Ionisation of Aluminium Halides in Alkyl Halides

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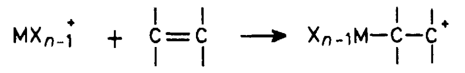
The ionisation of $AlBr_3$ in MeBr and of $AlCl_3$ in EtCl and CH_2Cl_2 between −78 and 0 °C have been studied by electrical conductance measurements *in vacuo*. Consistent results with these notoriously irreproducible systems were achieved by new purification methods, whose effectiveness was assessed by functional tests. The slow ionisation had previously been mistaken for, or obscured by, reactions of the aluminium halides with impurities. Always a randomly variable ' impurity conductivity ' κ_i is established very rapidly. The difference $\kappa - \kappa_i$ (κ = conductivity at any time) for most systems obeys the kinetics expected for ionisation of AlX_3 to AlX_2^+ and AlX_4^-, and the final equilibrium conductivity, κ_e, gives $\kappa_e - \kappa_i$ values which depend rectilinearly on the concentration of AlX_3. The equilibrium constant for the ionisation of the chloride in EtCl is *ca.* 100 times greater than that of the bromide in MeBr; for the ionisation in the chloride system $\Delta H^{\ominus} = -17.6 \pm 0.2$ kJ mol^{-1} and $\Delta S^{\ominus} = -217$ J K^{-1} mol^{-1}. The solubility of the chloride in CH_2Cl_2 at −78 °C (4.23×10^{-4} mol dm^{-3}) shows that it is monomeric. Previous results are discussed.

THE senior author's work on the mechanisms of cationic polymerisations initiated by metal halides includes one experimental study with aluminium chloride,[1] and several theoretical investigations based also on the experimental work of many other workers.[2-4] The theoretical work included a hypothesis [2,3] that in systems in which no co-catalyst is involved,[5] *i.e.* mainly those in which aluminium halides are concerned, the real initiating species is a metal-containing cation formed by self-ionisation of the metal halide [reaction (1)] which attacks the olefin, generating a carbenium ion, just as a proton or an organic cation would [reaction (2)].

$$2MX_n \rightleftharpoons MX_{n-1}^+ + MX_{n+1}^- \qquad (1)$$



$$MX_{n-1}^+ + \ce{>C=C<} \longrightarrow X_{n-1}M{-}C{-}C^+ \qquad (2)$$

The testing of this hypothesis required a preliminary study of the properties of aluminium halide solutions in alkyl halides, and especially of the ions present in them, because most of the information in the literature seemed contradictory. We used electrolytic conductivity for this study because of its sensitivity and convenience, and because no method of comparable sensitivity is applicable to totally closed systems. As some exploratory studies had alerted us to the difficulties of the intended work,[6] we started by perfecting purification techniques for the solvents, and by establishing criteria of purity. This was also done by means of conductivity because the conductivity of the solvent is a useful guide to its purity; however, it cannot reveal non-conducting impurities which generate ions by reacting with the aluminium halides. For this purpose the concentration dependence of the conductivity of AlX_3 solutions in the corresponding alkyl halide RX was found to be a very useful indicator. This is because in a system ionising according to equations (1) and (3) (two molecules

$$2AlX_3 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} AlX_2^+ + AlX_4^-,\ K = k_f/k_b \qquad (3)$$

generating two ions) the dependence of κ on $[AlX_3]$ is rectilinear, and any other dependence shows that at least some of the ions present have been generated by, or are involved in, ionogenic reactions of other types.

During these studies we found that the ionisation of the aluminium halides is a slow process with well defined kinetics, which had hardly been studied and which holds one clue to our understanding of the phenomenology of the catalytic activity of the aluminium halides.

In contrast to the lack of studies of the kinetics, there have been investigations of the ionisation equilibria, and the nature of the ions in various systems has been discussed frequently. Wertyporoch [7] found that the conductivity of $AlBr_3$ in EtBr varied with time and that the solutions were yellow, which we now know indicates that they were impure. Jacober and Kraus [8] studied solutions in MeBr and found that the conductivity changed little with concentration or temperature, but measurements were made at six concentrations only. Fairbrother and Scott [9] found that for ethyl bromide solutions the conductivity increased with time, and they assumed that this was caused by the slow formation of ethylene and hydrogen bromide. They therefore made conductivity measurements at 25 °C, by keeping the solutions at −78 °C, and then following the change in conductivity after the solution had been warmed rapidly to 25 °C. They obtained their conductivity values by extrapolating to zero time. Halpern and Polaczek [10] found that the conductivities of aluminium, gallium, and indium iodides in alkyl iodide solvents increased with time, and therefore they used Fairbrother's method of

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[1] J. H. Beard, P. H. Plesch, and P. P. Rutherford, *J. Chem. Soc.*, 1964, 2566.

[2] P. H. Plesch, *Makromol. Chem.*, 1974, **175**, 1065.

[3] P. H. Plesch, Macromolecular Chemistry–8, Internat. Symp. Helsinki 1973 (Suppl. to *Pure Appl. Chem.*), pp. 305—318.

[4] P. H. Plesch in ' Progress in High Polymers,' vol. 2, eds. J. C. Robb and F. W. Peaker, Iliffe Books, London, 1968, p. 139.

[5] M. Chmelir, M. Marek, and O. Wichterle, *J. Polymer Sci.*, 1967, **C16**, 833.

[6] P. H. Plesch and V. Shmarlin, unpublished work.

[7] E. Wertyporoch and A. Wohl, *Ber.*, 1931, **B64**, 1357; E. Wertyporoch, *ibid.*, p. 1369.

[8] W. J. Jacober and C. A. Kraus, *J. Amer. Chem. Soc.*, 1949, **71**, 2405.

[9] F. Fairbrother and N. Scott, *J. Chem. Soc.*, 1955, 425.

[10] A. Halpern and A. Polaczek, *Nature*, 1963, **199**, 1286; Institute of Nuclear Research, Report 491/V, Warsaw, 1963.

obtaining the 'real' conductivity. For AlI_3 in EtI the conductivity depended linearly on concentration, which suggests an ionisation according to equation (3).[11,12] These workers found Fairbrother's idea, that the steady increase in conductivity was due to dehydrohalogenation of the solvent, inapplicable because mass spectrometry showed no change in the ratio of the peak heights of HI and EtI even after 70 h, but they did not suggest an alternative explanation.

Transport numbers have been determined for $AlBr_3$ in methyl[13] and ethyl[14,15] bromide solutions. Of these, the most reliable appear to be Van Dyke's. His results, when interpreted according to the ionisation scheme (3), give $t_+ \approx t_-$, which indicates that the ions are of equal size; this brings the solvation by solvent into the picture, which can be represented very plausibly by equation (4).

$$2AlBr_3{\cdot}RBr \rightleftharpoons AlBr_2^+{\cdot}RBr + AlBr_4^- + RBr \quad (4)$$

Van Dyke's own ionisation scheme is incompatible with our results. Scheme (4) is clearly not the only one that would yield ions of near identical size, and the question whether, and how, one can decide between it and the obvious alternative (5) will be discussed later. Some of

$$2Al_2Br_6 \rightleftharpoons Al_2Br_5^+ + Al_2Br_7^- \quad (5)$$

the results in EtBr are reported to have been so irreproducible that one set of workers even refrained from publishing quantitative results.[9] The divergence of behaviour between different alkyl halides probably arises at least in part from the fact that with the same effort MeBr can be obtained more pure than EtBr, and that unless it is very pure the latter can react with $AlBr_3$ to give a variety of products *via* the intermediates ethylene and hydrogen bromide.

Since our kinetic studies had provided us with a self-consistent interpretation of the conductivity changes with time in pure systems and the techniques for obtaining these, we progressed to an investigation of the equilibria in these systems in an effort to clear up the contradictions and discrepancies mentioned above. The studies by means of which we proved subsequently the validity of the initiation mechanism (2) for aluminium chloride and bromide with several olefins will be published elsewhere.

EXPERIMENTAL

Materials.—Aluminium bromide, prepared conventionally under anhydrous nitrogen from the elements, was redistilled in a stream of dry nitrogen and was then resublimed several times under high vacuum in the presence of aluminium, finally into 1-cm^3 glass phials, whose contents were determined by the midpoint method.[16] Commercial pure aluminium chloride was resublimed five times under dry nitrogen, and was then resublimed and dosed into phials under high vacuum in the same way as $AlBr_3$.

Methyl bromide, ethyl chloride, and methylene dichloride, which had been purified, fractionated, and dried conventionally, were finally purified and dried further as follows, all the operations being made on a vacuum line. The alkyl halide (*ca.* 500 cm^3) was distilled on to the appropriate freshly sublimed aluminium halide (2 g). The aluminium halide solution became yellow overnight at room temperature. The alkyl halide was distilled from the aluminium halide on to well ground calcium hydride which had been kept under high vacuum for several hours, and was then distilled into a flask containing freshly sublimed aluminium halide and on this occasion no colour developed. The aluminium halide was always introduced into the purification vessel by direct sublimation from a side tube. In the first series of experiments the solvent was then distilled on to finely ground CaH_2 in a storage reservoir, but in later experiments an extra stage was added, and after the solvent had been kept over CaH_2 for a few days it was condensed on to a freshly prepared sodium mirror. The method of purification of halogenated solvents by means of a sodium mirror was originated by Medvedev for EtCl,[17] and was used for CH_2Cl_2 by Cheradame and Sigwalt.[18] **CAUTION:** It is extremely dangerous to use this method with alkyl halides unless they have been dried very well with, for example, CaH_2, and are free from oxygen. Methyl bromide kept over a sodium mirror for 10 months contained only a very small amount of ethane (*ca.* 1 : 10 000 v/v); no other impurities were observed by g.l.c. Trace amounts of ethane in the MeBr are probably of little consequence.

During the kinetic work the dominant role of the purification procedures became evident and therefore further stages were added for the later equilibrium work. The effect of added water on the conductivity of the alkyl halides was much less than expected, but trace amounts of acid added to them increased the conductivity considerably. As will be described below, the best test of the purity of the solvents was not so much their conductivity as the concentration, and temperature, dependence of the conductivity of aluminium halide solutions in them. We also found that it was important to have all the glass surfaces clean and neutral by washing them successively with chromic acid, water, aqueous alkali, acetone, and an alkyl halide.

Apparatus and Operation.—(*a*) *Kinetic measurements.* Several designs of vacuum conductivity cell were tried; the one most frequently used was similar to that described by Bertoli and Plesch,[19] but it also had a thermocouple pocket, and the leads were screened cable. The cells contained bright platinum electrodes (1 × 1 cm, 0.1 cm apart), with a cell constant (by KCl calibration) of *ca.* 0.1 cm^{-1}. A typical design is shown in Figure 1 and the rather critical arrangement of the internal leads is shown in Figure 2. The conductivity was measured with a Wayne–Kerr B.221 bridge with an AA-221 Autobalance Adaptor, the output of which was fed to a recorder. The bridge was capable of reading in the range from 1 to 10^{-11} S with an accuracy approaching five figures.

The cell was fused to a high-vacuum system without

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[11] O. Nuyken and P. H. Plesch, *Chem. and Ind.*, 1973, 379.

[12] D. W. Grattan and P. H. Plesch, unpublished work; D. W. Grattan, Ph.D. Thesis, Keele University, 1973.

[13] R. E. Van Dyke, *J. Amer. Chem. Soc.*, 1950, **72**, 3619; 1951, **73**, 2018.

[14] Z. A. Sheka and I. A. Sheka, *Ukrain. khim. Zhur.*, 1951, **17**, 911.

[15] Z. A. Sheka, I. A. Sheka, and E. I. Pechenaga, *Ukrain. khim. Zhur.*, 1950, **16**, 337.

[16] P. P. Rutherford, *Chem. and Ind.*, 1962, 1614.

[17] A. R. Gantmakher and S. S. Medvedev, *J. Phys. Chem. (U.S.S.R.)*, 1949, **23**, 516.

[18] H. Cheradame and P. Sigwalt, *Compt. rend.*, 1964, **259**, 4273; H. Cheradame, Ph.D. Thesis, Paris, 1966.

[19] V. Bertoli and P. H. Plesch, *J. Chem. Soc. (B)*, 1968, 1500.

joints or greased taps, thoroughly flamed and pumped for a minimum of 24 h before each experiment. A measured volume of solvent was distilled into it, and the conductivity was measured at the required temperature. When the temperature and conductivity were stable, a phial of aluminium halide was broken under the liquid and this was mixed rapidly. For $AlBr_3$ in MeBr the dissolution was almost instantaneous, whereas $AlCl_3$ took up to *ca.* 10 min to dissolve completely. The change in conductivity with time was measured.

(*b*) *Equilibrium measurements.* The conductivity meter was the same as that used for the kinetic work. Several types of conductivity cells were used, calibrated as described, the most successful one of which (Figure 3) had a usable volume range of 50—500 cm^3. The larger volume and different shape made it necessary to use a phial breaker different from that in Figure 1, but the electrodes were of the same type. The phial breaker was charged with a phial of aluminium halide and sealed into its socket with the virtually insoluble De Khotinsky cement. The cell was fused to the vacuum line which was devoid of greased joints or taps, was thoroughly flamed, and was then evacuated for at least 24 h before each experiment.

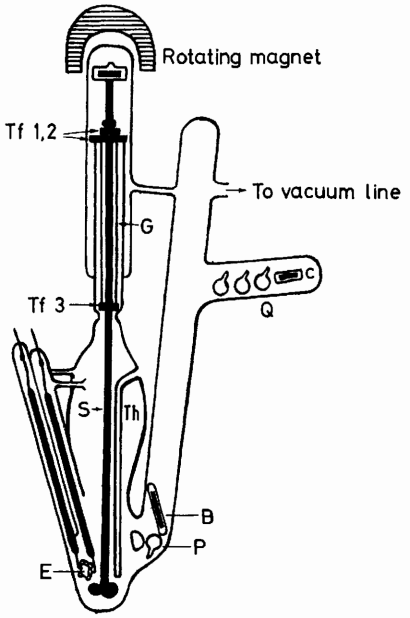

FIGURE 1 Vacuum conductivity cell for kinetics. Tf 1, 2, and 3 = Teflon bearings, G = glass spacer which holds Tf in position, S = stirrer shaft, Th = thermocouple pocket, B = glass-enclosed magnet to break the phial P containing the aluminium halide, Q = side tube containing several phials of aluminium halide which can be dropped one at a time by use of magnet C, for subsequent breaking by B, and E = pair of bright Pt electrodes

The alkyl halide was run in from the burette of a reservoir-and-burette assembly of the type described,[20] fitted only with all-metal valves, similar to those described,[21] in which the alkyl halide was under its own vapour pressure. When the solvent had attained the required temperature and its conductivity had been measured, the phial of aluminium halide was broken by withdrawing the retainer A1, thus letting the breaker drop upon the phial. When several phials were to be broken in succession, a cell with a phial-magazine (Figure 1) was used. When a solution had been diluted by the addition of solvent from the burette in order to obtain the concentration dependence of the conductivity in a dilution experiment, the solution could be concentrated

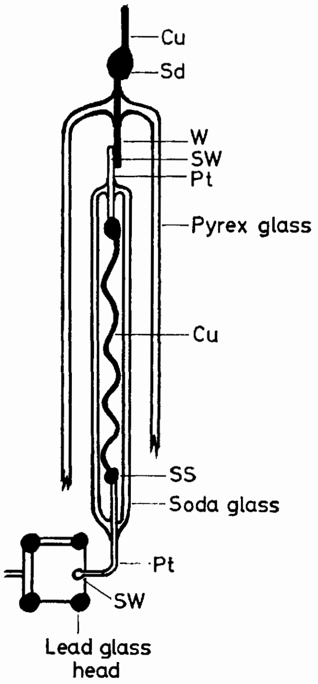

FIGURE 2 Arrangement of the leads inside the conductivity cell. Cu = copper wire, Sd = soldered joint, W = tungsten wire, SW = spot-weld, Pt = platinum wire, and SS = silver-soldered joint

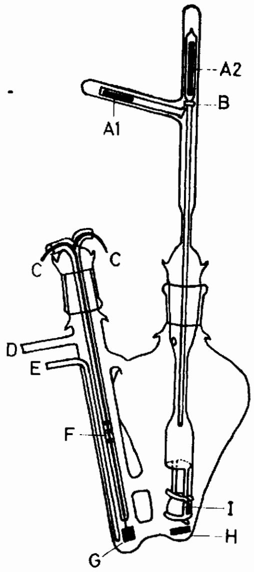

FIGURE 3 Conductivity cell for equilibrium measurements. A1 and A2 = glass-enclosed magnets, B = Teflon washer, C = screened cable, D = connection to vacuum line, E = thermocouple pocket, F = a soda glass–Pyrex graded seal, G = platinum electrodes, H = magnetic stirrer, and I = phial containing the aluminium halide

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[20] M. A. Hamid, M. Nowakowska, and P. H. Plesch, *Makromol. Chem.*, 1970, **132**, 1.

[21] R. H. Biddulph and P. H. Plesch, *Chem. and Ind.*, 1956, **569**.

again by distilling solvent from the cell into a hanging burette or a subsidiary reservoir on the vacuum line in order to test the reversibility of the conductivity–concentration relation. At the end of each experiment the solvent was pumped from the cell, the aluminium halide was hydrolysed and titrated, frequently both for halide ion and for aluminium. The amount of aluminium or halide or both always agreed with that which had been introduced, and the ratio was always 3 : 1, within the experimental error. This showed that the formation of volatile aluminium compounds was negligible and that irreversible substitutions at the aluminium atom forming involatile compounds could not have affected more than, at most, 0.1% of the aluminium atoms.

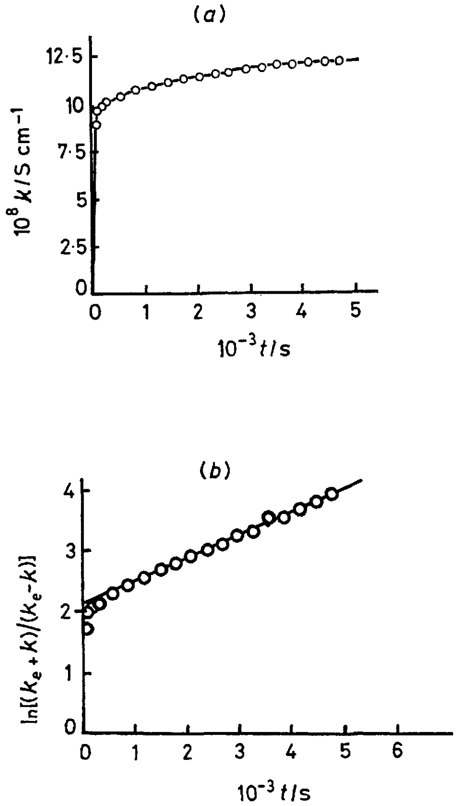

FIGURE 4 (*a*) Change in conductivity when a phial of $AlBr_3$ is broken into MeBr at 0 °C. $[AlBr_3] = 2 \times 10^{-3}$ mol dm^{-3}. (*b*) Plot of $\ln[(\kappa_e + \kappa)/(\kappa_e - \kappa)]$ against *t*, *i.e.* the kinetic plot, for the results shown in (*a*)

RESULTS AND DISCUSSION

The Kinetics of Ionisation.—The conductivity of aluminium bromide in methyl bromide: experiments at 0 *and* −23 °C. When a phial of $AlBr_3$ is broken into MeBr the conductivity κ is not stable, and the way in which it varies with time depends on the temperature. At 0 and −23 °C a two-stage process occurs (Figure 4), in that the conductivity increases very rapidly (half-life *ca.* 30 s) and then the increase becomes very slow (half-life *ca.* 1—2 h) as κ approaches an asymptote. At the start of this work it seemed unlikely that after several days at these temperatures an aluminium bromide solution would remain without some decomposition of the solvent, and therefore an experiment was carried out in which a 2×10^{-3} mol dm^{-3} solution of $AlBr_3$ in MeBr was prepared in a device fitted with a 1-cm silica cell, for measuring u.v.–visible absorption spectra under high vacuum.[19] The solution remained colourless and showed no u.v. absorption, even after 3 months at room temperature. This indicated that at least no conjugated carbenium ions or other conjugated compounds were formed. This observation agrees with that of Halpern and Polaczek,[10] who were unable to detect decomposition of an aluminium iodide solution in EtI when they repeatedly examined its mass spectrum over several days. In many subsequent experiments we found no evidence that under really clean conditions the alkyl halides studied by us reacted with aluminium halides. It therefore appeared that the slow increase of conductivity might be due to a very slow ionisation and therefore an analysis of the kinetics was undertaken.

In the simplest terms the ionisation of aluminium halides in alkyl halides can be represented as a self-ionisation or disproportionation [10,22,23] of single molecules [reaction (3), X = Br]. The form of the algebraic equations to be developed on this basis is independent of the existence and extent of solvation of molecules or ions by the solvent. However, the fact that $AlBr_2^+$ in MeBr is most probably $AlBr_2^+{\cdot}MeBr$ must of course be taken into account when attempts are made to interpret rate constants, activation parameters, *etc.* The nature of the ions in these systems will be discussed in greater detail later. The net rate of ionisation is given by (6) where a_0 is the total concentration of $AlBr_3$ and

$$dy/dt = k_f(a_0 - 2y)^2 - k_b y^2 \tag{6}$$

y is the concentration of each ion. The magnitude of the conductivity indicated that the fraction of the $AlBr_3$ which was ionised at equilibrium was <0.001%, and therefore as the ionisation proceeds the concentration of aluminium bromide molecules can be treated as constant. Thus $a_0 \gg y$ and therefore equation (6) can be simplified to give (7). But at equilibrium we

$$dy/dt = k_f a_0^2 - k_b y^2 \tag{7}$$

$$k_f a_0^2 = k_b y_e^2 \tag{8}$$

have (8) where y_e is the concentration of each ion at equilibrium. Thus we obtain (9). Integration of

$$dy/dt = k_b(y_e^2 - y^2) \tag{9}$$

equation (9) with the conditions $\kappa = \kappa_i$ at $t = 0$ and $\kappa = \kappa_e$ at $t = \infty$, and the substitutions (10) and (11)

$$\kappa = y\Lambda_i \tag{10}$$

$$\kappa_e/\Lambda_i = y_e = a_0 K^{\frac{1}{2}} \tag{11}$$

$$\ln[(\kappa_e + \kappa)/(\kappa_e - \kappa)] - \ln[(\kappa_e + \kappa_i)/(\kappa_e - \kappa_i)] = 2a_0 k_b K^{\frac{1}{2}} t \tag{12}$$

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[22] W. R. Longworth and P. H. Plesch, *J. Chem. Soc.*, 1959, 1887.

[23] H. Wendt, *Ber. Bunsengesellschaft Phys. Chem.*, 1964, **29**, 64.

where $K = k_f/k_b$, and Λ_i is defined by (10), yields (12). A plot of the first term against t should give a straight line whose intercept gives κ_i if κ_e is known and whose gradient can give k_b if K can be obtained by independent means. Since the approach to equilibrium is very slow, a computer was used to obtain that value of κ_e which gave the best straight line for the plot of equation (12). These κ_e values rarely differed by more than 5% from the value of κ at $t = 100$ min. In this way values of κ_i and of $k_bK^{\frac{1}{2}}$ were obtained.

The quantity κ_i is the conductivity due to the reaction of the aluminium halide with ionogenic impurities and it will be shown that extreme purification of the solvent can make κ_i considerably smaller than the conductivity due to self-ionisation, $\kappa_e - \kappa_i$. That κ_i is due to impurities was suspected quite early, as it varied randomly from experiment to experiment. On the other hand $\kappa_e - \kappa_i$ varies rectilinearly with a_0, as it should if the ionogenic process is one in which n (in this case two) molecules generate n ions (Figure 5).[11,12] In order to test this interpretation of the conductivity behaviour three phials of $AlBr_3$ were broken successively into the same reaction mixture. The conductivity curves together with the plots according to equation (12) are shown in Figure 6, and the gradient of these kinetic plots is shown as a function of a_0 in Figure 7. The relation is (approximately) rectilinear as demanded by our theory. A curious feature, not completely satisfactorily explained, is that κ_i is not zero for the second and third additions of $AlBr_3$, although it decreases markedly. It appears that the reaction of $AlBr_3$ with at least some of the impurities goes to equilibrium, and not to completion.

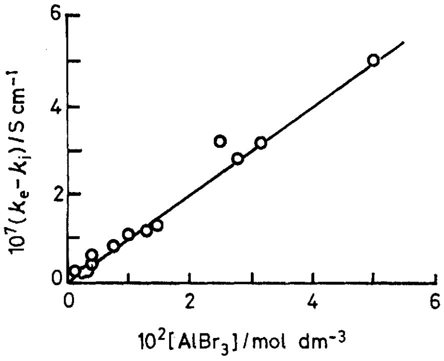

FIGURE 5 Plot of the conductivity due to self-ionisation ($\kappa_e - \kappa_i$) against $[AlBr_3]$ at 0 °C

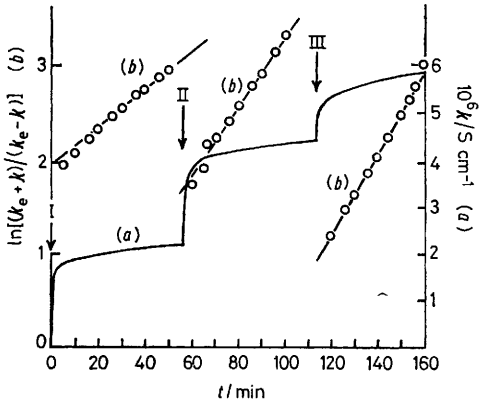

FIGURE 6 Experiment K2. The change in conductivity, and the associated kinetic plots, for the breaking of three phials of $AlBr_3$ into MeBr at 0 °C. The resulting individual concentrations produced by the contents of each phial were I 4.27×10^{-3}, II 8.55×10^{-3}, and III 10.13×10^{-3} mol dm^{-3}; therefore total $[AlBr_3] = 2.3 \times 10^{-2}$ mol dm^{-3}

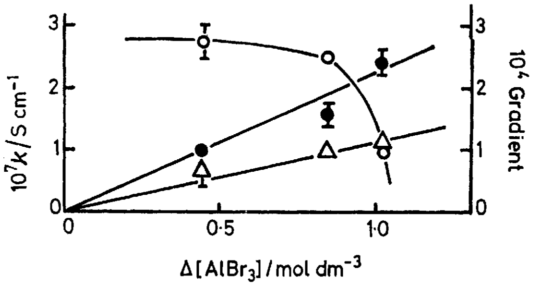

FIGURE 7 Experiment K2. The conductivities due to self-ionisation ($\kappa_e - \kappa_i$) (△), the impurity conductivities κ_i (○), and the gradients of the kinetic plots (●) for each phial broken as functions of $\Delta[AlBr_3]$, the concentration increment due to each phial, taken from Figure 6

From the values of $k_bK^{\frac{1}{2}}$ obtained from the kinetic plots and the corresponding values of K listed in Table 2, the values of k_f and k_b given in Table 1 were calculated.

TABLE 1

Velocity constants k_f and k_b for the ionisation of $AlBr_3$ and of $AlCl_3$ [equation (3)]. Wendt's values[23] are included for comparison

$\frac{\theta_c}{°C}$	Halide	Solvent	$\frac{k_f}{dm^3\ mol^{-1}\ s^{-1}}$	$\frac{k_b}{dm^3\ mol^{-1}\ s^{-1}}$	Expt. no.
0	$AlBr_3$	MeBr	$(4.5 \pm 1) \times 10^{-6}$	$(4 \pm 1) \times 10^2$	*a*
−23	$AlBr_3$	MeBr	1.8×10^{-6}	82	R2
0	$AlCl_3$	EtCl	5.5×10^{-4}	2.3×10^2	D2
−78	$AlCl_3$	EtCl	3.3×10^{-3}	11	R9
0	$AlCl_3$	CH_2Cl_2	9.2×10^{-4}	4	D4
−78	$AlCl_3$	CH_2Cl_2	1.4×10^{-1}	44	D1
25	$AlBr_3$	$PhNO_2$	8×10^{-1}	$(3.8 \pm 0.6) \times 10^2$	*b*
25	$AlCl_3$	$PhNO_2$	1.3×10^2	$(2.85 \pm 0.4) \times 10^4$	*b*

[a] The average of 12 experiments. [b] Ref. 23.

The value of K at 0 °C is the mean of many determinations with a mean deviation of *ca.* ± 20%, but that at −23 °C is a single determination. Thus all the rate constants have considerable uncertainty and therefore the calculation of activation energies would not be justified.

Experiments at −63 *and* −78 °C. On breaking the phial at −63 or −78 °C, there was an initial rapid increase in conductivity as at higher temperature, but this was followed by two main types of behaviour (Figure 8): (*i*) a gradual decrease in conductivity to an asymptote, sometimes reached in 10 or 20 min (*e.g.* R16 in Figure 8); or (*ii*) a rapid decrease in conductivity followed by a gradual decrease to an asymptote (*e.g.* K3 in Figure 8). However erratically the conductivity had behaved at first, it nearly always eventually became constant. Because of these differences in behaviour, and especially as the behaviour pattern of the reactions was so erratic, the kinetic scheme could not be applied at these temperatures. The reason for the decrease in κ with time has not been explored, but later experiments with purer MeBr lead us to think that it may be due to an association at these low temperatures of ions of all kinds with impurities. Because of the low concentrations of all the species concerned this would be slow, and the resulting increase in size of the ions would account for the decrease in κ.

TABLE 2

Ionisation constants for the self-ionisation of aluminium halides in alkyl halides, and calculated values of the limiting conductivity of the ions

Halide	Solvent	θ_c/°C	$10^2\eta$/P	Ion	$10r_-$/nm	Λ_0/S cm^{-1} mol^{-1} dm^3	K	Ref
$AlBr_3$	MeBr	0	0.397	$AlBr_4^-$	3.5	119	1.1×10^{-8}	
	MeBr	−23	0.54 [b]	$AlBr_4^-$	3.5	88	2.2×10^{-8}	
	MeBr	−63	1.15 [b]	$AlBr_4^-$	3.5	41	1.1×10^{-7}	
	MeBr	−78	1.7 [b]	$AlBr_4^-$	3.5	28	2.4×10^{-7}	
$AlCl_3$	CH_2Cl_2	0	0.54 [a]	$AlCl_4^-$	3.2	95	2.3×10^{-4}	
	CH_2Cl_2	−78	2.15 [a]	$AlCl_4^-$	3.2	24	3.3×10^{-3}	
	EtCl	0	0.34 [b]	$AlCl_4^-$	3.2	151	2.4×10^{-6}	
	EtCl	−78	1.85 [b]	$AlCl_4^-$	3.2	28	3.0×10^{-4}	
AlI_3	MeI	22	0.48 [b]	AlI_4^-	3.93	86.9	7×10^{-9}	
	EtI	22	0.67 [a]	AlI_4^-	3.93	62.3	3.6×10^{-9}	10
GaI_3	EtI	22	0.67 [a]	GaI_4^-	*ca.* 4	*ca.* 65	7×10^{-13}	10
InI_3	EtI	22	0.67 [a]	InI_4^-	*ca.* 4	*ca.* 65	4×10^{-9}	10
$AlBr_3$	$PhNO_2$	25		$AlBr_4^-$			$(2.2 \pm 0.5) \times 10^{-3}$	23
$AlCl_3$	$PhNO_2$	25		$AlCl_4^-$			$(4.5 \pm 1) \times 10^{-4}$	23

[a] Literature value. [b] Estimated value.

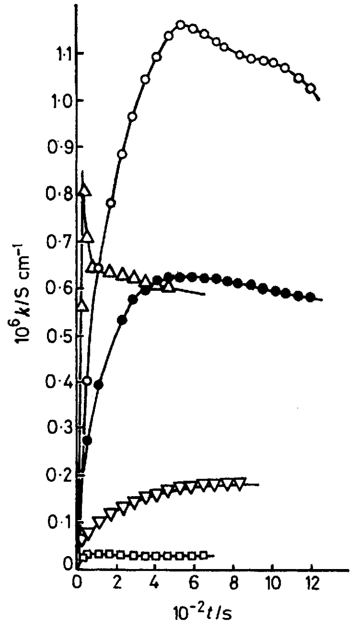

FIGURE 8 Some conductivity curves obtained when phials of $AlBr_3$ bromide are broken into MeBr at −63 °C. The concentrations are shown below:

Expt. no.	K5I(○)	R16(●)	K3(△)	K4II(□)	K4I(▽)
$10^3[AlBr_3]$/mol dm^{-3}	1.59	1.52	3.03	3.29	2.21

The conductivity of aluminium chloride in methylene dichloride and in ethyl chloride. In both solvents at 0 and at −78 °C the dissolution of $AlCl_3$ was slow (see Figure 9), and κ_i was much smaller than for the $AlBr_3$–MeBr system; when κ_i was relatively large, *i.e.* when the alkyl chloride was impure, the dissolution of the salt was faster. For both solvents at both temperatures the plots according to equation (12) were good straight lines, and the k_f and k_b values obtained from them and the K values in Table 2 are listed in Table 1. Because of the uncertainties in K, and because the rate constants are all from single determinations, no great significance can be attributed to their temperature coefficients and the calculation of activation energies is not justified. What does appear significant is that the forward (ionisation) component of reaction (3) (X = Cl) is much faster in CH_2Cl_2 than in EtCl, but the interpretation of this observation is not obvious at present. At 0 °C the ionisation of the chloride is much faster than that of the bromide. One might have attributed this to the polarity of MeBr being much smaller than that of the two chloride solvents were it not that the same ranking is found for the rates when both halides ionise in the same solvent nitrobenzene.[23]

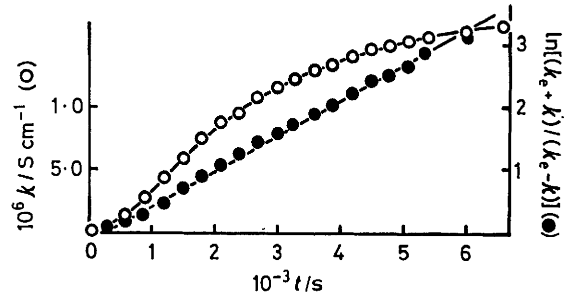

FIGURE 9 Ionisation and the plot of its kinetics for $AlCl_3$ at 0 °C. $[AlCl_3] = 1.1 \times 10^{-3}$ mol dm^{-3}

The state of aluminium chloride in solution. From our measurements we found the solubility of $AlCl_3$ in CH_2Cl_2 to be 4.23×10^{-4} mol dm^{-3} at −70 °C. This enables us to dismiss some much greater and unlikely looking literature values obtained evidently with inadequately purified solvents. It also enables us to settle the hitherto open question as to whether in these solutions the dominant form of the solute is monomeric or dimeric by reference to the ideal solubility calculated from the latent heat of fusion and the m.p. The latent heat of fusion of $AlCl_3$ at the m.p. (465.7 K) is 37.53 ± 0.8 kJ mol^{-1} and at 200 K it is 34.56 ± 0.8 kJ mol^{-1}. This gives an ideal solubility at -70 °C of 10^{-4} mol dm^{-3} which is reasonably close to our measured value. However, for Al_2Cl_6 the calculated ideal solubility is 2.3×10^{-9} mol dm^{-3}. We can conclude therefore that the chloride in CH_2Cl_2, like the bromide in MeBr,[24] is mainly monomeric, even at -70 °C. This finding of course does not affect the question of the extent to which molecules associate with ions to form $Al_2X_5^+$ and/or $Al_2X_7^-$.

Comparison with results of other workers. Many workers have noted that the conductivity of freshly prepared aluminium halide solutions increases with time and have attributed this to decomposition processes (see Introduction); it was considered a trivial nuisance, and often it was not even commented on. The only previous kinetic investigation of the ionisation of an aluminium halide in solution is by Wendt,[23] who studied the conductivity of aluminium bromide and chloride in nitrobenzene by pressure-shock relaxation. By this means he obtained values for k_f and k_b, which are included in Table 1 for comparison.

The Ionisation Equilibrium.—Aluminium bromide in methyl bromide: impurity effects and results at -63 *and* -78 °C. Because solutions of $AlBr_3$ in MeBr below *ca.* -63 °C usually attained a constant conductivity within *ca.* 30 min, we decided to study the conductivity as a function of concentration at this temperature. As was mentioned in the previous section, even with carefully purified solvents, solutions of approximately the same concentration can have very different conductivities, and the results of previous studies are in mutual disagreement and differ from ours. The only general consistent feature seemed to be that, as the system was purified progressively, the conductivity decreased. The most abundant impurities are likely to be those in the solvent, especially water, and the adsorbed water on the glass surfaces of the conductivity cell and its appendages. The aluminium halide was ruled out as an important source of impurities because of the purity of the materials from which it was prepared and because it was always resublimed many times before use. These considerations, originating in some exploratory experiments, induced us to study the effect of successive purifications of one batch of solvent on the concentration dependence of the conductivity. The experiment itself in effect paralleled a stage of the standard purification procedure.

The apparatus in which these experiments were carried out is shown in Figure 10. The experimental procedure was as follows. The MeBr was distilled from CaH_2 over a fresh sodium surface into the dosing reservoir V2, which had been well pumped and flamed out. From there it was dosed into the conductivity cell and the dependence of the conductivity on the concentration of $AlBr_3$ was measured at -63 and -23 °C. At the end of the experiment the solvent was distilled into V1, and the conductivity was measured during this process to see whether it changed in the same way during concentration

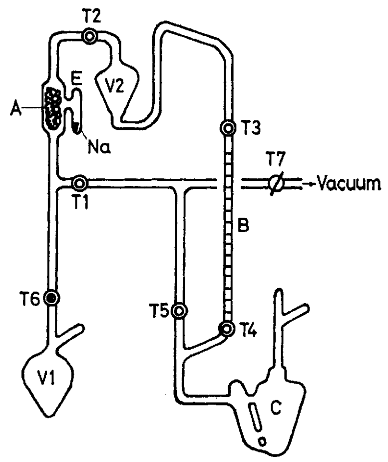

FIGURE 10 Apparatus in which one batch of MeBr could be used and purified alternately for many experiments. C = Conductivity cell, T1—T5 BiPl taps,[21] B = 20-cm³ burette, V1 = solvent reservoir containing CaH_2, T6 = Teflon tap, A = wad of glass wool coated with sodium by distillation from E, and V2 = secondary solvent storage

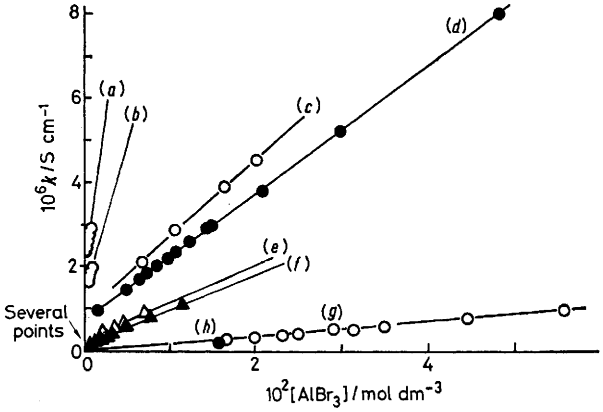

FIGURE 11 Effect of repeated purification of one batch of MeBr on the concentration dependence of the conductivity of $AlBr_3$ at -63 °C. In experiments C18 (*a*) and C19 (*b*) the solvent was cycled once, whereas in C24 (*g*) it had had seven cycles of purification with sodium. The results of experiments C23, 22, and 21 agreed closely (*e* and *f*). As each covered a different concentration range, this tended to conceal the effect of purification

Line	Expt. no	θ_c °C	$10^8\kappa$(solvent) S cm^{-1}
(*a*)	C18	−63	9
(*b*)	C19	−63	9
(*c*)	C20	−23	4.9
(*d*)	C20	−63	4.9
(*e*)	C21, C22, C23	−23	2.6, 2, 1.6
(*f*)	C21, C22, C23	−63	2.6, 2, 1.6
(*g*)	C24	−63	0.34
(*h*)	C24	0	0.34

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[24] (*a*) F. Fairbrother and N. Scott, *J. Chem. Soc.*, 1955, 452 and refs. therein; (*b*) D. G. Walker, *J. Phys. Chem.*, 1960, **64**, 939.

as it had during dilution of the $AlBr_3$. In all the experiments the two plots of κ against $[AlBr_3]$ were coincident within experimental error. This routine was repeated many times, each time with a fresh sample of $AlBr_3$. The results of this series of experiments (Figure 11) indicate that as the purity of the solvent improved: (*i*) its conductivity decreased; (*ii*) the conductivity of the aluminium bromide solutions decreased; (*iii*) the intercept on the conductivity axis diminished; and (*iv*) the temperature dependence of the conductivity became smaller. We conclude that a zero intercept on the κ axis and a rectilinear dependence of κ on $[AlBr_3]$ are proof that the concentration of ionogenic impurities has been reduced to a level where it is insignificant compared to the concentration of ions formed from the $AlBr_3$. The manner in which a rectilinear dependence of κ on $[AlBr_3]$ signals the existence of a two molecules $\rightleftharpoons$ two ions equilibrium such as (3) has been explained [11,12] and will be discussed further below.

The addition of water to give concentrations as high as *ca.* 10^{-4} mol dm^{-3} produced only a small increase in the conductivity of the alkyl halides, but the subsequent addition of an aluminium halide rapidly produced a relatively high conductivity. Whether this fast formation of ions occurs by enhancement of the self-ionisation [reaction (3)] by complexing of the cations by water, or whether it indicates formation of ions derived from hydrogen bromide formed by hydrolysis,[25] or both, or some other ionogenic reactions, is not clear. The occurrence of a fast hydrolysis in our conditions (reagents in solution in a polar solvent) would disagree with the results of Fairbrother and Frith,[25] who found that, although the hydration of aluminium bromide as vapour or as solid or in diethyl ether solution is fast, the subsequent hydrolysis under all those conditions is slow.

Whatever the origin of the ions formed in the presence of water, provided that the concentration of $AlBr_3$ exceeds that of water, it follows that as far as the water in the solvent is concerned the conductivity of the solution due to ions from this source is independent of the volume of the solvent added. On the other hand, the contribution to conductivity due to the water adsorbed on the walls of the cell will depend on the volume of liquid in it. This is represented schematically in Figure 12 where the line g—f represents the conductivity due to the products of reaction of the water in the solvent, g—e shows the extra conductivity arising from the products of the reaction of the water from the cell walls, and g—d represents the total conductivity including that from self-ionisation. The results in Figure 11 indicate that this somewhat oversimplified picture is an acceptable approximation. As the cell became drier, the gradient of the plots decreased, and as the solvent became more pure the intercept on the conductivity axis became smaller. However, from this experiment alone it is impossible to know whether all the water from the cell has been removed. This is even true for experiment C24, the most ' pure ' experiment. This difficulty can be overcome by using a constant volume of solvent and increasing the concentration of $AlBr_3$ by breaking successively several phials of it into the same volume of solvent. A typical result of such an experiment is shown in Figure 13. Since the concentration of water is now constant, the conductivity which arises from it will be constant, and therefore the total conductivity due to reaction with water will show up as an intercept on the plot of conductivity against concentration. In experiment K4 three phials of $AlBr_3$ were broken at 15-min intervals at −78 °C into solvent which had been stored over a sodium mirror. The solution was diluted with more MeBr after 1 h to see whether the conductivity was accurately reversible. On breaking phial I all the water reacted and therefore the conductivity consisted of (*a*) that due to self-ionisation and (*b*) that due to reaction with residual water. The increase in the conductivity following the breaking of phials II and III was due to self-ionisation alone. The plot of conductivity against concentration of $AlBr_3$ in Figure 14 (full circles) is linear with an intercept κ' on the conductivity axis, which represents the conductivity from reaction with impurities; if the latter is subtracted from the total conductivity, the remainder represents that due

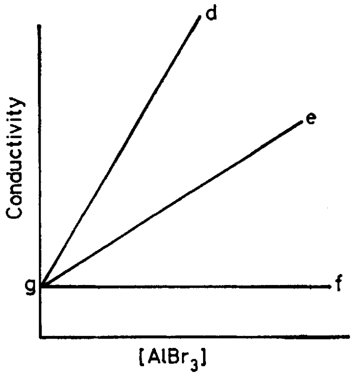

FIGURE 12 Schematic diagram of conductivity of aluminium halide solution as a function of its volume. For explanation see text

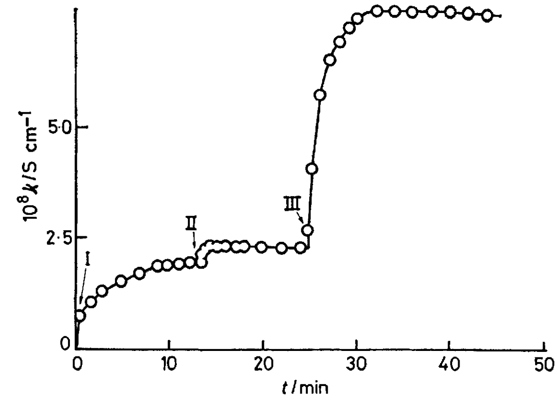

FIGURE 13 Experiment K4. The change of conductivity when three phials of $AlBr_3$ were broken into MeBr at −78 °C. The individual concentrations were: I 2.2×10^{-3}, II 3.3×10^{-3}, and III 3.8×10^{-2} mol dm^{-3}

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[25] F. Fairbrother and G. Frith, *J. Chem. Soc.*, 1953, 2975.

to self-ionisation (open squares in Figure 14). The plot of $\kappa - \kappa'$ against concentration was a straight line which agreed closely with that from the most pure experiment, C24 in Figure 11 (shown as a broken line in Figure 14). This shows that in experiment C24 virtually all the water from the solvent and the cell had been removed, and in addition confirms that there is a conductivity from the self-ionisation of $AlBr_3$ which is directly proportional to the solute concentration. In the experiment shown in Figures 13 and 14, when three phials of $AlBr_3$ had been broken, the solution was diluted with MeBr in order to examine whether the conductivity was reversible. The measured conductivity was corrected by subtracting a term $\kappa' V/V^0$, where V^0 was the initial volume. This correction removes the contribution to the conductivity which was due to the water present before more solvent was added, but any water in the additional solvent is not allowed for. The resulting conductivity (open circles in Figure 14) shows that this minuscule amount of water was of no consequence. We conclude from these results that the straight lines through the origin in Figures 14 and 15 represent the conductivity of $AlBr_3$ due to the self-ionisation.

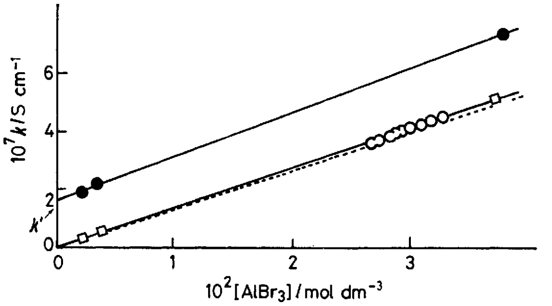

FIGURE 14 Plot of conductivity against concentration for the results shown in Figure 13. (●), The total conductivity when three phials of $AlBr_3$ were broken into MeBr at −78 °C. The intercept κ' is subtracted to give the points (□). (○), The results of a subsequent dilution after all the $AlCl_3$ had been added; the observed conductivity was corrected as described in the text. (— — —), Experiment C24 (see text)

We are aware that these results disagree in some details with those on multiple aluminium bromide additions recorded in the previous section and we attribute the differences to the greater purity of the solvent and improvements in the techniques used in the equilibrium experiments.

It is to be noted that κ' is distinguished from κ_i because this is an initial value of κ obtained by a kinetic calculation, whereas κ' is the intercept of κ at zero concentration in a plot of κ against $[AlX_3]$. However, both are due to impurity ions and are of the same order of magnitude.

Experiments at 0 *and* −23 °C. No dilution experiments were done at 0 °C because equilibrium is very slow. Instead, the $\kappa_e - \kappa_i$ values obtained as described in the previous section were plotted against the appropriate aluminium bromide concentration, and the resulting line for the self-ionisation at 0 °C coincided closely with that of experiment C24 (Figure 15).

Results for aluminium chloride. In Figure 16 a plot of κ against aluminium chloride concentration in EtCl at −78 °C is shown. The results were taken from three dilution experiments (D2, D5, and D6) each of which gave a linear plot of κ against $[AlCl_3]$. In experiments D2 and D5 the ionisation process consisted of a single stage only, and therefore κ_i was zero. In experiment D6 the ionisation was rapid, and did not obey the normal kinetics, probably because the EtCl contained trace amounts of water. Nevertheless, the subsequent dilutions gave a reasonably straight line which, after subtraction of κ', was coincident with the results of the other two experiments. Thus also for this system the conductivity depends rectilinearly on the concentration.

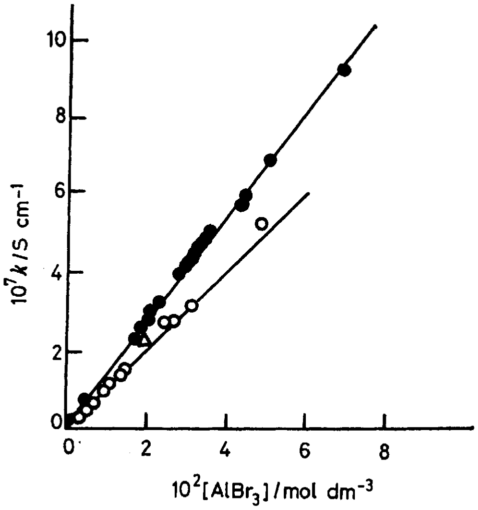

FIGURE 15 All the conductivity–concentration data for $AlBr_3$, at −63 and −78 (●) (there is little difference in conductivity at the two temperatures), −23 (△), and 0 °C (○)

Because the chloride dissolves so slowly, we obtained the required information for 0 °C and most of it for −78 °C in both chloride solvents *via* $\kappa_e - \kappa_i$ as described above.

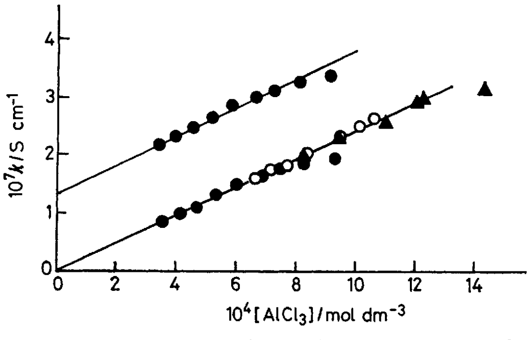

FIGURE 16 Plot of conductivity against concentration for $AlCl_3$ in EtCl at −78 °C. The results of experiment D6 (●) when corrected by subtraction of κ' agree with those of D2 (▲) and D5 (○)

The Ionisation Constants.—The fact that for all the systems examined the conductivity is a linear function of the concentration of the aluminium halide over a five- to ten-fold range shows that the number of ions generated must equal the number of molecules generating them.[2,11,12] For the present systems the most likely equilibria are (3) [of which (4) is a more realistic, but stoicheiometrically equivalent, version] and (5). The bromide is monomeric in methyl bromide [13,24b,26] and we have found the chloride to be so too in CH_2Cl_2. However, even at the low concentrations used here dialuminium ions may play some part in all the systems, especially at low temperatures, but the coexistence of equilibria (3)—(5) and the ' cross-equilibria ' would not give other than linear plots of κ against concentration; of course the value of the calculated equilibrium constant will depend on the model [(3) or (5)] used for the calculation. All our calculations are made according to equation (3) as this is dominant in our systems.

For equilibria of the n molecules $\rightleftharpoons$ n ions type, the conductivity–concentration relation is (13) where in these

$$\kappa = a_0\Lambda_i K^{\frac{1}{2}}/(1 + 2K^{\frac{1}{2}}) \qquad (13)$$

systems a_0 is the total [AlX_3]. In our systems y is of the order of 10^{-6} mol dm^{-3} (see below), so that for practical purposes $\Lambda_i = \Lambda_0$. It follows from (13) and the fact that $K \ll 1$, that to a good approximation the gradient of the plots of κ against a_0 is $\Lambda_i K^{\frac{1}{2}}$, and that these two terms cannot be separated. In order to obtain an estimate of K we can calculate $\Lambda_i(\simeq \Lambda_0)$ from the Stokes equation (14) where η is the viscosity of the solvent * and

$$\Lambda_0/\text{S m}^2\text{ mol}^{-1} = 8.2 \times 10^{-5}[r_+^{-1} + r_-^{-1})/\text{nm}^{-1}]/(\eta/\text{P}) \qquad (14)$$

the r are the radii of the ions. The r_- values were estimated from crystallographic data by standard methods and the r_+ were assumed to be the same. Unknown viscosities were estimated conventionally from those of closely related compounds. The results, together with those of Wendt [23] and of Halpern and Polaczek,[10] are shown in Table 2. They show that for $AlCl_3$ in EtCl, the extent of ionisation is 10^2—10^3 times greater than for $AlBr_3$ in MeBr. This accounts for our general observation that impurity effects are less, and reproducibility is easier to attain, in the chloride system. We can illustrate this with an order-of-magnitude calculation: it follows from equation (11) that for $a_0 = 10^{-2}$ mol dm^{-3} and $K = 10^{-4}$ (chlorides), y_e, the equilibrium concentration of ions of one kind, is 10^{-4} mol dm^{-3}; but $K = 10^{-8}$ (for $AlBr_3$) gives $y_e = 10^{-6}$ mol dm^{-3}. Thus the impurity level required to obtain reasonable results with the bromide system is about one hundredth of that which is adequate for the chloride system.

The smallness of the change of κ with temperature is the fortuitous result of the increase in the number of ions with decreasing temperature (because of increasing εT) being compensated by the concurrent increase in the viscosity of the solvent. A comparison of the results in Figures 11 and 15 shows that for the adequately pure systems κ *increases* slightly with decreasing temperature, whereas for the impure systems it *decreases* strongly; this is an additional useful practical test for the degree of purity achieved.

Thermodynamic Aspects.—The K values for $AlBr_3$ at four temperatures (Table 2) give a rectilinear van't Hoff plot, from which we calculate $\Delta H^\ominus = -17.6 \pm 0.2$ kJ mol^{-1}, independent of temperature between 0 and −78 °C. Whether this characterises only equilibrium (4) or whether it includes a component from an association equilibrium (15) and possibly also from (16) cannot be

$$AlBr_2^+{\cdot}RBr + AlBr_3 \rightleftharpoons Al_2Br_5^+{\cdot}RBr \qquad (15)$$

$$AlBr_4^- + AlBr_3 \rightleftharpoons Al_2Br_7^- \qquad (16)$$

decided on the basis of our data. The corresponding $\Delta S^\ominus = -217$ J K^{-1} mol^{-1} at 250 K.

Attempts to obtain further evidence on the energetics of these ionisations from the results of other workers are frustrated because the internal evidence of all the previous work on this subject, with the notable exception of that of Halpern and Polaczek,[10] indicates that it was so much affected by impurities that its re-evaluation would not be worthwhile. From Halpern and Polaczek's published curves of conductivity against time, approximate values of $\kappa_e - \kappa_i$ were calculated, and these showed that, for the iodides of aluminium and indium, half the measured conductivity was due to self-ionisation, but for gallium iodide this was only one third. From these conductivities we calculated ionisation constants (Table 2), which show that the trend towards lower ionisation constants for aluminium halides continues from bromide to iodide, that the iodides of aluminium and indium behave very similarly, and that the gallium iodide system is the least ionised of all those examined, which accounts for the large ' impurity contribution ' in this system noted above.

The interesting question, to what extent the marked trend in the dissociation constants from chloride through bromide to iodide is due to the different properties of the aluminium compounds and to what extent it reflects the different polarities, and thus solvation energies, of the solvents, requires for its resolution some analogous experiments with all the halides in the same solvent. Wendt's experiments with the chloride and bromide in nitrobenzene, also quoted in Table 2, although they are at one temperature only, seem to indicate that the differences in the K values arise principally from differences in the solvation energies of the ions in the two solvents.

Since, for our aluminium chloride systems, results are available at two temperatures only, we present the corresponding thermodynamic data with due reserve and we do not feel that their discussion is worthwhile at present.

$AlCl_3$ in	CH_2Cl_2	EtCl
$-\Delta H^\ominus$/kJ mol^{-1}	15	28
$-\Delta S^\ominus$/J K^{-1} mol^{-1}	125	208

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* 1 P = 10^{-1} Pa s.

[26] H. C. Brown and W. J. Wallace, *J. Amer. Chem. Soc.*, 1953, **75**, 6279; C. E. Jacobsen and B. B. Dumarevska, *Mem. Inst. Chem., Ukrain. Acad. Sci.*, 1946, **7**, 15; Z. A. Sheka and I. A. Sheka, *Doklady Akad. Nauk S.S.S.R.*, 1950, **73**, 739; J. J. Burbage and A. B. Garrett, *J. Phys. Chem.*, 1952, **56**, 730.

The Nature of the Ions.—The marked decrease in entropy which accompanies the ionisations shows that the ions (mainly of course the cation) bind the solvent much more strongly than do the molecules, which is in accord with expectation. From a slightly different point of view one can say that the unsolvated bare $AlBr_2^+$ ion with its high charge density is a most unlikely species in MeBr, and that the most abundant cation, at least at low concentrations, will be the ion $AlBr_2^+\cdot MeBr$. The reason for omitting the solvent from the equations is that the solvation of molecules and ions has no essential effect on the conductance behaviour of the systems, *i.e.* on the concentration dependence of rates and equilibria.

One other question needing clarification is why we have neglected consideration of the $BrMe_2^+$ ion which occurs in the $AlBr_3$–MeBr system under some conditions, the salt $BrMe_2^+AlBr_4^-$ having been characterised.[27] There are three reasons for this: (1) the cations formed under conditions similar to ours have been shown to contain aluminium;[13-15] (2) the $BrMe_2^+$ ion has not been shown to be an important constituent of the very dilute solutions used by us; and (3) if an important fraction of the ions had been generated by a reaction of the aluminium halide with the solvent, the dependence of κ on $[AlX_3]$ would have been of the Ostwald type, instead of linear, as we found it to be.

The only recent study of a related system by a similar method is that of Eley *et al.*[28] on the self-ionisation of antimony pentachloride in CH_2Cl_2. Their conductivities were very much higher than those of our aluminium halide solutions and not surprisingly a successful analysis of the data required use of an equation describing self-ionisation with formation of ion pairs, analogous to that of Grattan and Plesch.[12]

Conclusion.—We have shown that the kinetics of ion formation in solutions of aluminium halides in alkyl halides can be interpreted in terms of second-order forward and reverse reactions, provided that the system is adequately pure. Also, the corresponding equilibria are compatible with the kinetics and we have estimated the ionisation constants. Having thus cleared up the major features of the solution chemistry of these systems, we thought we knew what was necessary to attack our main objective, the mechanism whereby the aluminium halides initiate the polymerisation of olefins. The results of that investigation will be presented elsewhere.

We thank the British Council for the award of a scholarship to V. Shmarlin, who did some of the exploratory work, and the S.R.C. for equipment.

[6/961 *Received*, 20*th May*, 1976]

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[27] G. A. Oláh, J. R. De Member, Y. K. Mo, J. J. Svoboda, J. P. Schilling, and J. A. Oláh, *J. Amer. Chem. Soc.*, 1974, **96**, 884.

[28] D. D. Eley, D. F. Monk, and C. H. Rochester, *J.C.S. Faraday I*, 1976, 1584.