Acceptor Properties of Metal Halides. Part IV.[1] Group III Halides as Catalysts for the Racemisation of α-Methylbenzyl Chloride in Diethyl Ether

By **R. M. Evans** and **R. S. Satchell,*** Chemistry Department, Queen Elizabeth College, Campden Hill Road, London W.8

The catalytic efficiencies of boron chloride, boron fluoride, aluminium chloride, and gallium chloride in the racemisation of α-methylbenzyl chloride in diethyl ether have been compared kinetically at 25°. Gallium chloride has also been studied at 5 and 15°. With aluminium and gallium chlorides, and with boron fluoride, a simple first-order dependence of rate upon catalyst concentration is found. The catalytic efficiencies are in the order $GaCl_3 > AlCl_3 > BF_3$. Qualitative results with boron chloride indicate that its efficiency is approximately the same as that of boron fluoride. The mechanism of racemisation is discussed in the light of these results.

In continuation of our studies [1] of the racemisation of α-methylbenzyl chloride catalysed by covalent metal halides, we now report on the catalysis by boron fluoride, boron chloride, aluminium chloride, and gallium chloride in diethyl ether solution. There has been no comparable study with these catalysts since the early qualitative work of Bodendorf and Böhme.[2]

EXPERIMENTAL

Materials.—Optically active α-methylbenzyl chloride was obtained from the resolved alcohol by Gerrard's method [3] by use of phosphorus oxychloride and pyridine. The alcohol was resolved as previously described.[4] Diethyl ether and boron fluoride diether complex were purified as before.[5] Gallium chloride and aluminum chloride were purified by Mohammad and Satchell's method.[6,7] Boron chloride (Fluka) was used without further purification.

Preparation of Reaction Mixtures.—Stock solutions of boron fluoride were prepared and analysed as before.[5] Stock solutions of gallium and aluminium chlorides were prepared and analysed by methods similar to those used by Mohammad and Satchell.[6,7] Suitable aliquot portions of boron chloride were added to diethyl ether (with cooling) and the resulting stock solutions analysed by titration with alkali,[8] and by Volhard's method. To prepare a reaction mixture α-methylbenzyl chloride was added to a known volume of a catalyst stock solution in a volumetric flask, and the mixture made up with more solvent.

All operations involving the Lewis acids and their solutions were performed in a dry-box.

Kinetic Measurements.—The rate of loss of optical activity was measured as before.[4]

RESULTS AND DISCUSSION

Kinetic Form.—In the absence of a catalyst no racemisation of α-methylbenzyl chloride in diethyl ether

---

[1] Part III, R. S. Satchell, *J. Chem. Soc.*, 1965, 797.

[2] K. Bodendorf and H. Böhme, *Annalen*, 1935, **516**, 1.

[3] W. J. Gerrard, *J. Chem. Soc.*, 1945, 106.

[4] R. S. Satchell, *J. Chem. Soc.*, 1963, 5963.

[5] R. S. Satchell and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1967, 36.

[6] A. Mohammad and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1967, 403.

[7] A. Mohammad and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1968, 331.

[8] R. P. Bell and B. G. Skinner, *J. Chem. Soc.*, 1952, 2955.

is observed during 72 hr. at 25°. A similar result is obtained in other solvents.[4,9,10] In the presence of gallium, aluminium, or boron chloride, or of boron fluoride, racemisation takes place. For all the catalysts, at any fixed catalyst concentration, good first-order loss of optical activity was observed. However, the boron chloride solutions were deep orange and faded with time. For this reason, and because useful solutions of this catalyst were nearly saturated with boron chloride, we did not thoroughly investigate the reaction order in this case.

Results obtained at different catalyst concentrations are in Tables 1 and 2, in which k_{obs} is the observed first-order rate constant. For gallium and aluminium chloride, and for boron fluoride, a plot of k_{obs} against the stoicheiometric catalyst concentration is a straight line (Figure). However, for gallium chloride the plot shows an intercept on the catalyst concentration axis when $k_{obs} = 0$. This effect, we believe, is due to the presence of a small amount of water in the solvent. In other related systems the presence, in the ether, of water remaining after distillation from sodium leads to a certain amount of catalyst deactivation.[5,6] In the present work the intercept provides a value for the water concentration if we assume (as is probable) that the water reacts stoicheiometrically with the gallium chloride to form a 1 : 1 adduct. The water concentration so estimated varied from one batch of solvent to another, as would be expected, but was always in the range *ca.* 0·004—0·006M. We can therefore represent the dependence of k_{obs} on the gallium chloride concentration by equation (1). The slope of the plot of k_{obs} against $[GaCl_3]_{stoich}$ gives k_1, the catalytic rate constant.

TABLE 1

Racemisation of α-methylbenzyl chloride in the presence of gallium chloride in diethyl ether

$[PhCHMeCl] \simeq 0{\cdot}03$M and k_{obs} = observed first-order rate constant (sec.$^{-1}$) in all Tables. $[GaCl_3]_{stoich}$ represents the stoicheiometric concentration of $GaCl_3$ (see text).

At 5°		At 15°		At 25°	
$10^2[GaCl_3]_{stoich}$	10^3k_{obs}	$10^2[GaCl_3]_{stoich}$	10^3k_{obs}	$10^2[GaCl_3]_{stoich}$	10^3k_{obs}
2·00	0·58	1·00	0·43	0·70	0·43
2·50	0·84	1·50	0·85	0·90	0·88
3·00	1·02	2·00	1·40	1·16	1·39
3·50	1·24	2·52	1·88	1·40	1·83
				1·60	2·25
				1·86	2·73
				2·30	3·53

TABLE 2

Racemisation of α-methylbenzyl chloride in the presence of aluminium chloride, boron fluoride, and boron chloride in diethyl ether at 25°

$[AlCl_3]_{stoich}$	0·10	0·17	0·25	0·51	0·65	0·79
10^4k_{obs}	0·13	0·18	0·29	0·47	0·66	0·76
$[AlCl_3]_{stoich}$	1·01	1·39	1·46	1·58	1·76	1·81
10^4k_{obs}	0·99	1·30	1·44	1·57	1·82	1·88
$[BF_3]_{stoich}$	1·00	2·00	3·00	4·00	5·00	
10^6k_{obs}	0·81	1·55	2·08	2·98	4·31	
$[BCl_3]_{stoich}$	1·1	2·0				
10^6k_{obs}	2·3	6·7				

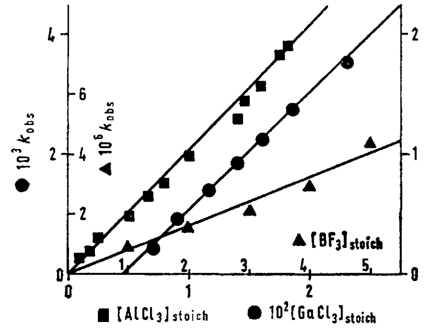
$$k_{obs} = k_1\,([GaCl_3]_{stoich} - [H_2O]) \qquad (1)$$

With both aluminium chloride and boron fluoride the catalyst concentration was always $\geqslant 0{\cdot}1$M, so that the residual water had an insignificant effect, with the result that the plot of k_{obs} against $[AlCl_3]_{stoich}$ or $[BF_3]_{stoich}$ goes through the origin (Figure). The slope is k_1. Values of k_1 are in Table 3.

Reaction Mechanism.—For catalysis by zinc and mercuric halides in acetone we previously concluded that the essential mechanism can be represented by reaction (2), where S represents the solvent.[9] We favour

$$RCl + MCl_xS_y \rightleftharpoons R^+[MCl_{x+1}]^-\,S_{y-1} + S \qquad (2)$$

the same scheme in ether, a solvent of even lower dielectric constant. The forward step will determine the rate of racemisation,[2,11] which should ideally, therefore, depend upon the first power of the catalyst concentration. This is found for those catalysts studied thoroughly in the present work. The entropy of activation now determined for catalysis by gallium chloride (—24 e.u., Table 3) is also compatible with reaction (2).



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

TABLE 3

Values of k_1

Catalyst	Temp.	k_1 (l. mole^{-1} sec.$^{-1}$)
$GaCl_3$ *	5°	$4{\cdot}25 \times 10^{-2}$
	15°	$9{\cdot}55 \times 10^{-2}$
	25°	$1{\cdot}92 \times 10^{-1}$
$AlCl_3$	25°	$1{\cdot}00 \times 10^{-4}$
BF_3	25°	$8{\cdot}2 \times 10^{-7}$

* From the three values for $GaCl_3$, we obtained $\Delta H^‡ = 12$ kcal. mole^{-1} and $\Delta S^‡$ —24 e.u. These quantities were not determined for $AlCl_3$ or BF_3 owing to the slowness of the reaction with these catalysts.

Comparison of Catalytic Efficiency.—Simple consideration of the concentration of catalyst required to bring about the racemisation leads to the order of effectiveness $GaCl_3 \gg AlCl_3 \gg BF_3$ (or BCl_3). Table 3 gives the k_1 values.

---

[9] R. S. Satchell, *J. Chem. Soc.*, 1964, 5464.

[10] H. Hart and W. L. Spliethoff, *J. Amer. Chem. Soc.*, 1955, **77**, 833; K. Heald and G. Williams, *J. Chem. Soc.*, 1954, 362.

[11] E. D. Hughes, C. K. Ingold, and A. D. Scott, *J. Chem. Soc.*, 1937, 1201.

In any discussion of the catalytic effects, factors that must be kept in mind are (i) that chlorine has two electron pairs potentially available for donation to a Lewis acid, (ii) that the boron halides can accept only one electron pair, whereas gallium and aluminium chlorides can make use of *d*-orbitals to accept a second electron pair,[12] (iii) that the atomic volumes of the central atoms are in the order Ga > Al > B, (iv) that the addition of the chloride ion to $M(Hal)_3$ may involve a steric effect, and (v) that in the absence of steric effects, and for the acceptance of a single electron pair from a base, the expected order of acidity is B > Al > Ga towards bases stronger than the solvent, and Ga > Al > B for bases weaker than the solvent.[12]

Whether chloride is to be considered a stronger or a weaker base than diethyl ether is a moot point. However, since towards N-bases, which are stronger than ether and which inevitably have one electron pair only available for donation, gallium[6] and aluminium[7] chlorides exhibit only comparable acidities; therefore gallium, which being larger should be able to make greater use than aluminium of *d*-orbitals, should exhibit the greater reactivity in the present reaction, as found. The size of the factor (2×10^3) is nevertheless surprising. We consider, therefore, that a steric effect is also involved: the greater size of gallium than aluminium will make more space available to the incoming chloride ion for the displacement of the co-ordinated ether molecule from the catalyst [reaction (2)].

The very low reactivity of the boron halides may also be largely steric in origin, although factor (ii) will also operate. Boron acids are relatively weak compared with gallium and aluminium acids towards other bases (*e.g.*, ketones) capable of donating two electron pairs.[12, 13]

The relative catalytic efficiencies found here for racemisation are in qualitative agreement with those found for the catalysed depolymerisation of paraldehyde in ether[8] (for which $AlCl_3 > BCl_3$) and, perhaps more relevantly, for the catalysed benzoylation of aromatic hydrocarbons in excess of benzoyl chloride[14] (where $GaCl_3 > AlCl_3 > BCl_3$). The significance of this agreement depends on the mechanism assumed for the various reactions.

Our results are surprisingly different from some obtained for the ionisation of triphenylmethyl chloride[15] in $PhPOCl_2$ and $POCl_3$ [reaction (3)] where equilibrium constants (4) lead to an order of acidity $BCl_3 > AlCl_3$.

$$Ph_3CCl + MCl_n \rightleftharpoons Ph_3C^+MCl^-{}_{n+1} \qquad (3)$$

$$K = \frac{[Ph_3C^+MCl^-{}_{n+1}]}{[Ph_3CCl][MCl_n]} \qquad (4)$$

This is the order expected, in the absence of complicating effects, when the solvent is very feebly basic.[12] Although steric factors resulting from the size of the incoming groups (a chloride ion in the forward direction and a solvent molecule in the reverse direction) will partly nullify each other so far as an equilibrium constant is concerned, nevertheless effect (ii) should still operate. More work on similar equilibria appears desirable.

[9/1061 *Received, June 23rd*, 1969]

---

[12] D. P. N. Satchell and R. S. Satchell, *Chem. Rev.*, 1969, **69**, 251.

[13] A. Mohammad, D. P. N. Satchell, and R. S. Satchell, *J. Chem. Soc.* (*B*), 1967, 723, 727.

[14] F. R. Jensen and H. C. Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 3039.

[15] M. Baaz, V. Gutmann, and J. R. Masaguer, *Monatsh.*, 1961, **92**, 582, 590.