Acceptor Properties of Metal Halides. Part VII.[1] Tin, Zinc, and Antimony Halides as Catalysts for the Racemisation of α-Methylbenzyl Chloride in Diethyl Ether

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The catalytic efficiencies of stannic chloride, stannic bromide, zinc chloride, zinc bromide, trichloro(phenyl)tin, and antimony trichloride in the racemisation of α-methylbenzyl chloride in ether have been compared. For all the catalysts the reaction is first order in the alkyl halide, but the order in the catalyst concentration depends upon the system. With stannic and zinc halides the order is a mixture of first and second, with trichloro(phenyl)tin a mixture of first and third, and with antimony trichloride fourth. The reaction mechanism is discussed. The first-order terms in catalyst concentration are interpreted as representing paths in which the transition state is solvated by ether molecules, and the higher order terms in catalyst concentration as representing paths in which the transition state is solvated by metal halide–ether molecules. The first-order catalytic rate constants are in the sequence $SnCl_4 > SnBr_4 > ZnBr_2 > ZnCl_2 > PhSnCl_3 > SbCl_3$. The enthalpy of activation and entropy of activation have been determined for both paths for the stannic halides and the zinc halides. The values generally support the suggested mechanism. The effect of water on the stannic chloride and on the zinc chloride catalysis has been studied. The racemisation rate is decreased: the reduction corresponds to the formation of $1SnCl_4,2H_2O$ and of $1ZnCl_2,1H_2O$ adducts. Addition of hydrogen chloride leads to an increase in the rate of the stannic chloride and of the antimony trichloride catalysed reactions. This increase probably results from transition state solvation by hydrogen chloride–ether molecules. Molecular weight determinations show that zinc bromide, zinc iodide, and stannic bromide are monomeric in ether, and that zinc chloride is monomeric in acetone.

IN continuation of our studies [2,3] of the racemisation of α-methylbenzyl chloride catalysed by covalent metal halides, we now report on the catalysis by stannic chloride, stannic bromide, trichloro(phenyl)tin, zinc chloride, zinc bromide, and antimony trichloride in diethyl ether solution. There have been no comparable studies with these catalysts since the early qualitative work of Bodendorf and Böhme.[4]

EXPERIMENTAL

The optically active chloride was a previous sample.[3] Diethyl ether,[5] acetone,[6] stannic chloride,[2] zinc chloride,[6] zinc bromide,[6] zinc iodide,[6] and antimony trichloride[1] were purified as before. Stannic bromide (B.D.H.), redistilled under vacuum, had b.p. 75° at 4 mmHg. Trichloro-

(phenyl)tin, anhydrous hydrogen chloride, and reaction mixtures were prepared and analysed by previous methods.[1,7] The loss of optical activity was followed, and the rate constant obtained as previously.[1,3,7] As in our earlier work all operations involving the Lewis acids and their solutions were performed in a dry-box.

The molecular weights of zinc chloride, zinc bromide, zinc iodide, and stannic bromide in ether were determined over a range of concentrations with a Gallenkamp semi-micro ebulliometer.[8] Naphthalene was used to determine the ebullioscopic constant. With the exception of zinc chloride, the metal halides were found to be accurately monomeric over the concentration ranges used ($ZnBr_2$, 0·01—0·10 mol dm^{-3}, $M = 225 \pm 1$, theoretical = 225; ZnI_2, 0·01—0·10 mol dm^{-3}, $M = 318 \pm 2$, theoretical = 319; $SnBr_4$, 0·02—0·30 mol dm^{-3}, $M = 440 \pm 2$, theoretical = 438). How-

[1] Part VI, R. M. Evans and R. S. Satchell, J. Chem. Soc. (B), 1970, 1667.

[2] R. M. Evans and R. S. Satchell, J. Chem. Soc. (B), 1970, 300.

[3] R. M. Evans and R. S. Satchell, J. Chem. Soc. (B), 1970, 298.

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

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

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

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

[8] C. Heitler, Analyst., 1958, 83, 223.

ever, for zinc chloride plots of the resistance change, ΔR (proportional to b.p. elevation), against the solute concentration were curves, rather than rectilinear. Moreover, sensible results could not be obtained on the assumption of a monomer–dimer equilibrium in the system. The molecular weight of zinc chloride was therefore determined in acetone over the concentration range 0·01—0·20 mol dm^{-3} to see whether similar behaviour would be found. However, in this solvent zinc chloride is clearly monomeric ($M = 137 \pm 2$, theoretical $= 136$). We suspect that the abnormal behaviour of zinc chloride in ether is due to the zinc chloride–ether adduct having a significant vapour pressure (the ebullioscopic method is based on the solute being involatile). Our reasons are: (i) zinc chloride is monomeric in acetone; (ii) zinc bromide and zinc iodide are monomeric in ether; (iii) observation indicates that the zinc chloride–ether adduct is a liquid, whereas other metal halide adducts are usually solids. We therefore believe that zinc chloride, in common with the other metal halides studied here, is monomeric in ether.

RESULTS AND DISCUSSION

Kinetics of the Reaction.—We have previously reported [3] that in the absence of a catalyst no racemisation of α-methylbenzyl chloride in diethyl ether occurs during 72 h at 25°. In the presence of stannic chloride, trichloro(phenyl)tin, zinc chloride, zinc bromide, and antimony trichloride, at any fixed catalyst concentration, good first-order loss of optical activity was observed. However, in the presence of stannic bromide such behaviour was restricted to the first 2—4 halflives, after which the reaction accelerated. This behaviour almost certainly resulted from halogen exchange. Such exchange has been observed in carbon tetrachloride solution.[9]

The first-order dependence of the reaction rate on the alkyl halide concentration was further shown for some of the catalysts by the independence of the observed first-order rate constant (k_{obs}) of the alkyl halide concentration at a fixed catalyst concentration (Tables 7 and 8); k_{obs} was reproducible to within $\pm 5\%$.

Catalysis by Stannic Chloride.—Values of k_{obs}, obtained at different catalyst concentrations and temperatures, are in Table 1. The concentration range for stannic chloride was limited by its solubility in ether (0·035 mol dm^{-3} at 25°). In past studies we have found that residual water in the dried solvent deactivates the catalyst.[1,3] In particular it was estimated in studies of the stannic chloride catalysed acylation of β-naphthol in ether distilled from sodium, that 0·002 mol dm^{-3} of stannic chloride are removed by the formation of a 1 : 2 adduct with residual water.[1] We therefore tested the effect of water on the present reaction. At a given stannic chloride concentration the intentional addition of water resulted in a decrease in k_{obs} (see Table 2). Values of [SnCl$_4$]$_{est}$, the apparent stannic chloride concentrations indicated by the values of k_{obs} obtained in the presence of added water, were obtained from a plot of k_{obs} versus [SnCl$_4$]$_{stoic}$, which is the apparent free stannic chloride concentration in the absence of added water. Within experimental error, the amount of

stannic chloride apparently lost in the presence of added water, Δ[SnCl$_4$] = [SnCl$_4$]$_{stoic}$ — [SnCl$_4$]$_{est}$, equalled half the concentration of water added. This result is in agreement with the formation of a catalytically inactive 1 : 2 adduct between stannic chloride and water. Since

TABLE 1

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

[PhCHMeCl] $\simeq$ 0·03 mol dm^{-3} (unless stated otherwise), k_{obs} = observed first-order rate constant (s^{-1}) in all Tables. [SnCl$_4$]$_{stoic}$ represents the stoicheiometric concentration of SnCl$_4$, and [SnCl$_4$]$_{free}$ = [SnCl$_4$]$_{stoic}$ — 0·002 (see text). All concentrations are in mol dm^{-3}

At 10°

10^2[SnCl$_4$]$_{stoic}$	1·00	1·50	2·00	2·50	
$10^4 k_{obs}$	0·18	0·32	0·48	0·68	
10^2[SnCl$_4$]$_{free}$	0·80	1·30	1·80	2·30	
$10^2 k_{obs}$/[SnCl$_4$]$_{free}$	0·225	0·246	0·267	0·296	

At 20°

10^2[SnCl$_4$]$_{stoic}$	1·00	2·00	3·00	4·00	
$10^4 k_{obs}$	0·40	1·08	2·22	3·36	
10^2[SnCl$_4$]$_{free}$	0·80	1·80	2·80	3·80	
$10^2 k_{obs}$/[SnCl$_4$]$_{free}$	0·50	0·60	0·79	0·88	

At 25°

10^2[SnCl$_4$]$_{stoic}$	1·10	1·45	1·70	1·85	2·20
$10^4 k_{obs}$	0·76	1·10	1·40	1·57	2·01
10^2[SnCl$_4$]$_{free}$	0·90	1·25	1·50	1·65	2·00
$10^2 k_{obs}$/[SnCl$_4$]$_{free}$	0·84	0·88	0·93	0·95	1·01
10^2[SnCl$_4$]$_{stoic}$	2·50	2·70	2·84	3·10	3·40
$10^4 k_{obs}$	2·50	2·85	3·05	3·50	4·09
10^2[SnCl$_4$]$_{free}$	2·30	2·50	2·64	2·90	3·20
$10^2 k_{obs}$/[SnCl$_4$]$_{free}$	1·09	1·14	1·16	1·21	1·28

At 32°

10^2[SnCl$_4$]$_{stoic}$	1·00	1·80	2·50	3·20	
$10^4 k_{obs}$	1·16	2·65	4·26	6·55	
10^2[SnCl$_4$]$_{free}$	0·80	1·60	2·30	3·00	
$10^2 k_{obs}$/[SnCl$_4$]$_{free}$	1·45	1·66	1·85	2·18	

TABLE 2

The effect of water and hydrogen chloride on the stannic chloride catalysis at 25°

For definition of [SnCl$_4$]$_{est}$ see text; Δ[SnCl$_4$] = [SnCl$_4$]$_{stoic}$ — [SnCl$_4$]$_{est}$ (all in mol dm^{-3})

Effect of water

10^2[SnCl$_4$]$_{stoic}$	2·70	2·70	2·74	2·80	2·84	2·84
10^2[H$_2$O]	0·60	2·50	1·75	1·20	0·76	1·00
$10^4 k_{obs}$/s^{-1}	2·45	1·06	1·60	2·07	2·42	2·30
[SnCl$_4$]$_{est}$	2·47	1·40	1·90	2·24	2·46	2·38
Δ[SnCl$_4$]	0·23	1·30	0·84	0·56	0·38	0·46

Effect of hydrogen chloride

[SnCl$_4$]$_{stoic}$ = 2·65 × 10^{-2}

10^2[HCl]	0·00	0·20	0·35	0·50	0·70	0·80
$10^4 k_{obs}$/s^{-1}	2·68	2·82	2·92	3·00	3·10	3·18

[SnCl$_4$]$_{stoic}$ = 2·20 × 10^{-2}

10^2[HCl]	0·00	1·00	1·20
$10^4 k_{obs}$/s^{-1}	2·01	2·62	2·65

in the previous study we estimated that 0·002 mol dm^{-3} of stannic chloride are removed by the residual water (0·004 mol dm^{-3}) in ether distilled from sodium, we

[9] J. Heald and G. Williams, *J. Chem. Soc.*, 1954, 362.

have allowed for this in our calculations *i.e.* $[SnCl_4]_{free} = [SnCl_4]_{stoic} - 0.002$.

Table 1 shows clearly that k_{obs} increases more rapidly than $[SnCl_4]_{free}$. The dependence of k_{obs} on the catalyst

TABLE 3

Values of rate constants for stannic halide catalysis

Units of k_1, k_2 [defined by equation (1)], and k [defined by equation (3)] are mol^{-1} dm^3 s^{-1}, mol^{-2} dm^6 s^{-1}, and mol^{-2} dm^6 s^{-1} respectively

Temp. (°C)	$10^3 k_1$	$10 k_2$	k	$10 k_1/k_2$
SnCl$_4$				
10	1·89	0·448		0·42
20	3·93	1·28		0·31
25	6·18	2·08	0·28	0·30
32	11·2	5·67		0·20
SnBr$_4$				
10	0·44	0·010		4·4
25	1·60	0·013		12·3
32	2·74			

concentration can be expressed by equation (1) which implies the existence of two catalysed reaction paths.

$$k_{obs} = k_1[SnCl_4]_{free} + k_2[SnCl_4]^2_{free} \qquad (1)$$

Values of k_1 and k_2 at different temperatures determined[7] from plots of $k_{obs}/[SnCl_4]_{free}$ *versus* $[SnCl_4]_{free}$ are in Table 3, and values for the entropy of activation and enthalpy of activation for the two paths are in Table 5.

The effect of hydrogen chloride on the stannic chloride catalysis was also examined. In agreement with observations in other solvents,[2,7] no racemisation of α-methylbenzyl chloride was observed in the presence of 0·03 mol dm^{-3} hydrogen chloride alone over 72 h at 25°. In the presence of stannic chloride concentrations of hydrogen chloride above $[SnCl_4]_{stoic}/2$ cannot be used owing to precipitation. At lower concentrations of hydrogen chloride the reaction rate increases (Table 2). At a fixed stannic chloride concentration k_{obs} is rectilinear in [HCl]. We can therefore write equation (2).

$$k_{obs} = k_1[SnCl_4]_{free} + k_2[SnCl_4]^2_{free} + k^1[HCl] \qquad (2)$$

The value of k^1, obtained from the plot of k_{obs} *versus* [HCl], increases with $[SnCl_4]_{free}$. When $[SnCl_4]_{free} = 0.0245$ mol dm^{-3} $k^1 = 0.67 \times 10^{-2}$ mol^{-1} dm^3 s^{-1}, and when $[SnCl_4]_{free} = 0.0200$ mol dm^{-3} $k^1 = 0.52 \times 10^{-2}$ mol^{-1} dm^3 s^{-1}. These values are roughly in the ratio of the stannic chloride concentrations. It is therefore probable, though not certain (owing to insufficient data) that equation (3) holds where $k = ca.\ 0.28$ mol^{-2} dm^6 s^{-1}.

$$k^1 = k[SnCl_4]_{free}[HCl] \qquad (3)$$

Catalysis by Stannic Bromide.—Results for stannic bromide have been treated in the same general way as those for stannic chloride; and the same allowance made for residual water. At 10 and 25° we find that, as for stannic chloride, k_{obs} increases more rapidly than does $[SnBr_4]_{free}$. At 32°, however, k_{obs} varies rectilinearly with $[SnBr_4]_{free}$ up to a concentration of 0·6 mol dm^{-3}

(Table 4). At the two lower temperatures the dependence of k_{obs} on $[SnBr_4]_{free}$ can be represented by equation (4), analogous to equation (1). Values of k_1 and k_2 are

$$k_{obs} = k_1[SnBr_4]_{free} + k_2[SnBr_4]^2_{free} \qquad (4)$$

in Table 3, and values of $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ are in Table 5. $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ were not determined owing to the disappearance of the term in k_2 at 32°. This effect is

TABLE 4

Racemisation of α-methylbenzyl chloride in the presence of stannic bromide in diethyl ether

$[SnBr_4]_{free} = [SnBr_4]_{stoic} - 0.002$ (see text) (concentrations in mol dm^{-3}).

At 10°

$[SnBr_4]_{stoic}$	0·300	0·500	0·700	0·900	1·12
$10^4 k_{obs}/s^{-1}$	2·16	4·53	7·70	11·7	16·8
$[SnBr_4]_{free}$	0·298	0·498	0·698	0·898	1·12
$10^3 k_{obs}/[SnBr_4]_{free}$	0·72	0·91	1·10	1·30	1·50

At 25°

$[SnBr_4]_{stoic}$	0·042	0·129	0·252	0·370	0·440
$10^4 k_{obs}/s^{-1}$	0·65	2·30	4·82	7·72	8·97
$[SnBr_4]_{free}$	0·040	0·127	0·250	0·368	0·438
$10^3 k_{obs}/[SnBr_4]_{free}$	1·63	1·81	1·93	2·10	2·05

$[SnBr_4]_{stoic}$	0·620	0·735	0·835		
$10^4 k_{obs}/s^{-1}$	14·8	20·0	24·1		
$[SnBr_4]_{free}$	0·618	0·733	0·833		
$10^3 k_{obs}/[SnBr_4]_{free}$	2·39	2·73	2·89		

At 32°

$[SnBr_4]_{stoic}$	0·100	0·206	0·310	0·404	0·450
$10^4 k_{obs}/s^{-1}$	2·73	5·50	8·28	11·1	12·5
$[SnBr_4]_{free}$	0·098	0·204	0·308	0·402	0·448
$10^3 k_{obs}/[SnBr_4]_{free}$	2·79	2·69	2·69	2·76	2·79

$[SnBr_4]_{stoic}$	0·496	0·600	0·700	0·760
$10^4 k_{obs}$	13·5	16·5	20·0	23·0
$[SnBr_4]_{free}$	0·494	0·598	0·698	0·758
$10^3 k_{obs}/[SnBr_4]_{free}$	2·73	2·76	2·87	3·03

TABLE 5

Summary of rate constants (25°) and activation parameters

Units of k_3 and k_4 are mol^{-3} dm^9 s^{-1} and mol^{-4} dm^{12} s^{-1} respectively. Units of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are kcal mol^{-1} and cal mol^{-1} K^{-1} respectively. See Table 3 for the other units, and text for definitions of k_1—k_4.

Rate constants

Acid	Solvent	$10^4 k_1$	k_2	$10^4 k_3$	$10^5 k_4$
SnCl$_4$	Benzene [a]	13,200			
SnCl$_4$	Ether	61·8	0·208		
SnBr$_4$	Ether	16·0	0·0013		
ZnCl$_2$	Ether	1·5	0·171		
ZnBr$_2$	Ether	4·0	0·0607		
PhSnCl$_3$	Ether	0·45		2·25	
SbCl$_3$	Ether	<0·01			5·49
GaCl$_3$	Ether [b]	1,920			
AlCl$_3$	Ether [b]	1·00			
BF$_3$	Ether [b]	0·008			

Activation parameters

Acid	Solvent	$\Delta H_1^{\ddagger}$	$\Delta S_1^{\ddagger}$	$\Delta H_2^{\ddagger}$	$\Delta S_2^{\ddagger}$
SnCl$_4$	Benzene [a]	8·5	−30		
SnCl$_4$	Ether	13	−26	17	−5
SnBr$_4$	Ether	14	−26		
ZnCl$_2$	Ether	22	−4	17	−6
ZnBr$_2$	Ether	18	−13	19	+1
GaCl$_3$	Ether [b]	12	−24		

[a] From ref. 2.   [b] From ref. 3.

different from that found for stannic chloride where k_1/k_2 decreases as the temperature rises (Table 3).

Catalysis by Trichloro(phenyl)tin.—Values of k_{obs} obtained at different catalyst concentrations are in Table 6. Since these concentrations are greatly in

TABLE 6

Racemisation of α-methylbenzyl chloride in the presence of trichlorophenyltin in diethyl ether at 25°

$[PhSnCl_3]_{stoic}/$ mol dm^{-3}	$10^4 k_{obs}/s^{-1}$	$10^4 k_{obs}/$ $[PhSnCl_3]_{stoic}$
0·200	0·09	0·45
0·400	0·37	0·93
0·660	0·97	1·47
1·00	2·85	2·85
1·41	7·18	5·09
1·66	10·7	6·45
1·78	13·3	7·47
2·20	25·0	11·4
2·33	29·6	12·7

excess of the residual water in the solvent, there is no need here to correct for catalyst deactivation by the water. The results in Table 6 show that k_{obs} increases very much more rapidly than does $[PhSnCl_3]_{stoic}$; a plot of $k_{obs}/[PhSnCl_3]_{stoic}$ against $[PhSnCl_3]^2_{stoic}$ is rectilinear, and the dependence of k_{obs} on $[PhSnCl_3]_{stoic}$ is best represented by equation (5). Values of k_1 and

$$k_{obs} = k_1[PhSnCl_3]_{stoic} + k_3[PhSnCl_3]^3_{stoic} \quad (5)$$

k_3 at 25°, obtained from the slope and intercept respectively are in Table 5.

Catalysis by Antimony Trichloride.—Values of k_{obs} for different catalyst concentrations are in Table 7. [As for

TABLE 7

Racemisation of α-methylbenzyl chloride in the presence of antimony trichloride in diethyl ether at 25°. The effect of hydrogen chloride on the catalysis; k_{obs} is s^{-1}, concentrations in mol dm^{-3}

Order in alkyl halide
$[SbCl_3]_{stoic} = 1·50$

[RCl]	0·01	0·03	0·09
$10^4 k_{obs}$	2·69	2·72	2·69

Order in antimony trichloride

$[SbCl_3]_{stoic}$	0·85	1·18	1·38	1·50	1·66	1·75
$10^4 k_{obs}$	0·25	0·99	1·80	2·72	4·25	5·22
$10^4 k_{obs}/[SbCl_3]_{stoic}$	0·29	0·84	1·32	1·81	2·56	2·98

$[SbCl_3]_{stoic}$	1·83	1·90	1·98
$10^4 k_{obs}$	6·25	7·20	8·70
$10^4 k_{obs}/[SbCl_3]_{stoic}$	3·42	3·79	4·39

Effect of hydrogen chloride
$[SbCl_3]_{stoic} = 1·50$

[HCl]	0·00	0·08	0·15	0·20	0·26	0·32
$10^4 k_{obs}$	2·72	3·50	4·33	4·84	6·22	8·75

trichloro(phenyl)tin it is unnecessary to allow for catalyst deactivation by the residual water in the solvent.] The observed increase in k_{obs} with $[SbCl_3]_{stoic}$ is very rapid; plots of $k_{obs}/[SbCl_3]_{stoic}$ against $[SbCl_3]^3_{stoic}$, and of k_{obs} against $[SbCl_3]^4_{stoic}$ are both straight lines passing through the origin. Therefore we can write

equation (6). The former plot gives an upper limit for

$$k_{obs} = k_4[SbCl_3]^4_{stoic} \quad (6)$$

the value of k_1; k_4 can be obtained from the slope of either plot (Table 5).

The effect of hydrogen chloride on the antimony trichloride catalysed reaction was also tested, although the concentration range that could be studied was limited by the formation of a precipitate. At a fixed antimony trichloride concentration (1·50 mol dm^{-3}), k_{obs} (Table 7) increases rectilinearly with [HCl] up to [HCl] *ca.* 0·20 mol dm^{-3}, but thereafter increases more rapidly.

Catalysis by Zinc Chloride.—The effect of deliberately added water on the zinc chloride catalysis was tested and, as for stannic chloride, resulted in a decrease in racemisation rate (Table 9). The amount of zinc

TABLE 8

Racemisation of α-methylbenzyl chloride in the presence of zinc halides in diethyl ether at 25°

$[Zn(Hal)_2]_{free} = [Zn(Hal)_2]_{stoic} - 0·004$ (see text). k_{obs} in s^{-1}, concentrations in mol dm^{-3}

(a) $ZnCl_2$

Order in RCl
$[ZnCl_2]_{stoic} = 0·025$

[RCl]	0·008	0·016	0·031	0·067
$10^4 k_{obs}$	0·62	0·60	0·59	0·59

Order in $ZnCl_2$
[RCl] = 0·03

$10^2[ZnCl_2]_{stoic}$	0·60	1·50	2·00	3·00	3·70	5·00
$10^4 k_{obs}$	0·014	0·18	0·44	1·15	2·00	3·71
$10^2[ZnCl_2]_{free}$	0·20	1·10	1·60	2·60	3·30	4·60
$10^3 k_{obs}/[ZnCl_2]_{free}$	0·70	1·64	2·75	4·42	6·06	8·04

$10^2[ZnCl_2]_{stoic}$	6·00	7·30	8·40
$10^4 k_{obs}$	5·30	8·20	11·20
$10^2[ZnCl_2]_{free}$	5·60	6·90	8·00
$10^3 k_{obs}/[ZnCl_2]_{free}$	9·46	11·9	14·0

(b) $ZnBr_2$

Order in RCl
$[ZnBr_2]_{stoic} = 0·030$

[RCl]	0·005	0·012	0·035	0·082
$10^4 k_{obs}$	0·48	0·47	0·47	0·48

Order in $ZnBr_2$
[RCl] = 0·030

$10^2[ZnBr_2]_{stoic}$	1·48	2·00	3·74	5·12	7·20	9·00
$10^4 k_{obs}$	0·09	0·24	0·75	1·53	3·09	4·60
$10^2[ZnBr_2]_{free}$	1·08	1·60	3·34	4·72	6·80	8·60
$10^3 k_{obs}/[ZnBr_2]_{free}$	0·83	1·50	2·25	3·24	4·54	5·35

$10^2[ZnBr_2]_{stoic}$	11·60	12·60
$10^4 k_{obs}$	7·98	9·60
$10^2[ZnBr_2]_{free}$	11·20	12·20
$10^3 k_{obs}/[SnBr_2]_{free}$	7·13	7·87

chloride deactivated by the water was calculated in the same way as for stannic chloride. The results indicate that zinc chloride and water form a 1 : 1 adduct. We can therefore assume that for solutions in the dried solvent $[ZnCl_2]_{free} = [ZnCl_2]_{stoic} - 0·004$ (see above).

The values of k_{obs} [Table 8; data at temperatures other than 25° are given in SUP No. 20646 * (4 pp.)]

TABLE 9

The effect of water on the zinc chloride catalysis at 25°

[ZnCl$_2$]$_{est}$ was obtained in the same way as for SnCl$_4$ from the data in Table 8; Δ[ZnCl$_2$] = [ZnCl$_2$]$_{stoic}$ − [ZnCl$_2$]$_{est}$. k_{obs} in s^{-1}, concentrations in mol dm^{-3}

10^2[ZnCl$_2$]$_{stoic}$	10^2[H$_2$O]	10^4k_{obs}	10^2[ZnCl$_2$]$_{est}$	10^2Δ[ZnCl$_2$]
6·80	1·00	5·44	6·05	0·75
7·60	2·50	4·02	5·18	2·42
7·60	3·50	2·51	4·22	3·38

TABLE 10

Values of rate constants for zinc halide catalysis

See Table 3 for units of k_1 and k_2

Temp. (°C)	10^4k_1	10k_2
ZnCl$_2$		
10		0·355
15	0·4	0·538
25	1·5	1·71
35	3·0	2·79
ZnBr$_2$		
10	0·8	0·110
20	2·2	0·352
25	4·0	0·607
32	8·5	1·46

increase more rapidly than [ZnCl$_2$]$_{free}$. Plots of k_{obs}/[ZnCl$_2$]$_{free}$ against [ZnCl$_2$]$_{free}$ are straight lines with small intercepts. Hence we can write equation (7).

$$k_{obs} = k_1[ZnCl_2]_{free} + k_2[ZnCl_2]^2_{free} \qquad (7)$$

Values of k_1 and k_2 at four different temperatures are in Table 10, and values of $\Delta H_1^{\ddagger}$, $\Delta S_1^{\ddagger}$, $\Delta H_2^{\ddagger}$, and $\Delta S_2^{\ddagger}$ are in Table 5. The value of k_1 at 10° was too small to detect.

Catalysis by Zinc Bromide.—Since, in general, the chemical behaviour of zinc bromide is very similar to that of the chloride, we have assumed that [ZnBr$_2$]$_{free}$ = [ZnBr$_2$]$_{stoic}$ − 0·004. Again k_{obs} increases more rapidly than [ZnBr$_2$]$_{free}$ (Table 8), and the dependence of k_{obs} on [ZnBr$_2$]$_{free}$ can be represented by equation (8). The values of k_1 and k_2 are in Table 10, and the values of

$$k_{obs} = k_1[ZnBr_2]_{free} + k_2[ZnBr_2]^2_{free} \qquad (8)$$

$\Delta H_1^{\ddagger}$, $\Delta S_1^{\ddagger}$, $\Delta H_2^{\ddagger}$, and $\Delta S_2^{\ddagger}$ are in Table 5.

Reaction Mechanism.—(i) *Terms first-order in catalyst.* We have concluded previously [3,6] that the mechanism of racemisation reflected by kinetic terms of the first-order in catalyst can be represented by reaction (9), where S

$$RCl + MCl_xS_y \rightleftharpoons R^+[MCl_{x+1}]^-S_{y-1} + S \qquad (9)$$
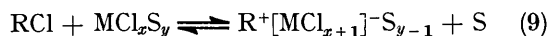
represents solvent. The forward step will determine the rate, which should depend upon the first power of the catalyst concentration. First-order terms only were found for the Group III halides in ether,[3] and also for catalysis by stannic chloride in benzene,[2] where the solvent is not co-ordinated to the acid and mechanism (9) simplifies to (10).

$$RCl + SnCl_4 = R^+SnCl_5^- \qquad (10)$$
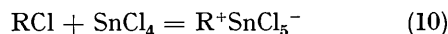
We consider that reaction (9), with S = ether, also represents the mechanism leading to the first-order terms in catalyst concentration in the present systems.

The values of $\Delta S_1^{\ddagger}$ for stannic chloride, stannic bromide (both −26 cal mol^{-1} K^{-1}), and gallium chloride [3] (−24 cal mol^{-1} K^{-1}) are compatible with this view, although the value for zinc bromide (−13 cal mol^{-1} K^{-1}), and in particular that for zinc chloride (−4 cal mol^{-1} K^{-1}), appear to be rather positive. Another relevant point is that $\Delta S^{\ddagger}$ for reaction (10) would be expected to be more negative than for reaction (9) in which extra bond-breaking in the transition state resulting from the displaced solvent molecule must occur. In keeping with this we find for stannic chloride that $\Delta S_1^{\ddagger}$ (ether) = −26 whereas $\Delta S^{\ddagger}$ (benzene) = −30 cal mol^{-1} K^{-1}.

Further comparisons of reactions (9) and (10) for a given catalyst suggest that although $\Delta S^{\ddagger}$ should be less favourable for (10), $\Delta H^{\ddagger}$ should have a more favourable value (since solvent does not have to be displaced). This is also found for stannic chloride catalysis: in benzene $\Delta H^{\ddagger}$ = 8·5 whereas in ether $\Delta H_1^{\ddagger}$ = 13 kcal mol^{-1}. The net result of the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ differences is that k_1 at 25° is appreciably greater in benzene than in ether.

(ii) *Terms of higher order in catalyst.* Terms in [M(Hal)$_n$]^2 have previously been observed in the rate equations for catalysis by zinc and mercuric halides in acetone [6] and in nitrobenzene.[7] We there favoured a mechanistic interpretation involving solvation of the transition state in (9), or (10), by a further molecule of catalyst. Support for this idea was found in the effect of arsenic trichloride (a weak chloride ion acceptor, but a molecule of similar polarity to mercuric chloride) on the mercuric chloride catalysed racemisation.[10] We now present further supporting evidence.

In benzene solution [equation (10)] additional stannic chloride molecules (formally non-polar) would not be expected to solvate the transition state; the simple first-order dependence of the racemisation rate on the stannic chloride concentration observed [2] under these conditions is therefore expected. In ether, however, further (polar) stannic chloride–solvent adducts could well solvate the transition state in (9), perhaps for example as in (I), and thus lead to a second-order term in stannic chloride. An alternative explanation, namely

$$\overset{\delta+}{R^+} \cdots Cl \cdots \overset{\delta-}{MCl_xS_{y-1}} \cdots S$$
$$\overset{\delta+}{S}-\overset{\delta-}{MCl_xS_{y-1}}$$
(I)
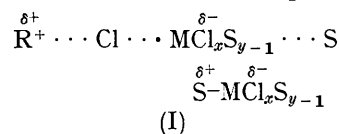
that the second-order term results from involvement of catalyst dimers, is not supported by a comparison between the two solvents: dimeric species, if they exist, are much more likely to be present in benzene, the solvent in which there is no second-order term. Moreover, molecular weight studies give no evidence for the presence of catalyst dimers in these systems (see Experimental section and ref. 1). We therefore believe that the kinetic terms of second-order in catalyst concentration are associated with solvation of the transition state of equation (9) by a single metal halide–ether

¹⁰ R. S. Satchell, *J. Chem. Soc.*, 1965, 797.

molecule, the third-order term in trichloro(phenyl)tin with solvation of the transition state by two trichloro-phenyltin–ether molecules, and the fourth-order term in antimony trichloride with solvation of the transition state by three antimony trichloride–ether molecules. Similar differences between the last two metal halides and the other metal halides, and correspondingly high orders, have also been found in the metal halide catalysed acylation of β-naphthol by acetyl chloride in ether.[1]

The factors which determine the solvation requirements with any particular metal halide are not obvious. At first sight the present results indicate that the feebler the catalyst, as judged by the magnitude of k_1, the greater the number of metal halide–ether molecules required for transition state solvation. However, this generalisation is not borne out if the results for the Group III halides are included (Table 5). In particular, the value of k_1 for boron trifluoride is smaller (or comparable with) the value for antimony trichloride, yet the order in boron trifluoride is very clearly unity.[3]

(iii) *The values of* $\Delta S_2^{\ddagger}$. Comparison between the values of $\Delta S_2^{\ddagger}$ and $\Delta S_1^{\ddagger}$ do not show the same trend. Whereas the former is more positive for zinc bromide and stannic chloride, the reverse is true for zinc chloride. The reason for this difference is not evident.

(iv) *Effect of hydrogen chloride.* In benzene solution hydrogen chloride leads to a slight increase in the rate of the stannic chloride catalysed racemisation.[2] This again is considered to result from solvation of the transition state by a hydrogen chloride molecule. In ether, hydrogen chloride leads to an increase in rate of both the stannic chloride and the antimony trichloride catalysed racemisations (Tables 2 and 7). In the presence of stannic chloride and initially (below 0·2 mol dm⁻¹ HCl) in the presence of antimony trichloride the increase is rectilinear in [HCl], and for stannic chloride the relevant rate equation is probably (11) (see above).

$$\text{Rate} = (k_1[\text{SnCl}_4]_{\text{free}} + k_2[\text{SnCl}_4]^2_{\text{free}} + k[\text{SnCl}_4]_{\text{free}}[\text{HCl}])[\text{RCl}] \quad (11)$$

This equation suggests the effect of hydrogen chloride arises from a route in which a hydrogen chloride–ether molecule solvates the transition state in place of a stannic chloride–ether molecule. It is noteworthy that k_2 and k are comparable in magnitude.

(v) *Comparison of the zinc halide catalysis in ether with that in acetone.* In both solvents the dependence of k_{obs} on the zinc halide concentration takes the form of

equation (7). For a given zinc halide concentration the catalysed racemisation is generally slower in acetone [6] than in ether. (The same is true for the formation of aniline–zinc halide adducts in these two solvents.[11]) This arises because, although k_1 is larger, k_2 is smaller in acetone than in ether. Two solvent properties that would be expected to markedly affect the value of k_1 are the basicity and the dielectric constant. Whereas the greater basicity of acetone should lead to a smaller k_1 value, the higher dielectric constant of acetone should lead to a bigger k_1 value. It thus appears in this comparison between acetone and ether that the difference in their dielectric constants is more important than their relative basicities. This, of course, ignores any differences in the entropy of activation for k_1 in these two solvents. The interesting feature is that k_1/k_2 is smaller for both halides in ether. The ratio $k_1 : k_2$ reflects the ability of the solvent to solvate the transition state of reaction (9) in competition with the more polar metal halide–solvent molecules. The more satisfactory the former is, the smaller will be the need for the latter. Acetone by virtue of its greater polarity and basicity would be expected to be the better solvating agent. Hence the smaller $k_1 : k_2$ values in ether are sensible. A similar comparison has been made between the solvents nitrobenzene and acetone.[6]

(vi) *Comparisons of catalyst activity.* Strictly, owing to the different kinetic orders observed, a quantitative comparison between the catalysts cannot be made. However, if our mechanistic interpretation is correct, comparison of the values of k_1, the rate constant for the forward step of reaction (9) when ether molecules solvate the transition state, should reflect the relative abilities of the catalyst to break the C–Cl bond. Table 5 shows that the values of k_1 are in the sequence $\text{GaCl}_3 > \text{SnCl}_4 > \text{SnBr}_4 > \text{ZnBr}_2 > \text{ZnCl}_2 \simeq \text{AlCl}_3 > \text{PhSnCl}_3 > \text{SbCl}_3$, BF_3. The available values of $\Delta H_1^{\ddagger}$ follow the same sequence; $\Delta S_1^{\ddagger}$ follows roughly the reverse sequence, but has less influence on k_1 at 25° than does $\Delta H_1^{\ddagger}$. This sequence is similar to those found for the ionisation of triphenylmethyl chloride [12] in PhPOCl_2 and in POCl_3 [reaction (12)], where equilibrium constants (13) lead to an order of acidity $\text{SnCl}_4 > \text{ZnCl}_2 \ggg \text{AlCl}_3 > \text{SbCl}_3$.

$$\text{Ph}_3\text{CCl} + \text{MCl}_n \rightleftharpoons \text{Ph}_3\text{C}^+\text{MCl}^-_{n+1} \quad (12)$$
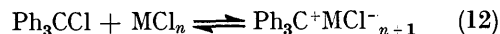
$$K = [\text{Ph}_3\text{C}^+\text{MCl}^-_{n+1}]/([\text{Ph}_3\text{CCl}][\text{MCl}])_n \quad (13)$$

[11] R. S. Satchell and D. P. N. Satchell, *Trans. Faraday Soc.,* 1965, **64,** 1118.

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