of Interaction of Styrene with Hydrogen Chloride.

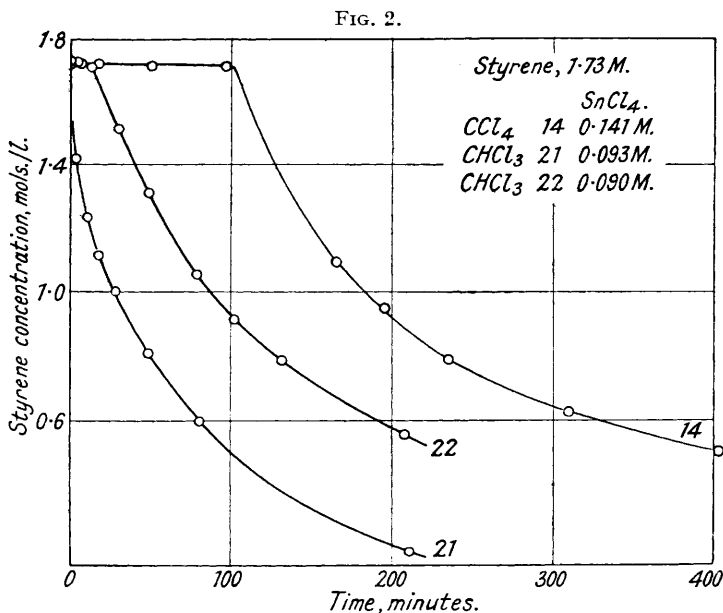
Expt. number	1A.		5A.		6A.		7A.		
Solvent	CCl ₄		CCl ₄		CHCl ₃		CHCl ₃		
Initial styrene, M	0.175		0.173		0.176		0.173		
Initial HCl, M	0.110		0.137		0.193		0.175		
SnCl ₄ , M	0		0.042		0		0.042		
Expt. 1A.			Expt. 5A.			Expt. 7A.			
Time, hrs.	C ₈ H ₈ , M.	Time, mins.	C ₈ H ₈ , M.	Change, %.	<i>k</i> ₂ , min. ⁻¹ .	Time, mins.	C ₈ H ₈ , M.	Change, %.	<i>k</i> ₂ , min. ⁻¹ .
0	0.175	0	0.173	—	—	0	0.173	—	—
1.5	0.177	3.65	0.170	—	—	1.92	0.123	29.5	1.24
18.3	0.175	11.0	0.155	13.1	0.080	2.83	0.104	40.4	1.37
49.3	0.177	21.8	0.143	21.9	0.072	4.10	0.094	46.2	1.20
Expt. 6A.		40.4	0.130	31.4	(0.054)	10.57	0.045	74.5	1.56
0	0.176	89.3	0.097	55.5	0.072	18.45	0.028	84.4	1.62
0.98	0.173	135.5	0.078	69.3	0.079	31.05	0.026	85.5	—
3.92	0.154	205	0.068	76.6	0.070				
20.2	0.110								

* Individual runs appear to be bimolecular. There is evidence that careful control of reagent purity is necessary to obtain reproducible results; the figures given are therefore provisional. In chloroform there appears to be slow interaction without a catalyst.

From Table II it may be calculated that the rate of consumption of styrene by hydrogen chloride at the point *E* of curve 13 (of the order 2×10^{17} mols./c.c./sec.) is greater than the over-all rate of consumption of styrene to form polymer just before addition of hydrogen chloride (7×10^{16} mols./c.c./sec.). Polymerisation must therefore be arrested. On the other hand, in an experiment with purified catalyst, when 0.005M-hydrogen chloride was added to 1.3M-styrene, polymerising at 4×10^{17} mols./c.c./sec., polymerisation was not totally arrested, but reduced to 4×10^{16} mols./c.c./sec., the calculated rate of removal of styrene by hydrogen chloride being 7×10^{15} mols./c.c./sec. The rate of chain initiation for these conditions thus lies between these last two figures, giving a value for the ratio (Rate of styrene consumption)/(Rate of chain initiation) of the same order of magnitude as the mean chain length (20—30) found by viscosity determinations on the polymer.

Calculations from the rates in Table II, based on the assumption that inhibition of polymerisation holds until the concentration of hydrogen chloride is reduced almost to zero, give estimates of the duration of the inhibition period which are much less than those shown in Fig. 1. This might be expected, since it is evident from Expts. VII and VIII of Table I that α -phenylethyl chloride can also inhibit long-chain polymerisation, and, in so doing, regenerate some hydrogen chloride.

Initial Inhibition.—It seems probable that the initial inhibition periods observed in polymerisations with unpurified stannic chloride are due to the presence of hydrogen chloride as impurity. Although not strictly proved, this explanation is supported by the following observations. (a) With purified catalyst, there is no initial inhibition (cf. curve 31, Fig. 1, and curves given in Part I, *loc. cit.*). (b) It is shown in Table II that hydrogen chloride reacts much more rapidly with styrene in chloroform than in carbon tetrachloride. Correspondingly, the initial inhibition of polymerisation is of much shorter duration in purified chloroform (9 mins. on curve 22 of Fig. 2) than in carbon tetrachloride (98 mins. on curve



Polymerisation of styrene in carbon tetrachloride and chloroform at 25°.

14). In commercial chloroform, used without purification, no initial inhibition occurred (curve 21). (c) In carbon tetrachloride, the inhibition period t_i decreases with increasing concentration of stannic chloride and of styrene, as shown below :

Initial Inhibition Periods at 25°.

No.	Styrene, 1.73—1.75M.							Styrene, 1.26M.
	7	8	10	12	14	9	11	
SnCl ₄ , M	0.013	0.030	0.089	0.107	0.141	0.157	0.193	0.108
t_i , hrs.	4.5	2.4	1.3	1.6	1.5	0.8	0.83	2.2

The variations are in the sense to be expected if hydrogen chloride, in amount proportional to the catalyst concentration, is the polymerisation inhibitor, and if it is removed in a pseudo-unimolecular reaction (styrene being in great excess) catalysed by stannic chloride.

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