

1041. *Acceptor Properties of Metal Halides. Part II.¹ Mercuric and Zinc Halides as Catalysts for the Racemisation of α -Methylbenzyl Chloride in Acetone.*

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The catalytic efficiencies of mercuric chloride, bromide, and iodide, and of zinc chloride, bromide, and iodide in the racemisation of α -methylbenzyl chloride in acetone have been compared kinetically at 25°. Mercuric iodide has also been studied at 42.5°. The catalysis is partly of the first order and partly of the second in each of the metal halides. For the first-order reaction the catalyst activities are in the sequence zinc iodide \geq zinc bromide > zinc chloride > mercuric bromide > mercuric iodide \geq mercuric chloride. For the second-order reaction the activities are in the sequence zinc iodide > zinc bromide > zinc chloride > mercuric iodide > mercuric bromide > mercuric chloride. Possible solvation effects are suggested as reasons for these observed sequences.

INVESTIGATION of the mercuric halide induced racemisation of α -methylbenzyl chloride in nitrobenzene¹ showed that with mercuric iodide the reaction was of the second order with respect to the catalyst, while with mercuric chloride and bromide it was partly of the first and partly of the second order. The rate constants for mercuric bromide catalysis were greater than those for mercuric chloride catalysis, a fact difficult to explain on the basis of their relative electrophilicities. Moreover the second-order dependence on catalyst concentration was not satisfactorily accounted for. Our suggested explanations of it were (i) a general salt effect, or (ii) catalysis by mercuric halide dimers. The latter explanation was favoured because with mercuric iodide two molecules *always* appear to be involved in the reaction. It was decided to study these reactions in a second solvent, first to test

¹ Part I, Satchell, *J.*, 1963, 5963.

whether the behaviour of mercuric iodide generally differs significantly from that of mercuric bromide and chloride, and secondly to examine further the relative magnitudes of the rate constants for the different catalysts. We chose acetone, in which the mercuric chloride catalysis had been studied by Bodendorf and Böhme² and by Read and Taylor.³ We demonstrated in Part I that their results (like ours in nitrobenzene) also show both a first- and a second-order dependence on mercuric chloride concentration. To compare also the behaviour of the mercuric halides with a second group of metal halides, which might reasonably be expected to behave similarly, we chose zinc halides.

EXPERIMENTAL

Materials.—Optically active α -methylbenzyl chloride was prepared as previously described.¹

AnalaR acetone, dried ("Drierite," 1 day), and finally distilled from "Drierite," had b. p. $56.4^{\circ}/760$ mm.

The mercuric halide samples have been described.^{1,4} AnalaR zinc chloride was used without further purification. Zinc bromide (Hopkin and Williams, G.P.R.) was sublimed *in vacuo*, and zinc iodide (B.D.H.) was heated at 200° (2—3 hr.), and allowed to cool in a desiccator.

Preparation of Reaction Mixtures.—Mixtures containing the mercuric halides in acetone were prepared as before,¹ except that a dry-box was not used.

Saturated solutions of the zinc halides in acetone were centrifuged in stoppered test-tubes to facilitate the removal of excess of solid without contact with the atmosphere. The solutions were pipetted to a dry flask and diluted with acetone. Portions of these stock solutions were placed in volumetric flasks, a small amount of α -methylbenzyl chloride added, and the solution made up.

The stock zinc halide solutions were analysed for halide volumetrically by Fajans's method (dichlorofluorescein) and by Volhard's method.

Measurement of the Loss of Activity.—The loss of optical activity was followed as before.¹ The observed rate constant (k_{obs}) of this process is a function of catalyst concentration (see Tables).

RESULTS AND DISCUSSION

Kinetic Form.—In the absence of a catalyst no racemisation of α -methylbenzyl chloride in acetone was observed during 100 hours at 25° . Similar results have been obtained in other solvents.^{1,5}

In the presence of zinc halides the loss of optical activity showed good first-order kinetics over several half-lives, but in the presence of mercuric halides this behaviour was limited to about three half-lives. After that time the mercuric halide reaction mixtures became brown, and the polarimeter readings unsteady. Such behaviour was observed by Read and Taylor.³ We also found unsteadiness in the polarimeter readings with *inactive* alkyl chloride in the presence of these catalysts under the same conditions. Since acetone solutions of the mercuric halides and of α -methylbenzyl chloride are stable, the brown colour must arise from interaction between the mercuric halide and α -methylbenzyl chloride. Since good straight lines were obtained over 2—3 half-lives, the first half-life probably represents a reasonably clean racemisation.

Values of k_{obs} for different catalyst concentrations are in Tables 1 and 2. All experiments were at 25° except those with mercuric iodide. The low solubility of this compound in acetone necessitated the use of a higher temperature (42.5°). One experiment was, however, made at 25° , in order to get a direct comparison with the other metal halides. Values reported by Bodendorf and Böhme for the zinc chloride system² are lower than ours. Their sample probably contained some impurity such as zinc hydroxide or water.

² Bodendorf and Böhme, *Annalen*, 1935, **516**, 1.

³ Read and Taylor, *J.*, 1940, 679.

⁴ Satchell, following Paper.

⁵ Hart and Spliethoff, *J. Amer. Chem. Soc.*, 1955, **77**, 833; Heald and Williams, *J.*, 1954, 362.

TABLE 1.

Racemisation of α -methylbenzyl chloride in the presence of mercuric halides in acetone.
[Ph·CHMeCl] *ca.* 0.05M in all Tables.

At 25°.

$10^3[\text{HgCl}_2]$ (M) ...	393	496	496	496	718	720	954	1164	
$10^6 k_{\text{obs.}}$ (sec. ⁻¹)	126	188	189	200	371	393	760	1251	
$10^6 k_{\text{calc.}}$ (sec. ⁻¹) * ...	128	192	192	192	374	376	632	918	
$10^3[\text{HgBr}_2]$ (M) ...	32.6	79.9	181	294	414	492	531	538	582
$10^6 k_{\text{obs.}}$ (sec. ⁻¹)	7.76	30.4	129	243	453	613	742	733	889
$10^6 k_{\text{calc.}}$ (sec. ⁻¹) * ...	8.86	30.1	108	249	460	631	727	744	861
$10^3[\text{HgI}_2]$ (M)	21.5								
$10^6 k_{\text{obs.}}$ (sec. ⁻¹)	7.8								

At 42.5°.

$10^3[\text{HgI}_2]$ (M)	10.8	19.4	27.3	27.6	32.1	36.8			
$10^6 k_{\text{obs.}}$ (sec. ⁻¹)	6.04	17.8	29.4	36.0	43.2	52.6			
$10^6 k_{\text{calc.}}$ (sec. ⁻¹) * ...	6.55	17.3	31.4	32.0	42.0	53.9			

* $k_{\text{calc.}}$ calculated from eqn. (1) with values of k_1 and k_2 in Table 3.

TABLE 2.

Racemisation of α -methylbenzyl chloride in the presence of zinc halides in acetone at 25°.

$10^3[\text{ZnCl}_2]$ (M)	46.4	104	171	258				
$10^5 k_{\text{obs.}}$ (sec. ⁻¹)	7.55	27.4	61.7	124				
$10^5 k_{\text{calc.}}$ (sec. ⁻¹) *	7.64	26.1	60.1	124				
$10^3[\text{ZnBr}_2]$ (M)	48.2	65.1	92.2	122	152	163	240	
$10^5 k_{\text{obs.}}$ (sec. ⁻¹)	16.7	23.6	39.5	56.8	73.9	90.2	161	
$10^5 k_{\text{calc.}}$ (sec. ⁻¹) *	16.5	24.1	38.4	57.0	78.8	87.5	162	
$10^3[\text{ZnI}_2]$ (M)	46.8	76.1	100	114	208			
$10^5 k_{\text{obs.}}$ (sec. ⁻¹)	19.2	35.9	50.6	63.5	169			
$10^5 k_{\text{calc.}}$ (sec. ⁻¹) *	18.3	35.6	53.0	64.6	169			

* See Table 1.

TABLE 3.

Values of k_1 and k_2 for catalysis by zinc and mercuric halides in acetone and nitrobenzene.

In acetone.	Temp.	$10^4 k_1$ ‡ (sec. ⁻¹ l. mole ⁻¹)	$10^3 k_2$ ‡ (sec. ⁻¹ l. ² mole ⁻²)	k_2/k_1 (l. mole ⁻¹)
ZnCl ₂	25°	9.5	1.5	16
ZnBr ₂	25	26	1.7	7
ZnI ₂	25	27	2.6	9
HgCl ₂	25	0.9 *	0.06 *	7 *
		0.4 †	0.084 †	21 †
HgBr ₂	25	2.0	0.22	11
HgI ₂	42.5	2.5	3.3	132
In nitrobenzene. †				
HgCl ₂	25°	5.1	2.9	57
HgBr ₂	25	13	3.9	30
	50	110	38	35
HgI ₂	50	7	79	1130

* See above. † See Part I. ‡ k_1 and k_2 were obtained from the intercept and slope of plots of $k_{\text{obs.}}/[\text{Me Hal}_2]$ against $[\text{Me Hal}_2]$, respectively.

In acetone (as for the mercuric halides in nitrobenzene¹) the dependence of k_{obs} on the catalyst concentration can be expressed by eqn. (1) for both the mercuric and the zinc halides. Values of the catalytic constants k_1 and k_2 , determined¹ by plotting $k_{\text{obs.}}/[\text{MeHal}_2]$

$$k_{\text{obs}} = k_1[\text{MeHal}_2] + k_2[\text{MeHal}_2]^2 \quad (1)$$

against $[\text{MeHal}_2]$, are summarised in Table 3. Also included for comparison are the values for the mercuric halides in nitrobenzene. The values for mercuric chloride in acetone are slightly different from those we calculated previously from Bodendorf and Böhme's, and Read and Taylor's results.¹ This is because the inclusion of our results shows that above

0.8M-mercuric chloride the plot is curved. Too much weight was given previously to the high-concentration values in determining k_1 and k_2 . The curvature indicates that, at catalyst concentrations above 0.8M, terms containing more than two molecules of mercuric chloride should be included in eqn. (1).

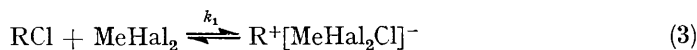
From the form of eqn. (1) we conclude that the reaction in acetone is partly of the first order and partly of the second in all the metal halides studied. This contradicts Bodendorf and Böhme's view that the reaction is simply of the second order in zinc chloride.²

The relative values of k_1 and k_2 are interesting; k_1 will be considered first, since conclusions concerning it affect the interpretation of k_2 .

First-order Dependence on Catalyst Concentration.—(a) *Reaction scheme.* We represented¹ the reaction scheme in nitrobenzene by eqn. (2), but in acetone, a solvent of lower dielectric



constant, ion-pairing is more likely. Racemisation of substituted diphenylmethyl chlorides in acetone in the presence of salts has been interpreted in terms of an ion-pair mechanism.⁶ Other strong support for ion-pair involvement has been drawn by Ledwith, Hojo, and Winstein,⁷ so we consider that the reaction probably does not involve free ions, and may be represented by eqn. (3). The forward step determines the rate of racemisation.



In practice the catalysts will doubtless be co-ordinated with the solvent (S) and (3) should therefore probably be written as:



(This mechanism is not complicated by the possibility of halogen exchange; see ref. 1 for arguments.)

(b) *Catalytic constants.* Values of k_1 in acetone follow the sequence $\text{ZnI}_2 \geq \text{ZnBr}_2 > \text{ZnCl}_2 > \text{HgBr}_2 > \text{HgI}_2 \geq \text{HgCl}_2$ (Table 3). In nitrobenzene¹ they are in the order $\text{HgBr}_2 > \text{HgCl}_2 \gg \text{HgI}_2$. The position of mercuric iodide in the acetone sequence was obtained as follows. The value of k_{obs} for 0.0215M-HgI₂ at 25° (Table 1) is *ca.* 2.6 times smaller than at 42.5°. Since the temperature effects on k_1 and k_2 for mercuric bromide in nitrobenzene (Table 3) are similar, it is assumed that division of k_1 and k_2 for mercuric iodide at 42.5° by 2.6 provides a rough estimate of their values at 25°. Hence k_1 and k_2 are roughly $1.0 \times 10^{-4} \text{ sec.}^{-1} \text{ l. mole}^{-1}$ and $1.3 \times 10^{-2} \text{ sec.}^{-1} \text{ l.}^2 \text{ mole}^{-2}$ respectively at 25°.

Four factors that will affect k_1 are now discussed. These are (i) the dielectric constant of the solvent, (ii) the basicity or donor character of the solvent, (iii) the electrophilic nature of the catalyst, and (iv) solvation of the transition state.

(i) Ionisation is favoured in media of high dielectric constant. In agreement with this, k_1 for mercuric chloride and bromide are both greater in nitrobenzene than in acetone (Table 3). On the other hand for mercuric iodide the change in k_1 is much smaller. A possible reason is suggested below. (ii) The more basic the solvent the less available will be the catalyst for acceptor behaviour towards other species. Nitrobenzene is a poorer electron donor than acetone,⁸ so this effect will supplement (i). (iii) In a given solvent, on their relative electrophilic character alone, the order predicted for k_1 is $\text{ZnCl}_2 > \text{ZnBr}_2 > \text{ZnI}_2 > \text{HgCl}_2 > \text{HgBr}_2 > \text{HgI}_2$. In fact the values of k_1 for the zinc halides in acetone are 10–25 times greater than those of the mercuric halides. However, within the two groups of halides the trend is in the opposite direction to that predicted. Reasons for this

⁶ Winstein and Gall, *Tetrahedron Letters*, 1960, No. 2, 31; Winstein, Hojo, and Smith, *ibid.*, 1960, No. 22, 12.

⁷ Ledwith, Hojo, and Winstein, *Proc. Chem. Soc.*, 1961, 241.

⁸ Baaz and Gutmann in "Friedel-Crafts and Related Reactions," ed. Olah, Vol. I, Interscience, 1963, p. 367.

reversed behaviour may be found in the remaining factor to be considered. (iv) Little is known concerning the solvation of transition states which are neutral overall. The transition state in the present reaction is $[\delta^+R \cdots Cl \cdots MX_2^{\delta-}]$. Since R is the same throughout it may be ignored for catalytic comparisons. The extent of solvation of the transition state is probably a function of its polarisability. By analogy with the solvation of anions⁹ we expect that the larger a transition state is, the greater will be its polarisability and hence the extent of its solvation (other factors, like permanent dipoles, being equal). In each series of the metal halides, polarisability will increase from the chloride to the iodide. If the relative polarisabilities of the transition states are the main determinants of their relative solvation, then the rates of reaction, which will be favoured by solvation, will be in the orders $ZnI_2 > ZnBr_2 > ZnCl_2$ and $HgBr_2 > HgCl_2$, *i.e.*, as found.

We conclude that for the present reaction, in a given solvent, catalytic activity seems determined by both catalyst electrophilicity and the demands of transition-state solvation. The latter can over-ride small variations in the former.

It is of interest that for the acetylation of toluene with acetyl bromide¹⁰ (a reaction involving a similar ionisation) the relative catalyst activities are also in the orders $ZnI_2 > ZnBr_2 > ZnCl_2$ and $HgBr_2 > HgCl_2$. It is particularly significant that the reverse sequence for the zinc halides has been found for the extent of I : I complex formation with substituted nitroanilines.¹¹ This is a different type of reaction, being less polar and not involving halogen ionisation. Presumably solvation effects are therefore less important, and the predicted electrophilic sequence can appear. The two sets of results emphasise the care necessary for making meaningful comparisons of catalytic activity.

The behaviour of mercuric iodide needs further comment. Its relatively small k_1 in nitrobenzene was attributed to a steric factor.¹ As noted above, the change from nitrobenzene to acetone produces a relatively small decrease in k_1 , despite the change in dielectric constant and donor character. However, acetone is a better solvating agent than nitrobenzene,⁹ and the greater transition-state solvation in acetone than in nitrobenzene, probably counteracts to some extent the reduction in k_1 otherwise expected. Further, if the necessity for transition-state solvation increases in the order chloride < bromide < iodide (see below) we can dispense with the steric factor explanation in nitrobenzene (where such solvation is little available and therefore the iodide is particularly badly hit) and yet accept the comparable values for the chloride and the iodide in acetone (where because of plentiful solvation their differences are somewhat levelled out).

Second-order Dependence on Catalyst Concentration.—We suggested¹ that the second-order term in catalyst resulted either from the presence of a general salt effect or from catalysis by dimeric molecules, and favoured the latter. We have since measured the molecular weights of the mercuric halides in acetone, and found no dimerisation,⁴ so we now discount catalysis by dimers. It was previously argued that a *general* salt effect is unlikely in view of the low dipole moments of the mercuric halides compared with that of the solvent. However, it was suggested (as an alternative model for dimer catalysis) that the transition state may be thought of as specifically solvated by mercuric halide molecules. Since solvation of the transition state by *solvent* molecules is probably an important feature of the reaction, this suggestion is now attractive. k_2 follows the sequence $ZnI_2 > ZnBr_2 > ZnCl_2 > HgI_2 > HgBr_2 > HgCl_2$ in acetone, and the sequence $HgI_2 > HgBr_2 > HgCl_2$ in nitrobenzene (Table 3 and p. 5467), *i.e.*, mercuric halides follow the same sequence in the two solvents. If our model is correct, the relative importance of solvation for the different catalysts will be reflected in the ratio $k_2 : k_1$ (Table 3). We note first that $k_2 : k_1$ for the mercuric halides is greater in nitrobenzene than in acetone. This implies that solvation by mercuric halide molecules is less important in the solvent which itself is a better solvating agent. That is sensible, and supports our model. Secondly, the great importance of solvation by

⁹ Parker, *Quart. Rev.*, 1962, **16**, 163.

¹⁰ Olah in "Friedel-Crafts and Related Reactions," Vol. I, Interscience, 1963, p. 861.

¹¹ Satchell and Wardell, *Chem. and Ind.*, 1963, 2011; *J.*, 1964, 4296.

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5469

mercuric iodide itself in nitrobenzene ($k_2 : k_1 = 1130$) supports our previous interpretation of the relative values of k_1 for mercuric iodide in the two solvents.

Since zinc halides are better ionising agents than those of mercury (cf. k_1 values), solvation in the former's reactions would be expected to be less important than in the latter's. Apart from the chlorides, the various values of $k_2 : k_1$ in acetone agree with this expectation also.

"Self-solvation" of the transition state by other metal halide molecules has also been suggested for the ionisation of triaryl halides in acetic acid,¹² chlorobenzene, and benzene.¹³ In acetic acid the effects were observed with both mercuric chloride and antimony trichloride, but not with stronger ionising agents such as ferric chloride. These findings are all compatible with our conclusions, and we suggest that self-solvation of the transition state is very important in ionisations catalysed by metal halides, especially in poorly solvating solvents. Such solvation by metal halide molecules might be expected to involve more than one halide molecule. Indeed in chlorobenzene Bayles, Evans, and Jones¹³ found that at the maximum concentration of mercuric chloride they used the average number of molecules involved in solvation was 1.4. We have also observed a similar effect with mercuric chloride in acetone. Like effects would probably have been observed with the other catalysts if sufficiently high concentrations could have been studied.

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¹² Cotter and Evans, *J.*, 1959, 2988.

¹³ Bayles, Evans, and Jones, *J.*, 1957, 1020.
