The Participation of Stannic Halide Catalysts in the Reactions of Styrene with Hydrogen Halides. Halogen Exchange between Stannic Halides and 1-Phenylethyl Halides.

By KATHLEEN HEALD and GWYN WILLIAMS.

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Some 1-phenylethyl bromide is formed when stannic bromide catalyses the addition of hydrogen chloride to styrene in carbon tetrachloride; and some 1-phenylethyl chloride is formed in the reaction between styrene and hydrogen bromide, in the same solvent, catalysed by stannic chloride. The cross halogen addition products are not necessarily formed during the actual process of addition because there is direct exchange of halogen between halides C_8H_9X and stannic halides SnY_4. In general, the proportion of cross halogenation increases with catalyst concentration. The reactions are best interpreted by carbonium-ion mechanisms.

In the polar solvent nitrobenzene, styrene and hydrogen chloride react, without a catalyst, to form mainly 1-phenylethyl chloride; but in the presence of stannic chloride the only product is polystyrene of molecular weight about 400.

IN carbon tetrachloride (Williams, *J.*, 1938, 246; 1940, 775), and in other solvents (*e.g.*, Pepper, *Trans. Faraday Soc.*, 1949, **45**, 397, 404), styrene polymerises in the presence of stannic chloride to long-chain polymers having molecular weights of the order 1000—10,000. When hydrogen chloride is present, however (Williams, *J.*, 1938, 1046; Williams and Thomas, *J.*, 1948, 1867), the long-chain polymerisation in carbon tetrachloride is replaced by a faster reaction producing 1-phenylethyl chloride and short-chain polystyrene. This is largely dimer for styrene < 2M, but the amount and average molecular weight of the polymer rise with increasing initial concentration of styrene. A similar difference between reactions in the absence and presence of hydrogen chloride is brought out clearly in the far more polar solvent, nitrobenzene (see Table 3). Carbonium-ion mechanisms have been proposed for the reactions in carbon tetrachloride (*idem, ibid.*; also Williams and Bardsley, *J.*, 1952, 1707). These are supported by the racemisation experiments on 1-phenylethyl chloride in carbon tetrachloride (following paper), and also by the following experiments, which show that the halogen atoms of a stannic halide catalyst participate in the reactions.

Participation of the halogen atoms of metal halide catalysts in Friedel–Crafts reactions has already been proved, in general, by Fairbrother (*J.*, 1937, 503; 1941, 293; *Trans. Faraday Soc.*, 1941, **37**, 763), by the use of catalysts containing radioactive halogen. A proof, on essentially similar lines, for hydrogen halide addition to styrene results from experiments in which hydrogen chloride addition is catalysed by stannic bromide, and hydrogen bromide addition is catalysed by stannic chloride.

TABLE 1. *Halogen exchange in addition of hydrogen halides in carbon tetrachloride at 20—25°.*

Expt. No.	Initial styrene, M	Catalyst concn., M	Duration of expt., hr.	% Styrene recovered as:			Total yield, %	% C_8H_9Br in C_8H_9X
				C_8H_8	C_8H_9X	$(C_8H_8)_n$ ¶		
			(a) *Adduct: hydrogen chloride. Catalyst:* $SnBr_4$. *Hydrogen chloride supply continuous.*					
18	0·34	0·0048	41	46	33·3	8·3	87·6	6·4 *
54	0·329	0·0136	$24\frac{1}{2}$	29·8	20·9	12·0	62·7	11·6 *
55	0·371	0·0171	$29\frac{3}{4}$	31·6	(75·9)	—	—	6·4 *
23	0·34	0·0264	48	15·6	35·5	22·7	73·8	7·2 *
89	0·333	0·105	$12\frac{1}{4}$	64·5	29	6·7	(100·2)	45·5
87	0·333	0·162	$10\frac{3}{4}$	48·6	33·1	7·8	89·5	63·0
88	0·333	0·170	$10\frac{3}{4}$	34·7	47·2	10	91·9	52·4
90	0·333	0·221	$10\frac{3}{4}$	35·2	42·3	17·8	95·3	54·0
19 †	0·34	0·0167	14	0	36	—	—	9·9 *
			(b) *Adduct: hydrogen bromide. Catalyst:* $SnCl_4$. *Hydrogen bromide supply continuous.*					
52	0·527	0·0104	$2\frac{3}{4}$	8·6	59·3	15·3	83·2	99·9 *
51	0·389	0·0202	3	0	78·7	15·8	94·5	98·6 *
53	0·793	0·0562	4	22·8	54·2	17·2	94·2	95·6 *
16	0·34	0·035	$3\frac{1}{4}$	0	69·2	16·7	85·9	96·4 *
81	0·34	0·0685	2	0	86·4	0	86·4	99·0
73	0·34	0·0857	$2\frac{1}{2}$	0	71·5	14·7	86·2	99·0
74	0·34	0·0857	$2\frac{1}{2}$	0	85·5	0	85·5	76·5
77	0·34	0·0857	7	0	89·4	0	89·4	82·5
17	0·34	0·186	$4\frac{3}{4}$	0	63·5	16·7	80·2	87·2 *
78	0·34	0·343	$2\frac{3}{4}$	0	80·1	9·4	89·5	50·5
79	0·34	0·343	3	0	81·4	9·4	90·8	60·1
			(c) *Adduct: hydrogen bromide. Catalyst:* $SnCl_4$. *Hydrogen bromide supply regulated.*					
72 ‡	0·34	0·0857	$3\frac{1}{4}$	40·0	26·3	34·3	(100·6)	11·1
69 ‡	0·34	0·171	$5\frac{1}{4}$	5·0	27·2	68·7	(100·9)	2·0
70 ‡	0·34	0·174	$3\frac{1}{4}$	18·4	34·2	42·9	96·0	4·7
71 ‡	0·34	0·343	3	0	49·7	39·5	89·2	2·3
76 §	0·34	0·175	4	27·9	68·4	0	96·3	20·0
75 §	0·34	0·175	$6\frac{1}{4}$	35·7	36·0	12·9	84·6	28·5
67 ‖	0·34	0·171	$4\frac{3}{4}$	5·0	57·0	32·6	94·6	35·7
65 ‖	0·34	0·343	$2\frac{1}{4}$	0	72·2	7·1	—	4·6

* Analysed by oxidation method: remainder by density method.
† Solvent: chlorobenzene.
‡ Very slow stream of HBr maintained throughout.
§ HBr supply stopped after 40 min. (76) and 15 min. (75).
‖ HBr supply stopped at once after addition of styrene and $SnCl_4$.
¶ Largely distyrene.

Halogen Exchange in Addition Reactions.—In the experiments listed in Table 1, the current of hydrogen halide was led through the solution of styrene and the stannic halide catalyst in carbon tetrachloride. The consumption of styrene was tested at intervals by removing samples and titrating the residual styrene with bromine (Williams, *J.*, 1938, 246). At the end of the experiment, the products were isolated by distillation, and the proportions of 1-phenylethyl chloride and 1-phenylethyl bromide in the hydrogen halide addition product were determined by methods described on p. 361.

In carbon tetrachloride, hydrogen chloride and styrene do not react in the absence of a catalyst (*locc. cit.*); but when hydrogen bromide is led through 0·33M-styrene, in the same solvent, 89—95% yields of 1-phenylethyl bromide are recovered after 1¾—3½ hr. The formation of substantial proportions of 1-phenylethyl chloride, when the addition of hydrogen bromide to styrene is catalysed by stannic chloride, is therefore particularly significant. The formation of cross halogen addition product is evident in a large proportion of the experiments in Table 1, from which the following conclusions may be drawn: (1) The addition of hydrogen bromide to styrene catalysed by stannic chloride is much more rapid than the addition of hydrogen chloride catalysed by stannic bromide; (2) in a general way, the proportion of cross halogen addition product formed increases with increase of catalyst concentration; the increase is not always strictly regular, but fluctuations may well be due to irregularities in the rate of supply of hydrogen halide; (3) from Table 1(c) as compared with Table 1(b), it is clear that the proportion of cross halogen product is increased by reduction of the rate of supply of hydrogen halide or by complete interruption of the supply.

Direct Halogen Exchange between 1-*Phenylethyl Halides and Catalyst.*—The results in Table 1 do not prove that the whole of the cross halogen addition product is formed in the actual process of addition; and indeed, the results of Table 1(c) indicate the possibility of direct interchange between catalyst and the organic halide after its formation. This possibility is confirmed by the results shown in Table 2.

TABLE 2. *Halogen exchange between* 1-*phenylethyl halides and stannic halides in carbon tetrachloride at* 20—25°.

Expt. No.	Initial C_8H_9Br, M	Concn. $SnCl_4$, M	Initial C_8H_9Cl, M	Concn. $SnBr_4$, M	Duration of expt., hr.	% C_8H_9X recovered	% C_8H_9Br in C_8H_9X
(a) *Interaction of* C_8H_9X *with* HY							
82 *	0·33	—	—	—	4	95·3	99·9
83 *	0·33	—	—	—	20	83·1	98·7
86 †	—	—	0·36	—	5	91·2	5·0
(b) *Interaction of* C_8H_9Br *with* $SnCl_4$							
56	0·33	0·164	—	—	6	91·1	4·5
95 ‡	0·33	0·164	—	—	4	94·3	45·5
58 †	0·33	0·164	—	—	6	88·7	88·5
57 †	0·33	0·164	—	—	13½	80·4	56·7
60 †	0·33	0·0164	—	—	4	68·2	96·6
(c) *Interaction of* C_8H_9Cl *with* $SnBr_4$							
65	—	—	0·34	0·0211	50	97·2	9·5
62 *	—	—	0·30	0·0331	48	73	10·9
33	—	—	0·30	0·036	12	78·1	6·0
93	—	—	0·30	0·111	12	94·6	21·9
92	—	—	0·30	0·114	12	96·7	24·4
94 *	—	—	0·17	0·242	12	92·5	39·7

* Current of dry hydrogen chloride supplied. † Current of dry hydrogen bromide supplied.
‡ Reagents added to solvent saturated with HBr, then gas supply discontinued.

Table 2(a) shows that interchange of halogen between C_8H_9X and HY is inconsiderable in the absence of catalyst. Table 2(b) and (c) shows that exchange of halogen between C_8H_9X and SnY_4 occurs, in carbon tetrachloride solution, in times comparable with those used for the addition experiments of Table 1, to an extent which increases with rising concentration of SnY_4 and falls in presence of HX.

For some addition experiments the reagents were specially dried and the reaction was conducted in a totally enclosed apparatus, with an internal arrangement for breaking phials of specially pure catalyst without contact with the atmosphere. The results of these experiments did not seem to be significantly different from those conducted without these special precautions; but, even so, the extent of drying achieved in the special experiments was probably insufficient to exclude the possibility of co-catalysis by traces of moisture.

DISCUSSON

In the addition reactions it is not known whether the catalyst acts first upon styrene or upon the hydrogen halide. The *result* of the (no doubt, stepwise) interaction of the three reagents may be represented formally by equation (1). Subsequent steps may be those shown in equations (2)—(6):

$$\mathrm{CHPh{:}CH_2 + SnY_4 + HX = {}^{+}CHPh{\cdot}CH_3\}SnXY_4{}^{-}} \qquad (1)$$

$$\mathrm{{}^{+}CHPh{\cdot}CH_3\}SnXY_4{}^{-}} \rightleftharpoons \left\{\begin{array}{ll}\mathrm{CHPhX{\cdot}CH_3 + SnY_4} & (2)\\ \mathrm{CHPhY{\cdot}CH_3 + SnXY_3} & (3)\end{array}\right.$$

$$\mathrm{HX + {}^{+}CHPh{\cdot}CH_3\}SnXY_4{}^{-} = CHPhX{\cdot}CH_3} + \left\{\begin{array}{l}\mathrm{SnY_4 + HX}\\ \mathrm{SnXY_3 + HY}\end{array}\right. \qquad (4)$$

$$\mathrm{CHPh{:}CH_2 + {}^{+}CHPh{\cdot}CH_3\}SnXY_4{}^{-} = {}^{+}CHPh{\cdot}CH_2{\cdot}CHPh{\cdot}CH_3\}SnXY_4{}^{-}} \qquad (5)$$

$$\mathrm{{}^{+}CHPh{\cdot}CH_2{\cdot}CHPh{\cdot}CH_3\}SnXY_4{}^{-} = CHPh{:}CH{\cdot}CHPh{\cdot}CH_3 + HX + SnY_4} \qquad (6)$$

Interaction of the carbonium ion with styrene (5) can form (slowly) a polymeric ion, which may be stabilised by reaction with the anion (6). One of the stages in process (1) determines the rate of addition, as is shown by the kinetics of the reaction (Williams and Bardsley, *loc. cit.*). The forward processes (2) and (3) are fast, whilst the reverse actions have a measurable speed, as is shown by the racemisation experiments (following paper), in which $X = Y = Cl$.

The logic of the proof, by demonstration of halogen exchange (Table 1), that the halogen atoms of the catalyst participate in the addition reactions, is marred only by the possibility of direct halogen exchange between HX and SnY_4. This exchange is known to occur very slowly between HBr and $SnCl_4$ below 0°; the halides $SnCl_3Br$, $SnCl_2Br_2$, and $SnClBr_3$ are less stable than $SnCl_4$ and $SnBr_4$ (Besson, *Compt. rend.*, 1897, **124**, 683). However, the proof of halogen exchange between catalyst and organic halide (Table 2) shows that the presence of hydrogen halide is not essential to halogen interchange, which may occur by the back reaction (2) and forward reaction (3). The reaction (4) may account for the effect of hydrogen halide in reducing halogen exchange.

Hydrogen halides play no part in the normal polymerisation of styrene by stannic halides to give long-chain polymers. Formation of long-chain polystyrene, insoluble in methyl alcohol, was not observed in any of the reactions shown in Tables 1 and 2. If the long-chain polymers, produced in the *absence* of hydrogen halide, are also formed through carbonium ions of the form $^{+}CHPh{\cdot}[CH_2{\cdot}CHPh]_n{\cdot}CH_3$, then the higher rate of consumption of styrene in *presence* of hydrogen halide may be due to the readier supply of carbonium ions by process (1), when hydrogen halide is available as a co-catalyst; and the absence of long-chain polymers in these conditions must be due to the efficiency of reactions of type (6) in destroying growing polymer ions. That forward step (2) is much faster than polymer growth is shown by the racemisation experiments (following paper). No hydrogen halide addition products of distyrene or other polymer have been isolated in any addition experiments.

Experiments in Nitrobenzene.—These considerations are shown in extreme form in the solvent nitrobenzene (Table 3), which is much more favourable to ionisation than carbon tetrachloride. In this solvent, styrene reacts with hydrogen chloride, without an added catalyst, to form 1-phenylethyl chloride [Table 3(*c*)]. Formation of carbonium ion through attack of a solvated proton, $Ph{\cdot}NO_2H^+$, upon the olefin is not improbable. When stannic chloride is present, in nitrobenzene solution, the only product isolated from a very rapid reaction with hydrogen chloride is quite short-chain polystyrene [Table 3(*b*)]. Growth of polymeric ions—by steps such as (5)—is thus efficient enough to destroy all hydrogen halide

TABLE 3. *Reactions in nitrobenzene. Temp.* 20—25°.

Reagents	$SnCl_4$, M	Duration of expt., min.	% Styrene recovered as C_8H_9Cl	% Styrene recovered as $(C_8H_8)_n$	*n*
(*a*) Styrene, 0·392M	0·0307	200	—	89·2	26
(*b*) Styrene, 0·34M; HCl satd.	0·034	3	—	94·5	(I) 4·4 (II) 4·2 (III) 3·3
(*c*) Styrene, 0·34M; current of HCl	—	70	72·8	4·1	Small

addition product; but chain termination, presumably of type (6), is so effective that only short-chain polymers are formed, in contrast with the long-chain polymers produced in absence of hydrogen halide [Table 3(*a*)].

The solvent used clearly plays an important part in determining what products are formed when styrene is exposed to the action of stannic halides and to the combined action of stannic halides and hydrogen halides. Pepper and Somerfield have recently shown (in "Cationic Polymerisation," ed. Plesch, Heffer, Cambridge, 1953, p. 75) that hydrogen chloride and hydrogen bromide will initiate the polymerisation of styrene in the absence of stannic halide, in solvents of relatively high dielectric constant.

EXPERIMENTAL

Materials.—Pure commercial styrene stabilised with quinol was distilled under reduced pressure before use. Commercial stannic chloride and stannic bromide were distilled in a vacuum, essentially as described previously (Williams, *loc. cit.*). "AnalaR" carbon tetrachloride was stored over phosphoric oxide and distilled immediately before use. 1-Phenylethyl chloride and 1-phenylethyl bromide were made, respectively, by the action of purified thionyl chloride (McKenzie and Clough, *J.*, 1913, **103**, 694) and phosphorus tribromide (Rupe and Toni, *Ber.*, 1914, **47**, 3074) upon 1-phenylethyl alcohol, prepared from phenylmagnesium bromide and acetaldehyde (Found, for the two compounds: Cl, 25·1, 25·3; Br, 43·2, 43·4. Calc. for C_8H_9Cl and C_8H_9Br: Cl, 25·3 and Br, 43·2%, respectively).

Addition and Halogen-exchange Experiments.—A current of dry hydrogen chloride (generated from hydrochloric and sulphuric acid) or hydrogen bromide (generated by allowing bromine to drop on a mixture of red phosphorus and water, or on purified tetralin) was led through a solution of styrene and catalyst in carbon tetrachloride at known concentrations. In both the addition experiments and the direct halogen-exchange experiments, the products were separated by distillation as described by Williams and Thomas (*loc. cit.*).

Products.—The hydrogen chloride addition product had composition C, 68·8; H, 6·5; Cl, 25·3 (Calc. for C_8H_9Cl: C, 68·3; H, 6·4; Cl, 25·3%). The compound has already been proved to be 1-phenylethyl chloride (Williams and Thomas, *loc. cit.*). The hydrogen bromide addition product (Found: Br, 43·2%) was shown to be 1-phenylethyl bromide by conversion, through the alcohol, into the 3 : 5-dinitrobenzoate (m. p. 94—95°; mixed m. p. with authentic specimen 94—95°: cf. Ashworth and Burkhardt, *J.*, 1938, 1798). The short-chain polystyrenes, (largely) distyrene, have been identified by Williams and Thomas (*loc. cit.*).

Analysis of Mixed 1-*Phenylethyl Halides.*—(a) *Oxidation method.* 0·2—0·4 G. of the mixed 1-phenylethyl chloride and bromide was hydrolysed by refluxing it for 3 hr. with a slight excess of 0·2N-alcoholic sodium hydroxide. After removal of all organic material by steam-distillation (½ hr.), sulphuric acid to make up to 7N and chromium trioxide (5 g.) were added to the residual mixed sodium chloride and bromide, and air was led through for 3 hr. (Evans, *Analyst*, 1930, 590), to carry the liberated bromine into 20 ml. of approx. 0·2N-arsenious oxide (excess), together with sodium hydrogen carbonate (5 g.) and water (200 ml.). Completeness of bromine absorption was checked by passing the exit gas through a second arsenious oxide solution. The excess of arsenious oxide was titrated against 0·1N-iodine solution. Control experiments on synthetic mixtures are shown in Table 4.

TABLE 4. *Analysis of mixed* 1-*phenylethyl chloride and bromide by oxidation.*

Mixture	Wt. bromide, g.	0·0439	0·1316	0·1804	0·3236
	Wt. chloride, g.	0·2345	0·3042	0·1673	0·0407
% C_8H_9Br	Calc.	15·70	30·11	51·60	88·62
	Found	15·77	30·19	51·88	88·81

(b) *Density method.* The densities of pure 1-phenylethyl chloride and bromide, and of artificial mixtures of them, were determined by pycnometer (Table 5). The relationship between density and composition is linear. The composition of halide mixtures derived from reaction products was determined by reference to these results.

TABLE 5. *Densities of mixtures of* 1-*phenylethyl chloride and bromide.*

C_8H_9Br, %	0	24·2	49·2	80·7	100
d^{25}_{25}	1·0631	1·136	1·212	1·302	1·3584

When applied to the same sample of mixed halides from a reaction product, the oxidation and the density method gave concordant results for the proportion of bromide present (Table 6).

TABLE 6. *Comparison of analytical methods.*

C_8H_9Br present. %	By oxidation	6·35	9·85	54·2	87·1
	By density	6·70	9·90	55·0	87·5

The total halogen present in reaction products was frequently determined. The results were consistent with those for the proportions of bromide and chloride present.

Experiments in Nitrobenzene.—At the end of the experiment of Table 3(*c*) the reaction mixture was washed with water and dried and then distilled at <0·1 mm., leaving a small residue of undistillable polymer. The 1-phenylethyl halide in the distillate was determined by hydrolysis with water, followed by Volhard estimation of halide in the aqueous layer. In the experiment of Table 3(*b*), the polymer fractions (I) and (II) were precipitated with much methyl alcohol; and fraction (III) was a distillation residue. The molecular weights were determined cryoscopically in benzene. The polymer of Table 3(*a*) was precipitated in methyl alcohol.

ROYAL HOLLOWAY COLLEGE (UNIVERSITY OF LONDON),
ENGLEFIELD GREEN, SURREY.

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