

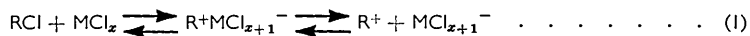
1133. *Acceptor Properties of Metal Halides. Part I. Mercuric Halides as Catalysts for the Racemisation of α -Methylbenzyl (1-Phenylethyl) Chloride.*

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The efficiencies of mercuric chloride, bromide, and iodide as catalysts for the racemisation of α -methylbenzyl (1-phenylethyl) chloride in nitrobenzene have been compared kinetically at 25° and 50°. Negligible racemisation occurs in the absence of a catalyst. The reaction is always of the first-order in α -methylbenzyl chloride, but of the second-order in mercuric iodide, and partly of the first-order and partly of the second-order in both mercuric chloride and mercuric bromide. The catalytic effect of mercuric chloride is slightly reduced by the addition of hydrogen chloride. The latter alone does not induce racemisation. Possible mechanisms for the catalysed racemisation are suggested. Dimeric catalyst molecules may be involved. The activities of the monomers are in the order, iodide \ll chloride $<$ bromide.

To compare the strengths of different Brønsted acids is a straightforward problem,¹ but for Lewis acids it is less so. For the latter case several qualitative comparisons have been made on the basis of product yield in reactions *catalysed* by Lewis acids. For example, the order of catalyst activity for the acetylation of toluene with acetyl chloride² is $\text{AlCl}_3 \approx \text{FeCl}_3 > \text{SbCl}_5 > \text{TiCl}_4 > \text{TeCl}_4 > \text{SnCl}_4 > \text{BiCl}_3 \approx \text{ZnCl}_2 > \text{HgCl}_2$, and for acetylation with acetyl bromide³ it is $\text{AlBr}_3 > \text{FeBr}_3 > \text{SbBr}_3 > \text{ZnBr}_2 > \text{TiBr}_4 > \text{TeBr}_4 > \text{SnBr}_4 > \text{HgBr}_2$; for the reaction of acetophenone with methyl chloride⁴ it is $\text{AlCl}_3 > \text{SbCl}_5 > \text{FeCl}_3 > \text{TeCl}_2 > \text{SnCl}_4 > \text{TiCl}_4 > \text{TeCl}_4 > \text{BiCl}_3 > \text{ZnCl}_2$; for the polymerisation of isobutene⁵ it is $\text{BF}_3 > \text{AlBr}_3 > \text{TiCl}_4 > \text{TiBr}_4 > \text{SnCl}_4$; and for the Gatterman-Koch reaction⁶ it is $\text{AlBr}_3 > \text{AlI}_3 > \text{AlCl}_3 > \text{FeCl}_3$. These orders of efficiency show fairly good, though not complete, agreement for the different reactions. This is somewhat surprising, for attempts to compare the catalytic efficiencies quantitatively, for example, by kinetic measurements, have shown that the reactions are often complex and that the mechanisms vary from one catalyst to another. For example, three distinct types of kinetic behaviour have been observed in the decomposition of benzoyl azide in benzene,⁷ and other, similar complexities are well known.⁸ It is clear, therefore, that the qualitative comparisons noted above, and others like them, may be ambiguous, since all meaningful comparisons of efficiency must refer to reactions with identical kinetic behaviour. One example of this is the depolymerisation of paraldehyde in ether,⁹ a reaction found to be of the second order in each catalyst studied: the catalyst efficiency is $\text{TiCl}_4 > \text{FeBr}_3 > \text{AlCl}_3 > \text{FeCl}_3 > \text{SnCl}_4 > \text{BCl}_3 > \text{ZnCl}_2$.

Another type of investigation of the relative strengths of Lewis acids is based on their ability to ionise polar halides, especially triaryl halides:



¹ Bell, "The Proton in Chemistry," Cornell Univ. Press, New York, 1959.

² Dermer and Billmeier, *J. Amer. Chem. Soc.*, 1942, **64**, 464.

³ Dermer, Mori, and Suguitan, *Proc. Oklahoma Acad. Sci.*, 1948, **29**, 74 (*Chem. Abs.*, 1952, **46**, 7538g).

⁴ Dermer, Wilson, Johnson, and Dermer, *J. Amer. Chem. Soc.*, 1941, **63**, 2881.

⁵ Plesch, Polanyi, and Skinner, *J.*, 1947, 257.

⁶ Dilke and Eley, *J.*, 1949, 2613.

⁷ Coleman, Newman, and Garrett, *J. Amer. Chem. Soc.*, 1954, **76**, 4534.

⁸ Jensen and Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 3039.

⁹ Bell and Skinner, *J.*, 1952, 2955.

In glacial acetic acid,¹⁰ where ion pairs predominate, the observed order is $\text{SbCl}_5 \gg \text{FeCl}_3 \gg \text{SnCl}_4 \gg \text{BiCl}_3 > \text{HgCl}_2 > \text{SbCl}_3$. Gutmann¹¹ has similarly studied the acceptance of chloride ions by many chlorides in both phosphorus oxychloride and phenylphosphonic dichloride; in the former solvent the acceptor strength is $\text{FeCl}_3 > \text{SbCl}_5 > \text{SnCl}_4 > \text{BCl}_3 > \text{HgCl}_2 > \text{TiCl}_4 > \text{AlCl}_3 > \text{ZnCl}_2$. The unusual positions of mercuric chloride and aluminium chloride in this list, compared with their positions in the lists given above, should be noted.

Since the efficiency of Lewis acid catalysts is usually considered to be associated with their acceptor properties, comparisons of results of studies such as those just mentioned with unambiguous catalytic efficiencies is obviously important. In the present work we chose a system having aspects of both types of study.

The racemisation of alkyl halides in the presence of Lewis acids may occur, depending on the dielectric constant of the medium, by the formation of either ion pairs or free ions [cf. reactions (1)]. Bodendorf and Böhme¹² studied the racemisation of α -methylbenzyl chloride in the presence of several metal halides in a variety of solvents. The general order of catalytic activity of the metal halides fits reasonably with those quoted above. Yet close examination of their results reveals some startling facts: *e.g.*, reaction orders of 14 are reported for boron trichloride in nitrobenzene and for titanium tetrachloride in chloroform. It was, therefore, felt that re-examination of their potentially valuable systems would be profitable. No other extensive kinetic studies of the rate of ionisation of alkyl halides induced by Lewis acids exist. As a starting point, mercuric chloride was chosen as the catalyst and nitrobenzene as the solvent. For this system Bodendorf and Böhme reported that the reaction order in mercuric chloride is 1.5 (apparently based on three rate measurements). It will be seen below that, although their actual rate measurements agree with ours, their conclusions concerning the reaction order do not. Since very few comparisons have been made of catalysis by chlorides with bromides and iodides, under identical conditions, we also compared catalysis by mercuric chloride with that by mercuric bromide and mercuric iodide in the same system.

EXPERIMENTAL

Materials.—Optically active α -methylbenzyl (1-phenylethyl) chloride was obtained from the resolved alcohol ($[\alpha]_D + 39.7^\circ$ in 95% alcohol; b. p. 102—104°/22 mm.) by Gerrard's method.¹³ Its activity varied from one preparation to another ($[\alpha]_D + 7^\circ$ to $+22^\circ$ in nitrobenzene). α -Methylbenzyl alcohol (B.D.H) was dried (Na_2CO_3) and distilled (b. p. 88.5—89.5°/12.5 mm., n_D^{23} 1.5260), and then resolved through the brucine phthalate by Downer and Kenyon's method.¹⁴ The optically active chloride was dried (K_2CO_3), distilled under reduced pressure (b. p. 89—91°/30 mm., n_D^{24} 1.5260), and stored in a dry atmosphere.

"AnalaR" nitrobenzene was purified by three methods: (1) it was dried over calcium hydride for 24 hr., decanted, and fractionally distilled (b. p. 51.5—53.0°/1.5 mm.); (2) it was fractionally crystallised three times, dried over phosphorus pentoxide, filtered, and fractionally distilled (b. p. 65.2°/3.5 mm.); (3) it was shaken with 1 : 1 sulphuric acid (twice), with water (once), with 10% aqueous sodium hydroxide (three times), and with water (three times). After drying over calcium sulphate and then over activated calcium sulphate ("Hi-drite"), it was fractionally distilled (b. p. 62.5—63.0°/3.5 mm.). All liquid transferences were performed in a dry-box. The middle fraction of each distillation was kept for use.

Mercuric chloride ("AnalaR"), mercuric bromide (Hopkin and Williams, reagent grade), and mercuric iodide (Harrington, reagent grade) were used without purification.

Gaseous hydrogen chloride was produced by addition of concentrated aqueous hydrochloric acid to concentrated aqueous sulphuric acid. Stock solutions of hydrogen chloride in nitrobenzene were prepared by bubbling the gas, after prior passage through concentrated aqueous

¹⁰ Cotter and Evans, *J.*, 1959, 2988.

¹¹ Gutmann, *Oesterr. Chem. Ztg.*, 1961, **62**, 326; Gutmann and Hampel, *Monatsh.*, 1961, **92**, 1048.

¹² Bodendorf and Böhme, *Annalen*, 1935, **516**, 1.

¹³ Gerrard, *J.*, 1944, 85; procedure 7.

¹⁴ Downer and Kenyon, *J.*, 1939, 1156.

sulphuric acid, through the solvent until it was *ca.* 0.2M in hydrogen chloride. The vessel containing the resulting solution was immediately stoppered and placed in a dry-box.

Analysis of Hydrogen Chloride Stock Solutions.—Solutions were analysed for hydrogen chloride by Volhard's method. Analyses were reproducible within $\pm 2\%$. Since hydrogen chloride tended slowly to escape from the more concentrated stock solutions, these were analysed at their times of use.

Preparation of Reaction Mixtures.—Volumetric flasks containing weighed amounts of mercuric halide were placed in the dry-box and solvent (nitrobenzene) added to them. After dissolution of the halide and addition (by pipette) in relevant experiments of a portion of a stock hydrogen chloride solution, a small amount (volume approximately known) of α -methylbenzyl chloride was added. The mixture was immediately made up to the mark with solvent, and a polarimeter cell was filled.

For the experiments at 50°, whilst the mercuric halide was dissolving, the flask and contents were warmed at 60°, together with pipettes and the polarimeter cell. On complete dissolution, all these items were quickly transferred to the dry-box, and the α -methylbenzyl chloride was added, etc. This operation took *ca.* 5 min. Speed was essential, first, to ensure that the concentration of the solution at 50° was known with reasonable accuracy and, secondly, in the case of mercuric iodide to avoid its crystallisation.

General Details of the Measurement of Loss of Activity.—Polarimeter cells, which were all-glass, were of three types. Cells A and B (2 cm. path-length) were placed in an aluminium container, which fitted into a brass jacket through which water circulated from a thermostat-controlled bath. Cell C (1 cm. path-length) fitted directly into the brass jacket. It was possible to measure the temperature *inside* one cell only, and this temperature is the one quoted throughout (all the cells gave identical kinetic results). The loss of optical activity was followed with an automatic polarimeter (ETL-NPL type 143A) used in conjunction with a moving-coil microammeter. With cell C it was found that for the faster runs the optical activity always eventually fell to zero, and so it was assumed to do so also in the longer experiments where it was inconvenient to follow the reaction to completion. However, with cells A and B it was always essential to follow the racemisation to infinity, since the cells themselves had rotations which depended on their position in the instrument and this was not exactly reproduced from run to run.

The loss of activity was always a first-order process. The observed rate constants (k_{obs}) were obtained from plots of $\log (R_t - R_\infty)$ against time, where R_t and R_∞ were the readings on the microammeter at time t and ∞ , respectively, and R was proportional to the optical rotation.

RESULTS AND DISCUSSION

Catalysis by Mercuric Chloride at 25°.—In the absence of a catalyst no racemisation of α -methylbenzyl chloride in nitrobenzene was observed (the rotation of a solution was unchanged after 7 weeks at room temperature). Similar results have previously been obtained for solvents of lower dielectric constant.¹⁵

In the presence of mercuric chloride the loss of optical activity showed good first-order kinetics over four half-lives (Fig. 1). The observed rate-constant was independent of the total concentration of α -methylbenzyl chloride (0.03—0.37M), since all the experimental values fall on the same curve (Table 1 and Fig. 2). If two molecules of the alkyl chloride were involved in the racemisation [reaction (2)],



then, although the racemisation would follow the first-order rate law, the rate constant would depend on the total concentration of the organic chloride. Therefore, only one, and not two, molecules of α -methylbenzyl chloride is involved in the reaction.

Values of k_{obs} for different concentrations of mercuric chloride are in Table 1 together with those obtained by Bodendorf and Böhme.¹² In Fig. 2, k_{obs} is plotted against the stoichiometric concentration of mercuric chloride. The values obtained with nitrobenzene purified by the three methods fall on the same curve; so also do the results of

¹⁵ Hart and Spliethoff, *J. Amer. Chem. Soc.*, 1955, **77**, 833; Heald and Williams, *J.*, 1954, 362.

Bodendorf and Böhme. We, therefore, conclude that no interfering basic ions were present in the nitrobenzene dried over calcium hydride, since the results otherwise would have differed from those obtained with nitrobenzene dried over phosphorus pentoxide, which would have removed such ions. Therefore, calcium hydride-dried solvent was used in the experiments with mercuric bromide and mercuric iodide.

Fig. 2 shows that the rate constant increases more rapidly than does the stoichiometric concentration of mercuric chloride. Bodendorf and Böhme concluded that the

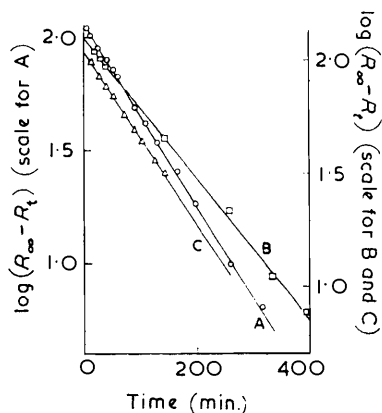


FIG. 1. Examples of first-order loss of optical activity.

(A) $6.18 \times 10^{-2}M$ - $HgCl_2$. (B) $4.13 \times 10^{-2}M$ - $HgBr_2$. (C) $1.28 \times 10^{-2}M$ - HgI_2 .

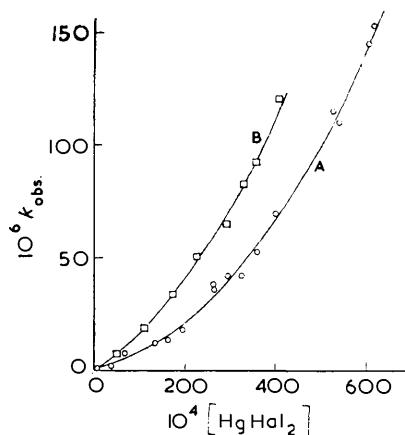


FIG. 2. Dependence of k_{obs} on catalyst concentration at 25° .

(A) $HgCl_2$. (B) $HgBr_2$.

TABLE I.

Racemisation of α -methylbenzyl chloride in the presence of mercuric chloride in nitrobenzene at 25° .

Purifn. of solvent *	[RCl] † (M)	$10^4[HgCl_2]$ (M)	$10^6 k_{obs}$ (sec. ⁻¹)	Purifn. of solvent *	[RCl] † (M)	$10^4[HgCl_2]$ (M)	$10^6 k_{obs}$ (sec. ⁻¹)
2	0.15	618	153	1	0.12	265	38.1
1	0.03	609	145	3	0.15	196	18.2
	0.35 ‡	540 ‡	110	1	0.03	164	13.7
1	0.15	531	115	2	0.15	134	12.2
2	0.15	403	69.1	1	0.12	67.3	7.16
	0.35 ‡	360 ‡	53		0.35 ‡	36 ‡	2
1	0.05	326	42.2	2	0.14	5.6	0.8
3	0.03	298	41.8	1	0.12	5.5	0.7
1	0.12	265	36.1				

* See Experimental section. † R = CHPhMe. ‡ These values are approximate; Bodendorf and Böhme expressed their results as moles of $HgCl_2$ per mole of PhCHMeCl and stated that their solutions contained *ca.* 0.75 g. of PhCHMeCl per 15 ml.

racemisation has an order of 1.48 in mercuric chloride. They reached a similar conclusion from their results for anhydrous acetone solutions. If this were so, a plot of $\log k_{obs}$ against $\log [HgCl_2]$ should be a straight line of slope 1.48. However, a straight line is not obtained either for nitrobenzene or for acetone when Bodendorf and Böhme's values are considered together with some values from Read and Taylor,^{16a} who concluded that the reaction is of the second order in mercuric chloride. The rate constant is properly expressed by equation (3) in which k_1 and k_2 are constants.

$$k_{obs} = k_1[HgHal_2] + k_2[HgHal_2]^2 \dots \dots \dots (3)$$

In Fig. 3 the linear relations of $k_{obs}/[HgHal_2]$ with $[HgHal_2]$ are shown; for nitrobenzene

¹⁶ (a) Read and Taylor, *J.*, 1940, 679; (b) Ledwith, Hojo, and Winstein, *Proc. Chem. Soc.*, 1961, 241.

solution the values of k_1 and k_2 obtained from the intercept and the slope are 5.1×10^{-4} sec.⁻¹ l. mole⁻¹ and 2.9×10^{-2} sec.⁻¹ l.² mole⁻², respectively; for acetone the values are 4×10^{-5} sec.⁻¹ l. mole⁻¹ and 8.4×10^{-4} sec.⁻¹ l.² mole⁻², respectively.

It is concluded, therefore, that the reaction has neither an order of *ca.* 1.5 in mercuric chloride, as stated by Bodendorf and Böhme, nor of 2, as stated by Read and Taylor, but that it has two components, one of the first-order and the other of the second-order in mercuric chloride. Ledwith, Hojo, and Winstein have also found evidence for a first-order dependence on catalyst concentration for the racemisation of the related compound *p*-chlorobenzhydryl chloride in acetone.^{16b}

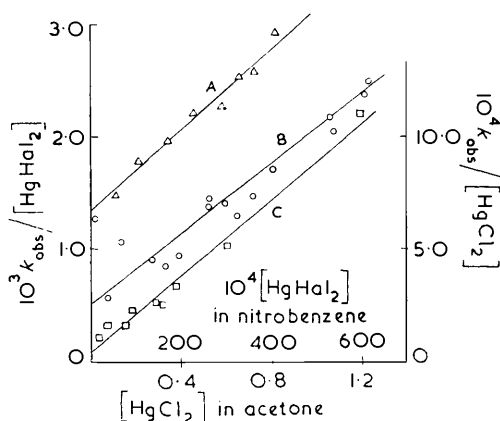


FIG. 3. Plots for determination of k_1 and k_2 , at 25°.

(A) HgBr_2 in nitrobenzene. (B) HgCl_2 in nitrobenzene. (C) HgCl_2 in acetone (from refs. 12 and 16; values from ref. 16 recalculated for 25° by using the activation energy given in ref. 12).

Since, the first-order term is easier to explain (see p. 5963) than the second-order term, we shall consider it first. The ions, HgCl_3^- and HgCl_4^{2-} , are both well-known¹⁷ but, in view of the conclusion above concerning the molecularity for the alkyl chloride, equation (1) will in this case be expected to take the form:

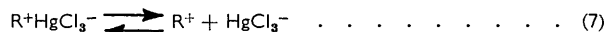


The rate of racemisation will then be given by:

$$\begin{aligned} \text{Rate} &= k_1[\text{RCl}][\text{HgHal}_2] \\ \text{or } k_{\text{obs}} &= k_1[\text{HgHal}_2] \dots \dots \dots (5) \end{aligned}$$

Thus the observed first-power dependence on catalyst and alkyl chloride concentration is accounted for.

Bayles, Evans, and Jones¹⁸ interpreted their results concerning the ionisation of triaryl chlorides by mercuric chloride in nitromethane in terms of two equilibria, the first involving ion-pair formation [reaction (6)], and the second the dissociation of the ion pairs into free ions [reaction (7)].



However, there is a general discrepancy between results of Evans, Price, and Thomas¹⁹ and of Price and Lichtin²⁰ for the ionisation of triaryl halides in nitroaromatic solvents. The former claim that their results (from spectrophotometric studies) show the formation of ion pairs only and indicate no dissociation to free ions. Lichtin and Price (who used

¹⁷ (a) Marcus, *Acta Chem. Scand.*, 1957, **11**, 599; (b) Garrett, *J. Amer. Chem. Soc.*, 1939, **61**, 2744.
¹⁸ (a) Bayles, Evans, and Jones, *J.*, 1955, 206; (b) *J.*, 1957, 1020.
¹⁹ Evans, Price, and Thomas, *Trans. Faraday Soc.*, 1954, **50**, 568.
²⁰ Price and Lichtin, *Tetrahedron Letters*, 1960, No. 18, 10.

conductivity and spectrophotometric methods to distinguish between ion pairs and free ions) found, however, no difference between the free-ion concentration and the total-ion concentration. Other evidence also favours the latter conclusion.²¹

In the present system it therefore seems probable that free carbonium and HgCl_3^- ions are obtained, and not ion pairs. This is the justification for expressing the racemisation by reaction (4).

The second-order dependence on the mercuric chloride concentration poses a number of problems. It could be caused either by a general or specific salt effect or by the presence of a dimeric species of mercuric chloride. These possibilities will be discussed in turn.

General salt effects for S_N1 reactions have been observed.²² They result from changes in the ionic character of the medium owing to dissociation of the salts into ions. Mercuric chloride shows little tendency to ionise either in water^{23a} or in nitrobenzene.^{23b} Therefore, a salt effect could occur only by dipole-dipole interactions and not as a result of changes in the ionic strength of the medium. In order to test whether the observed kinetics could reasonably be explained on such a basis, experiments were performed with hydrogen chloride. Since the dipole moments in benzene are very similar (HgCl_2 $\mu = 1.23$ D,²⁴ HCl $\mu = 1.25$ D²⁵), and also because hydrogen chloride is undissociated in nitrobenzene, it should show a salt effect similar to that of mercuric chloride.

No racemisation of α -methylbenzyl chloride was observed in the presence of hydrogen chloride (2×10^{-4} to 0.4 M) in nitrobenzene at 25° over a period of 70 hr. This shows that the ability of hydrogen chloride to break a carbon-chlorine bond is very small compared with that of mercuric chloride.

TABLE 2.

Racemisation of α -methylbenzyl chloride in the presence of hydrogen chloride and mercuric chloride in nitrobenzene at 25° .

$10^3[\text{HgCl}_2]$ (M)	$10^2[\text{HCl}]$ (M)	$10^5 k_{\text{obs}}$ (sec. ⁻¹)	$K_1 \uparrow$ (l. mole ⁻¹)
3.02	0.0	4.18 *	
3.02	3.95	4.01	16
3.02	19.1	3.90	20

* Calc. by using equation (3) with $k_1 = 5.1 \times 10^{-4}$ sec.⁻¹ l. mole⁻¹ and $k_a = 2.9 \times 10^{-2}$ sec.⁻¹ l.² mole⁻². † See equations (9) and (11); calc. on the basis of a salt effect.

The addition of hydrogen chloride somewhat decreased the catalytic effect of mercuric chloride (Table 2). The decrease could perhaps be due to experimental error, but seems to us too large for this. It is significant also that the decrease is largest for the highest concentration of hydrogen chloride. We believe that the effect is real, and that it probably results from complex formation between the hydrogen chloride and mercuric chloride [reaction (8)], thus removing some of the latter. Similar complexes between zinc chloride and hydrogen chloride have been proposed:²⁶



The equilibrium constant (K_1) for this reaction is given by:

$$K_1 = [\text{H}\cdot\text{HgCl}_3]/[\text{HCl}][\text{HgCl}_2] \quad \dots \dots \dots (9)$$

²¹ Pocker, *J.*, 1958, 240.
²² See, e.g., Winstein, Smith, and Darwish, *Tetrahedron Letters*, 1959, No. 16, 24; de la Mare, Hughes, Ingold, and Pocker, *J.*, 1954, 2930.
²³ (a) Lindgren, Jonsson, and Sillen, *Acta Chem. Scand.*, 1947, **1**, 479; (b) Kessler and Mendeleev, *Izvest. Akad. Nauk S.S.S.R.*, 1956, 513.
²⁴ Tourky and Rizk, *Canad. J. Chem.*, 1957, **35**, 630.
²⁵ Weith, Hobbs, and Gross, *J. Amer. Chem. Soc.*, 1948, **70**, 805.
²⁶ Bethell, Gold, and Satchell, *J.*, 1958, 1918.

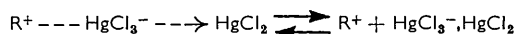
If a general salt effect operates, and if its magnitude is linearly related to the salt concentration (as found in S_N1 reactions²²), equation (3) can be expressed in the form:

$$k_{\text{obs}} = k_1[\text{HgHal}_2](1 + b[\text{HgHal}_2]), \dots \dots \dots (10)$$

where $b = k_2/k_1$. If it is assumed that the salt-effect constant b is the same for hydrogen chloride as for mercuric chloride (on the basis of their similar dipole moments), then the observed rate constant in the presence of a mixture of these compounds will be given by

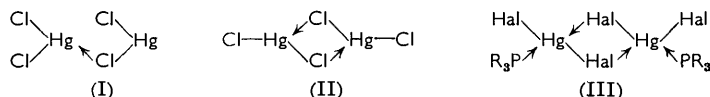
$$k_{\text{obs}} = k_1[\text{HgCl}_2](1 + b[\text{HgCl}_2] + b[\text{HCl}]). \dots \dots \dots (11)$$

From the experimental results it is possible to obtain values of K_1 . These are given in Table 2. The good agreement between the two values obtained for K_1 supports the idea of a general salt effect. On the other hand, the small dipole moments of mercuric chloride and of hydrogen chloride relative to that of the solvent²⁷ perhaps argue against such an effect, which might be expected to be related to changes in the dielectric constant of the medium. A specific salt effect, in which the transition state is specifically solvated by molecules of mercuric chloride or of hydrogen chloride, rather than by the solvent, may obtain. (A similar effect has been proposed for the ionisation of triaryl halides in the presence of mercuric chloride in solvents of lower dielectric constant.^{10,18b}) Such an effect may be imagined in which the mercuric chloride interacts with the HgCl_3^- part of the transition state in such a way as to aid its removal:



This idea becomes very close to a dimeric species of mercuric chloride interacting with the alkyl chloride.

There is evidence that an aqueous solution of mercuric chloride contains a small amount of dimer.^{17b,28} Approximately 10% appears to be dimerised in a saturated solution at 25°. Linhart^{28a} claims that no dimerisation occurs in benzene. However, examination of his results for the distribution of mercuric chloride between water and benzene shows that, because of its low solubility in benzene, the presence of *ca.* 10% of the mercuric chloride in benzene as a dimer would have no appreciable effect on his calculations. Also cryoscopic measurements in benzene,^{18b} again owing to the low solubility of mercuric chloride, would not reveal the presence of as much as 10% of dimer. In acetone, there is some indication of polymeric species,^{28b} but generally there is no definite evidence for or against the presence of mercuric chloride dimers in organic solvents. At least two structures (I/II) can be envisaged for the dimer. The mercuric halides are known to form bridged structures with tertiary phosphines and arsines, *e.g.*, (III).²⁹



In view of the symmetry of form (II), it appears at first sight to be the more favourable structure. However, support for structure (I) lies in the dipole moments in benzene and dioxan.^{24,30} It has been suggested that the dipole moment in dioxan is due to either distortion of the Hg-Cl bonds or to complex formation.³⁰ Although mercuric chloride does form complexes with dioxan,³¹ it has also been argued that, since the dipole moment in that solvent is very similar to that in benzene, it is unlikely that it arises from complex

²⁷ Smith, "Electric Dipole Moments," Butterworths, London, 1955.

²⁸ (a) Linhart, *J. Amer. Chem. Soc.*, 1915, **37**, 258; (b) Bhagwat and Tosniwal, *J. Indian Chem. Soc.*, 1942, **19**, 492.

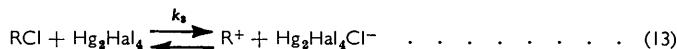
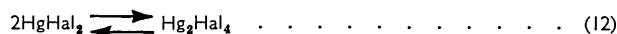
²⁹ Evans, Mann, Peiser, and Purdie, *J.*, 1940, 1209.

³⁰ (a) Tourky and Rizk, *J. Phys. Chem.*, 1960, **64**, 565; (b) Curran, *J. Amer. Chem. Soc.*, 1941, **63**, 1470.

³¹ Daasch, *Spectrochim. Acta*, 1959, 726.

formation.^{30a} We suggest that dimers such as (I) could be the reason for the finite dipole moment in both solvents since, whereas structure (II) (assuming sp^2 -hybridisation of the mercury bonds) would have zero dipole moment, the unsymmetrical structure (I) would have an appreciable moment. Moreover, the extent of dimerisation is likely to be of the same order in the two solvents, which have similar dielectric constants.

If dimeric molecules of mercuric chloride are a reactive species in the racemisation, the following reaction scheme can be set up [in addition to that represented by (4) and (5)]:



The rate of racemisation resulting from this reaction is given by

$$\begin{aligned} \text{Rate} &= k_3[\text{RCl}][\text{Hg}_2\text{Hal}_4] \\ &= k_3K_2[\text{RCl}][\text{HgHal}_2]^2 \quad \dots \dots \dots (14) \end{aligned}$$

$$\text{where } K_2 = [\text{Hg}_2\text{Hal}_4]/[\text{HgHal}_2]^2 \quad \dots \dots \dots (15)$$

The second-order rate constant k_2 will be equal to k_3K_2 . An idea of the magnitude of k_3 compared with k_1 [equation (5)] is obtained in the following way. From equation (3) (which is based on the stoichiometric concentration of mercuric chloride) it follows that the extent of dimerisation must be small. Linhart²⁸ found the value of 0.3 mole l.^{-1} for K_2 in aqueous solution at 25° . Since k_2 is $2.9 \times 10^{-2} \text{ sec.}^{-1} \text{ l.}^2 \text{ mole}^{-2}$ (K_2 being assumed to be 0.3 mole l.^{-1}), we find a value of $0.1 \text{ sec.}^{-1} \text{ l. mole}^{-1}$, for k_3 . On this basis, k_3 is 200 times greater than k_1 . Thus, if this mechanism is real, the dimer is a much more effective catalyst than the monomer. This is further support for structure (I) in view of the larger positive charge that will be induced on one of the mercury atoms, which will also be less shielded than in structure (II).

If we assume dimers to provide the second-order term, hydrogen chloride will not be expected to have any effect other than as a complexing agent (p. 5968). K_1 can again

TABLE 3.

Calculation of K_1 on the basis of catalysis by dimeric mercuric chloride molecules.

$[\text{HgCl}_2]_s$ *	$[\text{HCl}]_s$ *	k_{obs}	$[\text{HgCl}_2]$ free †	$[\text{H}\cdot\text{HgCl}_2]$	$[\text{HCl}]$	K_1
(M)	(M)	(sec.^{-1})	(M)	(M)	(M)	(l. mole^{-1})
0.0302	0.0395	4.01	0.0287	0.0015	0.0380	1.4
0.0302	0.191	3.90	0.0284	0.0018	0.189	0.3

* Stoichiometric concentrations. † Obtained from Fig. 2.

be calculated (Table 3). The values now obtained do not show the good agreement they do when calculated instead on the basis of salt effects.

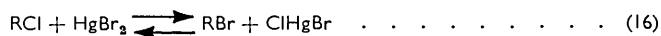
We conclude then that the second-order dependence on catalyst concentration can be interpreted either in terms of a salt effect or in terms of catalysis by a dimeric species of structure (I). The effects of added hydrogen chloride point to the former, though this explanation seems dubious on other grounds (p. 5969). The separation of complexes of mercuric chloride and tri-*p*-tolylmethyl chloride from benzene solution in which the ratio of mercuric chloride to the alkyl chloride is greater than two^{18b} lends some support to the idea of catalysis by dimers. More light is thrown on this problem in the following section.

Comparison of the Catalytic Behaviour of Mercuric Chloride, Mercuric Bromide, and Mercuric Iodide.—As noted earlier (p. 5964), most previous comparisons of the catalytic activities of metallic chlorides, bromides, and iodides have been ambiguous. Our results, which are unambiguous, provide the first comparison of the activities of the mercuric

halides, and also the first for any metal, based on kinetic measurements, which includes an iodide.

Mercuric iodide has a low solubility in nitrobenzene, and therefore experiments with it were carried out at 50°. In order to compare the three halides mercuric bromide was studied at both 25° and 50°.

Good first-order kinetic behaviour was again obtained for the loss of optical activity in the presence of either mercuric bromide or iodide (Fig. 1). It can thus be inferred that the catalytic power of these compounds did not change during a racemisation, as it would have been expected to do if either mercuric chloride or a mixed halide had been formed. This means that the halogen-exchange equilibria (16) and (17) lie well to the left-hand side.



Values of k_{obs} for different concentrations of mercuric bromide at 25° and at 50° are summarised in Table 4. Values for mercuric iodide are in Table 5. As for mercuric

TABLE 4.
Racemisation of α -methylbenzyl chloride in the presence of mercuric bromide in nitrobenzene.

At 25°.									
$10^4[\text{HgBr}_2]$ (M)	413	361	330	289	229	173	111	52	
$10^6 k_{\text{obs}}$ (sec. ⁻¹)	120.7	92.7	83.1	65.4	50.4	33.9	19.6	7.7	
At 50°.									
$10^4[\text{HgBr}_2]$ (M)	309	192	130	62.4					
$10^6 k_{\text{obs}}$ (sec. ⁻¹)	728	356	211	90.5					

TABLE 5.
Racemisation of α -methylbenzyl chloride in the presence of mercuric iodide in nitrobenzene at 50°.

$10^4[\text{HgI}_2]$ (M)	145	128	98.1	49.7	32.6
$10^6 k_{\text{obs}}$ (sec. ⁻¹)	174	150	80.5	20.2	12.7

chloride, k_{obs} increases more rapidly than does the stoichiometric concentration of catalyst (Figs. 2 and 4). Plots of $k_{\text{obs}}/[\text{HgHal}_2]$ against $[\text{HgHal}_2]$ [equation (3)] are shown in Figs. 3 and 5. The values of k_1 , k_2 , and b [see equations (3) and (10)] are summarised in Table 6. It may be seen that k_1 increases in the order $\text{HgI}_2 \ll \text{HgCl}_2 < \text{HgBr}_2$ and k_2 in the order $\text{HgCl}_2 < \text{HgBr}_2 < \text{HgI}_2$. At 25° the value of the salt-effect constant b is greater for mercuric chloride than for mercuric bromide. The general pattern of the results suggests that mercuric chloride and bromide react in essentially the same manner, but that the behaviour of mercuric iodide is significantly different. This is seen in the very low value of k_1 (and consequently the very large value of b) for the iodide compared with that for the bromide at 50°.

Since the covalent character of the mercuric halides increases (and thus the electrophilic nature of the mercury atom decreases) from the chloride to the iodide, k_1 might, at first sight, be expected to be in the order $\text{HgI}_2 < \text{HgBr}_2 < \text{HgCl}_2$. The results make it clear, therefore, that other factors influence the value of k_1 . It is possible that its small value for mercuric iodide-catalysis is due to a steric factor.

The presence of dimeric molecules of either mercuric bromide or iodide seems perhaps less likely than for the chloride. Indeed, in aqueous solution it is generally considered that, whereas a small amount of mercuric chloride dimerises (see p. 5969), the bromide and iodide do so inappreciably.^{17b,32} On the other hand, if the dipole moments in benzene

³² Marcus, *Acta Chem. Scand.*, 1957, **11**, 330.

and dioxan are indeed due to the presence of a small number of dimeric molecules of structure (I) (as suggested on p. 5970), then, as the moments of the three halides^{24,30} are of the same order of magnitude, the extent of their dimerisation would also be expected to be similar. In any event the second-order region, interpreted on a dimer basis, leads to

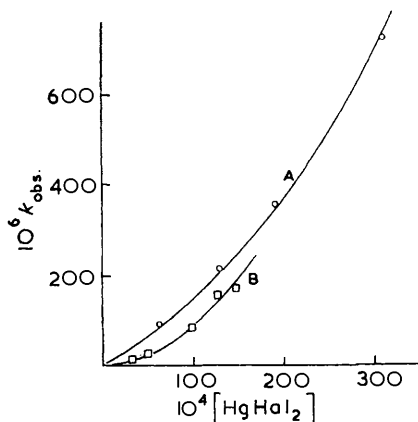


FIG. 4. Dependence of k_{obs} on catalyst concentration at 50° .
(A) HgBr_2 . (B) HgI_2 .

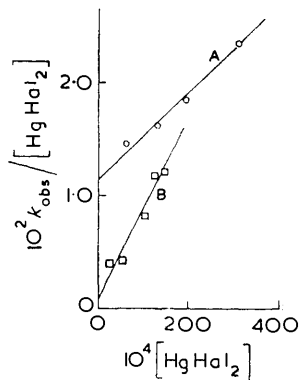


FIG. 5. Plots for determination of k_1 and k_2 at 50° .
(A) HgBr_2 . (B) HgI_2 .

the order $\text{HgI}_2 > \text{HgBr}_2 > \text{HgCl}_2$ for k_3 (k_2/K_2 ; Table 6). This is the reverse of that naïvely expected if the polarity of the dimer decreases, as for the monomer, from the chloride to the iodide.

Alone, the results for chloride and bromide are at least compatible (even if they are difficult to rationalise completely) with the occurrence of either a salt effect or of dimerisation, but those for the iodide cannot easily be reconciled with the operation of a salt effect. This is because the value of b for the iodide would be so large, and so very much larger than for the chloride and bromide (Table 6). It seems clear that, under our condi-

TABLE 6.

Values of k_1 , k_2 , and b for catalysis by mercuric chloride, mercuric bromide, and mercuric iodide.

	HgCl_2	HgBr_2	HgBr_2	HgI_2
Temp.	25°	25°	50°	50°
$10^4 k_1$ (sec. ⁻¹ l. mole ⁻¹) *	5.1	13	110	<7
$10^2 k_2$ (sec. ⁻¹ l. ² mole ⁻²) *	2.9	3.9	38	79
b (l. mole ⁻¹) †	57	30	35	

* Calc. from Figs. 3 and 5. † $b = k_2/k_1$.

tions, two molecules of mercuric iodide are effectively always involved in the reaction with α -methylbenzyl chloride. This points to catalysis by dimeric species, even if these are only formed transiently. Dimers of type (I) would, in fact, relieve any steric shielding of the mercury atom experienced by the monomer—shielding we have suggested as a possible reason for its inactivity (p. 5971). By analogy, catalysis by dimers should at least contribute to the second-order terms for the chloride and bromide, and, seen as a whole, therefore, all the second-order terms are perhaps best interpreted in this way.

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