# *The Racemisation of* (–)-1-*Phenylethyl Chloride by Stannic Chloride in Carbon Tetrachloride and its Bearing on the Cationic Polymerisation of Styrene.*

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[Reprint Order No. 4589.]

Stannic chloride catalyses the racemisation of (–)-1-phenylethyl chloride in carbon tetrachloride, which makes it very probable that carbonium-ion mechanisms can occur in this solvent of low dielectric constant. The rate of racemisation is substantially unaffected by the presence of excess of styrene. It follows that the recombination of the $CHPhMe^+$ ion to form the halide is faster than its reaction with a styrene molecule. This conclusion is confirmed by direct observation on the rate of interaction of the halide with styrene in presence of stannic chloride. The interaction of this carbonium ion with monomeric styrene is an essential growth step in the polymerisation of styrene. Polymerisation is very largely inhibited by 1-phenylethyl chloride.

IN liquid sulphur dioxide (Bergmann and Polanyi, *Naturwiss.*, 1933, **21**, 378; Hughes, Ingold, and Scott, *J.*, 1937, 1201, 1271) and in formic acid (Bodendorf and Böhme, *Annalen*, 1935, **516**, 1), optically active 1-phenylethyl chloride racemises without further catalytic aid. Bodendorf and Böhme (*loc. cit.*) showed that, in less polar solvents, the Friedel–Crafts catalysts mercuric chloride, zinc chloride, boron trichloride, titanium tetrachloride, stannic chloride, and antimony pentachloride, were effective catalysts for the racemisation. The compound antimony trichloride had little activity, whilst silicon tetrachloride and arsenic trichloride had none. The racemising influence of zinc chloride was lessened and almost inhibited by the presence of lithium chloride; and the action of stannic chloride in benzene was greatly reduced by the presence of hydrogen chloride (Böhme and Siering, *Ber.*, 1938, **71**, 2372). With a given catalyst, the rate of racemisation in different solvents generally ran roughly parallel with dielectric constant; and a carbonium-ion mechanism was proposed for the reaction.

Bodendorf and Böhme examined the action of stannic chloride in nitromethane, nitrobenzene, benzene, ether, and chloroform, but not in the still less polar solvent carbon tetrachloride. Since carbonium-ion mechanisms have been suggested for reactions of styrene, hydrogen chloride, and 1-phenylethyl chloride, in this solvent, in presence of stannic chloride (cf. preceding paper), we have verified that stannic chloride does bring about the racemisation of (–)-1-phenylethyl chloride in carbon tetrachloride and we have measured rates of racemisation.

*Racemisation Reactions.*—The results are shown in Table 1. Racemisation is normally of the first order with respect to (—)-1-phenylethyl chloride; for (*a*) the half-period of racemisation (in a given experiment) is nearly equal to the time needed to pass from one-third to two-thirds of completion, the reaction periods being derived from curves of observed rotation against time (Fig., *c*, *d*); (*b*) log $a_t$ is linear with time (Fig., *a*, *b*), and velocity coefficients may be computed graphically for the expression $k_1t = 2{\cdot}303 \log (a_0/a_t)$, where $a_0$ and $a_t$ are the rotations observed for times zero and *t*, respectively; (*c*) rates of reaction with a stannic chloride catalyst are seldom exactly reproducible, but the values of $k_1$ and the periods for fractional completion of racemisation are nearly the same for different initial concentrations of the halide.

In all the experiments the catalyst concentration was nearly the same. Each group of experiments in Table 1 is a series performed with catalyst solutions derived from the same sample of stannic chloride. Between each series of experiments, the reaction vessel (polarimeter tube) was dried particularly thoroughly (see p. 366). In a few experiments, at the beginning of a series, racemisation was unusually slow and did not conform to first order. An example is Expt. 15 (Table 1) which was slow in its later stages, and another is given by a series (not shown in the Table) in which the half-periods and periods for one-third to two-thirds completion in successive reactions were 31, 112; 11·0, 21·5; 14·5, 18·5; and 11·7, 12·8 min. There is evidence (*e.g.*, Plesch, *Research*, 1949, **2**, 267) that the action of Friedel–Crafts catalysts is sometimes influenced by traces of a polar " co-catalyst " (such as water). The reagents used in the racemisations were thoroughly dried by normal methods. It has not been established whether the abnormal racemisations, which occurred, if at all, at the beginning of a series, were due to the removal of moisture by the rigorous drying of the polarimeter tube between series, or to the presence of adventitious anti-catalyst. In any event, it appears (Table 1) that reasonable (though not necessarily exact) reproducibility of reaction rate is obtainable by ordinary careful treatment of reagents and apparatus, as is also true of the polymerisation of styrene by stannic chloride in carbon tetrachloride (Williams, *J.*, 1940, 775).

TABLE 1. *Rates of racemisation in carbon tetrachloride at 25°.*

| Expt. No. | $[\alpha]_D$ for $C_8H_9Cl$ used | $C_8H_9Cl$, initial concn., M | $SnCl_4$, M | Concn. of styrene, M | | Reaction time: | | 100 $k_1$, min.$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| | | | | Initial | Final | 0—½ completion | ⅓—⅔ completion | |
| 3 | −50·1° | 0·3447 | 0·0712 | — | — | 13·8 | 15·1 | — |
| 4 | — | 0·3447 | 0·0712 | — | — | 10·3 | 10·0 | — |
| 5 | −36·5 | 0·2187 | 0·0584 | — | — | 13·0 | 15·1 | 4·8 |
| 6 | — | 0·2081 | 0·0556 | 0·413 | — | 15·0 | 14·0 | 4·8 |
| 11 | −45·3 | 0·2070 | 0·0739 | — | — | 10·5 | 13·2 | (3·7) |
| 12 | — | 0·2070 | 0·0739 | — | — | 8·7 | 9·2 | 6·9 |
| 13 | — | 0·1972 | 0·0704 | 0·413 | — | 7·8 | 8·2 | 6·6 |
| 14 | — | 0·1972 | 0·0704 | 0·413 | — | 8·0 | 8·5 | 6·9 |
| 15 | −51·9 | 0·1250 | 0·0778 | — | — | 12·5 | 27·5 | — |
| 16 | — | 0·1250 | 0·0778 | — | — | 10·0 | 15·9 | (6·2) |
| 17 | — | 0·1190 | 0·0741 | 0·413 | 0·394(90) * | 11·0 | 9·9 | 7·4 |
| 18 | — | 0·1190 | 0·0741 | 0·413 | 0·385(75) * | (11·0) | (11·5) | (7·6) |
| 19 | −51·9 | 0·1144 | 0·0618 | — | — | 9·0 | 14·3 | 4·9 |
| 20 | — | 0·1089 | 0·0589 | 0·413 | 0·419(21) *<br>0·393(54) * | 9·5 | 14·5 | 6·5 |
| 21 | — | 0·1089 | 0·0589 | 0·413 | — | (7·5) | (9·7) | 5·9 |
| 22 | — | 0·1144 | 0·0618 | — | — | 11·2 | (14·3) | 5·5 |

* Times (min.) at which styrene concentration was determined are in parentheses.

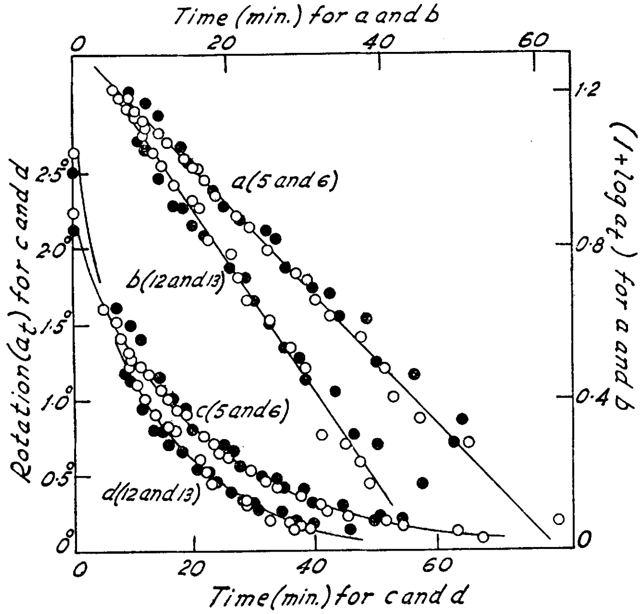
In Bodendorf and Böhme's experiments with stannic chloride (*loc. cit.*), racemisation was slowest in chloroform. It is slower still in carbon tetrachloride. Extrapolation from their results (with the aid of their unusual expression for the dependence of racemisation rate upon catalyst concentration) gives $k_1 \sim 0{\cdot}4$ for catalysis by 0·074M-stannic chloride in chloroform. The corresponding result (Table 1) for carbon tetrachloride is $k_1 \sim 0{\cdot}07$.

*Mechanism of Racemisation.*—Previous investigators (*locc. cit.*) have taken the observed rates of racemisation to be the rates of formation of carbonium ions. Prior elimination of hydrogen chloride, possible in formic acid solvent (Hughes, Ingold, and Scott, *loc. cit.*), is unlikely in racemisation by Friedel–Crafts catalysts (Böhme and Siering, *loc. cit.*). On this view the rates of racemisation in Table 1 are the rates of carbonium-ion formation in processes of type (1) :

$$(-)\text{-CHPhCl·CH}_3 + \text{SnCl}_4 \rightleftharpoons \overset{+}{\text{C}}\text{HPh·CH}_3\}\text{SnCl}_5^- \rightleftharpoons (+)\text{-CHPhCl·CH}_3 + \text{SnCl}_4 \qquad (1)$$

The rate of disappearance of (−)-1-phenylethyl chloride is measured by $k_1/2$ ; but the total rate of interaction of the chloride with stannic chloride is given by $k_1$ (cf. Bartlett and Pöckel, *J. Amer. Chem. Soc.*, 1938, **60**, 1585). Reconversion of the ion-pair into halide and catalyst must be rapid.

*Racemisation in Presence of Styrene.*—The rate of racemisation of (−)-1-phenylethyl chloride is substantially unaffected by the presence of excess (0·41M) of styrene (Table 1; Fig. *a*, *b*, *c*, *d* ); and the bulk of the styrene is still present at the end of the reaction (Table 1).



*Open circles : Progress of racemisation in absence of styrene.*
*Full circles : Racemisation in presence of excess of styrene.*

*Reaction of* (±)-1-*Phenylethyl Chloride with Styrene.*—Stannic chloride has been shown to catalyse a reaction between styrene and racemic 1-phenylethyl chloride, in carbon tetrachloride, to form distyrene and other short-chain polystyrenes (Williams and Thomas, *J.*, 1948, 1867). The results of new experiments on the rate of this reaction are shown in Table 2. The consumption of styrene was followed by titration with bromine (Williams, *J.*, 1938, 246). Up to about 15% consumption of styrene, the fraction of styrene consumed in a given time is nearly independent of the initial styrene concentration, which indicates that the reaction rate is proportional to the first power of the styrene concentration. At later stages of the reaction, when polymers larger than the dimer are accumulating, the fraction consumed in a given time increases with increasing styrene concentration.

*Relative Rates of Reactions.*—Rates of racemisation are known from Table 1 ; those for the reaction between halide and styrene may be inferred from Table 2 ; and rates for the long-chain polymerisation of styrene, in presence of stannic chloride, and for the action of hydrogen chloride upon styrene, are known from earlier work (Williams, *J.*, 1940, 775; Williams and Bardsley, *J.*, 1952, 1707). Calculated rates for comparable concentrations of the reagents are shown in Table 3, from which it is clear that neither interaction between styrene and 1-phenylethyl chloride (*b*) nor long-chain polymerisation of styrene (*c*) will be expected to occur to an appreciable extent in the time required for complete racemisation of halide (*a*) in presence of 0·41M-styrene, in agreement with the results of Table 1. However, reactions (*b*) and (*c*) proceed, in independent systems, at comparable speeds. Since long-chain polystyrene is not detected among the products of (*b*) (Williams and Thomas, *loc. cit.*), it is evident that (*b*) can interfere with the long-chain polymerisation of styrene. This is still more obvious when 1·74M-styrene is present. As shown in Table 3(*e*), long-chain polymerisation would be rapid at this concentration, in the absence of halide.

TABLE 2. *Reaction of* 1-*phenylethyl chloride with styrene.*

| | Expt. No. | 84 | 85 | 86 |
|---|---|---|---|---|
| Initial concn., M | Styrene | 0·385 | 0·743 | 1·378 |
| | (±)-$C_8H_9Cl$ | 0·179 | 0·171 | 0·157 |
| | $SnCl_4$ | 0·0666 | 0·0636 | 0·0582 |

| Time (hr.) | | 0·833 | 1·67 | 3·33 | 4·17 | 10 | 20 | 30 | 40 |
|---|---|---|---|---|---|---|---|---|---|
| % Consumption of styrene in Expt. No. | 84 | 4·0 | 7·8 | 13·0 | 14·5 | 19·0 | 27·5 | 35·0 | 41·0 |
| | 85 | 3·5 | 6·0 | 12·0 | 14·0 | 22·0 | 36·0 | 46·5 | 55·0 |
| | 86 | 3·0 | 6·4 | 12·6 | 16·0 | 33·5 | 57·0 | 72·0 | 82·5 |

TABLE 3. $[C_8H_8]$ = 0·41M (except in *e* and *f*); $[C_8H_9Cl]$ = 0·18M; $[SnCl_4]$ = 0·065M.

| Reaction | $10^4$ × rate, mole l.$^{-1}$ min.$^{-1}$ |
|---|---|
| (*a*) (−)-$C_8H_9Cl(+ SnCl_4) \longrightarrow$ racemate | 108 |
| (*b*) $C_8H_9Cl + C_8H_8(+ SnCl_4) \longrightarrow (C_8H_8)_2$ | 3·0 |
| (*c*) $C_8H_8(+ SnCl_4) \longrightarrow (C_8H_8)_{12}$ | 1·3 |
| (*d*) $C_8H_8 + HCl(+ SnCl_4) \longrightarrow C_8H_9Cl$ | 128 |
| (*e*) 1·74M-$C_8H_8(+ SnCl_4) \longrightarrow (C_8H_8)_{23}$ | 417 |
| (*f*) 1·7M-$C_8H_8 + C_8H_9Cl(+ SnCl_4) \longrightarrow$ small polymers | 12·4 |

## DISCUSSION

The occurrence of racemisation in carbon tetrachloride makes it very probable that carbonium-ion mechanisms are possible even in this solvent of low dielectric constant. If the rate of reaction (*a*) of Table 3 is the rate of formation of the carbonium ion $CHPhMe^+$ [cf. equation (1)], then the rate of recombination of this ion to form 1-phenylethyl halide [faster than (*c*)] is much faster than the combination $CHPhMe^+ + CHPh{:}CH_2$, which is the probable rate-determining step of reaction (*b*) of Table 3 [cf. equation (5) of preceding paper]. The latter process is a growth step in the cationic polymerisation of styrene (Table 3, *c*). The rate of (*c*) is essentially the rate of combination of all growing polymer cations with monomeric styrene. With 0·41M-styrene the rates of (*b*) and (*c*) are (fortuitously) nearly the same, although there is no necessary relation between the carbonium-ion concentrations in the two processes. With 1·74M-styrene, the rate of polymer growth (*e*) is much greater than the rate of combination of 1·74M-styrene with halide $C_8H_9Cl$ (*f*) (estimated by extrapolation from Table 2), when these two reactions occur independently, yet distyrene is the main product of (*f*) and very little non-distillable polymer is formed (Williams and Thomas, *loc. cit.*). Presumably polymer growth in (*f*) is cut short by the effective chain-breaking combination of carbonium ion with $SnCl_5^-$ ion (cf. preceding paper). The rate of reaction (*d*) is that of the essential step in the formation of carbonium ion from styrene, hydrogen chloride, and stannic chloride, shown as equation (1) in the preceding paper, whilst the rate of (*a*) is the rate of the back step in (2).

## EXPERIMENTAL

*Materials.*—1-Phenylethyl alcohol (from phenylmagnesium bromide and acetaldehyde) was converted by phthalic anhydride and pyridine (Pickard and Kenyon, *J.*, 1911, **99**, 45; Houssa and Kenyon, *J.*, 1930, 2260) into its hydrogen phthalate; and this was resolved with brucine (Ott, *Ber.*, 1928, **61**, 2140). The less soluble brucine salt (m. p. 150—152°, $[\alpha]_{5461}^{15}$ −46·8°, $[\alpha]_{5890}^{15}$ −34·0°; cf. $[\alpha]_{5461}^{17}$ −47·7°, found by Houssa and Kenyon, *loc. cit.*) was reconverted with hydrochloric acid into the hydrogen phthalate (m. p. 81—81·5°, $[\alpha]_{5461}^{16}$ +42·1°, $[\alpha]_{5890}^{16}$ +35·7°; cf. m. p. 81—82°, $[\alpha]_{5461}^{20}$ +39·8°, found by Houssa and Kenyon, *loc. cit.*), and this was hydrolysed to the alcohol (b. p. 90—91°/16 mm., $[\alpha]_{5461}^{15\cdot4}$ −49·7°, $[\alpha]_{5890}^{15\cdot4}$ −40·9°; Houssa and Kenyon found $[\alpha]_{5893}^{20}$ −43·8°).

The action of thionyl chloride upon the alcohol (McKenzie and Clough, *J.*, 1913, **103**, 946) gave (−)-1-phenylethyl chloride (b. p. 82·5°/17 mm., $[\alpha]_{5890}^{15}$ −50·1°). The rotatory power of the chloride obtained varied in different preparations, as shown in col. 2 of Table 1. The highest value recorded was $[\alpha]^{17}_{5890}$ −51·9°.* A previous value for the (+)-isomer was $[\alpha]^{20}_{D}$ 50·6° (*idem, ibid.*).

Samples were dried ($K_2CO_3$) and redistilled, and their rotatory power was measured, immediately before use.

The stannic chloride was collected in sealed glass bulbs after repeated distillation in a high-vacuum apparatus, as in previous work (*e.g.*, Williams, *J.*, 1938, 246). Carbon tetrachloride (" AnalaR "), after several weeks' storage over phosphoric oxide, was refluxed over this reagent for 12 hr. and then fractionally distilled into a storage flask (having phosphoric oxide protection) whence it was displaced by dry nitrogen when required for reaction mixtures. Styrene was twice dried over sodium and redistilled.

*Racemisation Experiments.*—Reaction mixtures, made up in a stoppered bottle from previously prepared solutions of phenylethyl chloride and of stannic chloride in carbon tetrachloride, were displaced into a jacketed 2-dm. polarimeter tube by dry nitrogen. Between each *series* of experiments (see Table 1), the polarimeter tube and the vessel used for mixing the reagents were washed with several solvents, dried at 110° for 12 hr., and allowed to cool in a stream of dry nitrogen. Between individual experiments of a series they were washed similarly and dried at 110° for 30 min. The glass end-plates of the polarimeter tube (also pipettes used) were covered with a thin film of dimethyl silicone as water repellent. In only a few experiments (disregarded) did a faint opalescence (or even turbidity) develop in the reaction mixtures. Normally these remained perfectly clear throughout the experiment.

In the absence of stannic chloride, no racemisation occurred in carbon tetrachloride, as the following figures show :

Concn. of 1-phenylethyl chloride ($[\alpha]^{25}_{5890}$ −36·5° for specimen used) = 0·0925M ; temp. 25° ; $l$ = 2 dm.

| | | | | | |
|---|---|---|---|---|---|
| Time (hr.) ..................... | 0·05 | 0·1 | 4·0 | 33·0 | 48·0 |
| Rotation ....................... | 0·95° | 0·96° | 0·96° | 0·97° | 0·96° |

We thank the Distillers Company Limited for gifts of styrene, and Imperial Chemical Industries Limited for financial help towards the work described in this paper and the preceding one.

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[*Received, August* 17*th*, 1953.]