The Equilibrium in Solution among Tetrachloroaluminate, Tetrabromoaluminate, and the Mixed Bromochloroaluminate Ions

By **D. E. H. Jones**, I.C.I. Ltd., Petrochemical and Polymer Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire

The equilibrium in acetonitrile solution among the five ions $AlCl_nBr_{4-n}^-$ ($0 \leqslant n \leqslant 4$) at 26 °C has been examined by ^{27}Al n.m.r. spectroscopy, and the equilibrium constants for the system have been determined.

THE set of five ions $AlCl_nBr_{4-n}^-$ ($0 \leqslant n \leqslant 4$) is known to form an equilibrium mixture, so that compounds of the individual mixed bromochloroaluminate ions cannot be isolated from solution. Bradley, Brier, and Jones[1] found that mixtures of $AlCl_4^-$ and $AlBr_4^-$ rapidly equilibrated in solution to give the five ions; they analysed the vibrational spectra of mixtures of overall composition NMe_4^+ $AlCl_xBr_{4-x}^-$ ($0 \leqslant x \leqslant 4$) into contributions from each of the five. Kidd and Truax[2] prepared solutions of tetrabromoaluminate salts in dichloromethane and found them to contain all five ions, which they recognised by their individual ^{27}Al n.m.r. signals. They found that in the presence of aluminium bromide, the signals coalesced into a broad band indicative of rapid exchange between the ions. This paper reports a study of the equilibrium among the ions $AlCl_nBr_{4-n}^-$ in acetonitrile solution and against NMe_4^+ as counterion, using ^{27}Al n.m.r. spectroscopy.

EXPERIMENTAL

Preparation of Samples.—Reagents were purified and specimens of tetramethylammonium tetrahalogenoaluminates were prepared as before,[1] using the reaction between aluminium trihalide and tetramethylammonium halide in acetonitrile. Because of the sensitivity to water of these reagents and of the products, dry-box and vacuum-line techniques were employed. Five solid specimens of different compositions were prepared for the n.m.r. studies: analytically pure samples of tetramethylammonium tetrachloroaluminate and of tetramethylammonium tetrabromoaluminate, and three samples obtained by crystallising mixtures of these salts from acetonitrile. Analytical results on the mixed specimens are shown in Table 1.

TABLE 1

Analytical results on solid samples $NMe_4^+AlCl_xBr_{4-x}^-$

Sample formula	1 $NMe_4AlCl_{3\cdot05}Br_{0\cdot95}$		2 $NMe_4AlCl_{2\cdot45}Br_{1\cdot55}$		3 $NMe_4AlCl_{0\cdot85}Br_{3\cdot15}$		4 $NMe_4AlCl_{2\cdot82}Br_{1\cdot18}$	
Analysis	Found	Required	Found	Required	Found	Required	Found	Required
%C	16·8	16·8	15·4	15·4	12·4	12·5	16·7	16·3
%H	4·2	4·2	3·9	3·9	3·4	3·1	4·2	4·1
%Cl	31·7 *	37·9	27·8	27·85	7·5	7·9	34·0	33·85
%Br	28·3 *	26·6	39·7	39·7	65·7	65·7	32·4	31·9
Total halogen (mmols/g)	13·9	14·0						
Cl : Br ratio	3·3 : 1 †	3·21 : 1						

* Believed to be erroneous determinations, see text. † Determined on a solution of this sample in acetonitrile.

The halogen values given in Table 1 for sample 1 are in poor agreement with those required by the formula there given, $NMe_4^+AlCl_{3\cdot05}Br_{0\cdot95}^-$. Unfortunately all this sample had been dissolved in acetonitrile and the ^{27}Al n.m.r. experiments completed, before this discrepancy was noticed. The C, H, and total-halogen values are in agreement with the composition quoted, as also is the halogen ratio determined subsequently on a remaining sample of the solution. The adoption of this formula gives much greater self-consistency to the interpretation of the spectroscopic results than does one based on the halogen values of Table 1. Since these were determined by a total-halide titration, followed by a separate oxidation step and determination of bromine as bromate to give the chlorine value by difference, an error in this individual bromine analysis would explain the discrepancy. A second sample of the same approximate stoicheiometry (sample 4 of Table 1) was prepared and analysed satisfactorily, but was too late to be included in the n.m.r. experiments.

Solutions (*ca.* 30% by weight) of the tetramethylammonium salt specimens were made up in dry acetonitrile for n.m.r. examination. Solutions in dry nitromethane were also prepared, but even in sealed tubes these solutions slowly became cloudy due to some secondary reaction, and were therefore not examined.

N.m.r. Spectroscopy.—The acetonitrile solutions were examined using a Bruker Spectrospin HFK-6 instrument equipped with a ^{27}Al probe. The sample area, although not thermostatted, was fairly constant in temperature at 26 ± 1 °C. The signals saturated readily (particularly those of the highly symmetrical ions $AlCl_4^-$ and $AlBr_4^-$), and the runs to determine the relative signal intensities of the ions in each solution had to be carried out with low power levels. As a consequence, the maximum signal : noise ratio of these runs was only of the order of 15 : 1. and in order to improve the precision of the measurements of the signal intensities (derived by subsequent area integration), several runs were taken on each solution.

RESULTS AND DISCUSSION

The chemical shifts of the five ions [relative to $Al(H_2O)_6^{3+}$] are shown in Table 2, and agree well with

---

[1] R. H. Bradley, P. N. Brier, and D. E. H. Jones, *J. Chem. Soc.* (*A*), 1971, 1397.

[2] R. G. Kidd and D. R. Truax, *J. Amer. Chem. Soc.*, 1968, **90**, 6867.

those found by Kidd and Truax. The relative signal intensities of the ions in each solution, expressed as percentages of the total Al signal, are also shown in Table 2; the limits of error shown span the maximum variation between the ratios encountered in several runs on each solution.

The linewidths of the $AlCl_4^-$ and $AlBr_4^-$ signals were *ca.* 4 Hz in solutions containing these species as sole anions, but broadened to 5—6 Hz in the mixed solutions, indicating an exchange-time of equilibration between the ions of *ca.* 0·2 s. An upper limit to this exchange-time was obtained in a mixing experiment, in which a solution of $NMe_4^+AlCl_4^-$ was carefully decanted onto one of $NMe_4^+AlBr_4^-$ in the sample tube, so that only the lower layer of the stratified solution projected into the r.f. field of the spectrometer, and only the one peak due to $AlBr_4^-$ was observed. Rapid inversion of the tube then mixed the two layers, and a fast scan was commenced within 2 s, within which time the peaks of all five ions had established themselves at their equilibrium intensities, unchanged on subsequent scanning.

TABLE 2

^{27}Al N.m.r. results obtained at 23·45 MHz and 26 ± 1 °C. Chemical shifts and relative signal intensities of ions $AlCl_nBr_{4-n}^-$ ($0 \leqslant n \leqslant 4$); equilibrium constants and heats of disproportionation of mixed ions ($1 \leqslant n \leqslant 3$)

Ion		$AlCl_4^-$	$AlCl_3Br^-$	$AlCl_2Br_2^-$	$AlClBr_3^-$	$AlBr_4^-$
Chemical shift (p.p.m.)						
This work:		103	99	94	87·5	80
Ref. 2:		104	98	93	87	80
Signal intensities (% of total), for overall Cl : Br ratios below						
3·21 : 1	obs:	39 ± 4	43 ± 2	18 ± 1		
	calc:	35·4	41·4	17·0	5·5	0·7
1·58 : 1	obs:	17 ± 2	35 ± 3	30 ± 3	16 ± 3	2 ± 1
	calc:	16·5	35·9	27·2	16·3	4·1
0·27 : 1	obs:		9 ± 1	22 ± 2	40 ± 2	29 ± 2
	calc:	1·5	9·8	21·7	38·4	28·6
Mixed ion equilibrium constants of disproportionation giving the above calculated compositions			K_3: 0·35 ± 0·03	K_2: 0·8 ± 0·1	K_1: 0·425 ± 0·045	
Heats of disproportionation corresponding to these equilibrium constants (cal mol^{-1})			ΔH_3: 40 ± 50	ΔH_2: −350 ± 80	ΔH_1: −70 ± 60	

Derivation of Equilibrium Constants.—The equilibrium among the five molecules MCl_nBr_{4-n} capable of undergoing halogen redistribution reactions, can be expressed in terms of three equilibrium constants. Each one is associated with a disproportionation of type (1).

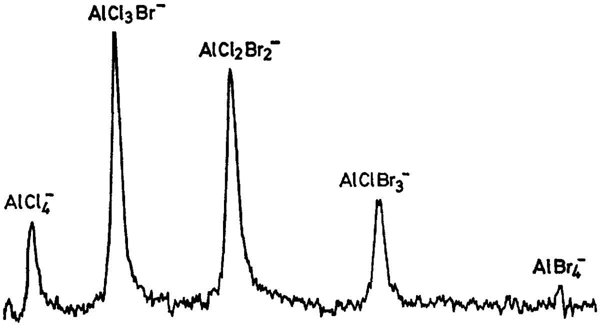
$$2MCl_nBr_{4-n} = MCl_{n+1}Br_{3-n} + MCl_{n-1}Br_{5-n} \quad (1)$$

Applied to these three disproportionations, the simple law of mass action defines each equilibrium constant in terms of molecular concentrations:

$$K_n = [MCl_{n+1}Br_{3-n}][MCl_{n-1}Br_{5-n}]/[MCl_nBr_{4-n}]^2$$
(n is 1, 2, or 3)

In the case where the chlorine and bromine atoms are 'indistinguishable' to the central metal atom, a binomial or Calingaert distribution[3] would be expected, in which the concentration of each ion would be proportional to the corresponding term in the binomial expansion of $([Cl] + [Br])^4$, the symbols representing the respective halogen contents of the mixture. For this distribution $K_1 = K_3 = 0{\cdot}375$ and $K_2 = 0{\cdot}444$. Liquid mixtures of $SnCl_4$ and $SnBr_4$ reach an equilibrium in which the distribution of mixed $SnCl_nBr_{4-n}$ halides has been shown to be approximately random in this sense, by ^{119}Sn n.m.r. spectroscopy.[4] Clark and Willis[5] have more recently studied the equilibrium between $TiCl_4$ and $TiBr_4$ both as liquid mixtures and in cyclohexane solution, by Raman spectroscopy; their results again indicate a nearly random distribution of the mixed halides $TiCl_nBr_{4-n}$ with $K_1 = 0{\cdot}32$, $K_2 = 0{\cdot}60$ and $K_3 = 0{\cdot}34$.

For the system $AlCl_nBr_{4-n}^-$, each ^{27}Al n.m.r. spectrum exhibits at least three consecutive halogenoaluminate ion signals with measurable intensity, thus enabling at least one of the constants K_n to be estimated immediately; solutions of sample 2 showed the signals of all five ions with measurable intensity (Figure). Since for each mixed solution the three equilibrium



^{27}Al n.m.r. spectrum (23·45 MHz) of sample 2 (overall stoicheiometry: $NMe_4^+AlCl_{2\cdot45}Br_{1\cdot55}^-$) in acetonitrile

---

[3] C. Calingaert and H. A. Beatty, *J. Amer. Chem. Soc.*, 1939, **61**, 2748.

[4] J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 326.

[5] R. J. H. Clark and C. J. Willis, *Inorg. Chem.*, 1971, **10**, 1119.

constants and the Cl : Br ratio together determine the relative signal intensities of all five ions, the experimental data of Table 2 considerably overdetermine the three constants K_1, K_2, and K_3. To determine the values of these constants which best fitted all the data, a computer optimisation routine was employed which, given the observed signal intensities and halogen-ratios, and starting-values of the equilibrium constants obtained from individual spectra, optimised the constants to give the smallest sum of squared errors between the calculated and observed intensities. For this exercise, peaks lost in background noise were assigned zero intensity. Computations were also made in which the halogen-ratios were similarly optimised, taking their observed values as starting-points. These optimisations had little effect on the ratios for solutions 2 and 3, but showed that for solution 1 the halogen-ratio implied by the formula $NMe_4{}^+AlCl_{3\cdot05}Br_{0\cdot95}{}^-$ gave a much better fit to the data than one based on the original halogen determinations on this sample. The above formula was therefore adopted in the optimisation giving the final values of the calculated intensities and the equilibrium constants shown in Table 2, as it is supported by other analytical data (see above) which suggest that the original bromine estimation on this sample had been in error.

TABLE 3

Calculated ionic distributions, and calculated and observed relative intensities of the strong a_1 Raman band of each halogenoaluminate ion, in solid samples $NMe_4{}^+AlCl_xBr_{4-x}{}^-$; expressed as percentages of total

x	Ion	$AlCl_4{}^-$	$AlCl_3Br^-$	$AlCl_2Br_2{}^-$	$AlClBr_3{}^-$	$AlBr_4{}^-$
3·0	Calc. molar percentage:	33	42	18	6	1
	Calc. intensity:	31	40	21	7	1
	Obs. intensity:*	29	42	23	6	0
2·0	Calc. molar percentage:	9	27	29	26	9
	Calc. intensity:	8	25	32	26	9
	Obs. intensity.*	5	20	36	30	9
0·96	Calc. molar percentage:	1	6	18	39	36
	Calc. intensity:	1	6	19	39	35
	Obs. intensity:*	1	4	14	41	40
Mechanical mixture of 3·0 and 0·96 samples	Calc. molar percentage:	17	23	18	23	19
	Calc. intensity:	15	22	20	24	19
	Obs. intensity:*	20	27	20	19	14
Effective intensity factors for each a_1 band. Calc. intensities are derived from the five $k_n \times$ (Calc. molar percentage)$_n$ values by renormalising to 100		k_4: 0·91	k_3: 0·94	k_2: 1·12	k_1: 1·03	k_0: 1·00

* Data taken from ref. 1.

Table 2 shows that, within the limits of error of the observations, the optimum values of K_1, K_2, and K_3 account completely for the observed signal intensities of the ^{27}Al n.m.r. spectra. The error limits shown for the K values were obtained by calculations in which each equilibrium constant in turn was displaced from its optimum position until the most sensitive relative intensity had altered by its limit of error. The uncertainty in the equilibrium constants is seen to be of the order $\pm10\%$.

Relative Raman Intensities of Characteristic $AlCl_nBr_{4-n}{}^-$ *Bands in Equilibrated Mixtures.*—Tetrahalide molecules MCl_nBr_{4-n} exhibit a strong a_1 Raman band arising from the symmetric stretching vibration of the halogen atoms, and this characteristic band has been used to identify the mixed tetrahalides of a number of elements (ref. 5 and refs. cited therein). These a_1 bands in the ions $AlCl_nBr_{4-n}{}^-$ occur at 352, 308, 278, 247 and 214 cm^{-1}, and have been assigned [1] to the ions with $n = 4$—0 respectively by consideration of their relative intensities in solid samples of various compositions $NMe_4{}^+AlCl_xBr_{4-x}{}^-$. From K_1, K_2, and K_3, and the known overall composition of these samples, the ionic distribution in each of them can be calculated (assuming that this distribution is the same in the solid as in the solution from which it was prepared). By a calculation similar to that of Clark and Willis [5] for the a_1 Raman intensities of the five molecules $TiCl_nBr_{4-n}$ $(0 \leqslant n \leqslant 4)$, it is then possible to seek an ' effective intensity factor ' for the a_1 band of each halogenoaluminate ion, such that together these five factors account for the observed relative intensities of the a_1 bands in the Raman spectra of the $NMe_4{}^+AlCl_nBr_{4-n}{}^-$ samples.

The results of this exercise are shown in Table 3. The relative intensity of the a_1 band of each ion is nearly proportional to its concentration (expressed as the percentage contribution of that ion to the total mol fraction of aluminium in the sample), for all four mixtures studied in ref. 1. This indicates that the effective ionic intensity factors (k_4—k_0 in Table 3) are all about the same. These factors will include any correction for changing photomultiplier sensitivity between $\Delta\nu = 352$ and 214 cm^{-1}, and are normalised to an average of unity in the absence of a reliable internal spectral standard in terms of which to express them (the *ca.* 752 cm^{-1} band of $NMe_4{}^+$ is unfortunately of variable position and contour). Most of the differences between the observed and calculated a_1 Raman intensities in Table 3 are within the $\pm 15\%$ uncertainty which the calculations retain by their derivation from the similarly uncertain K_1, K_2, and K_3. The assignments of the Raman spectra in ref. 1, and the intensities reported therein, are therefore fully consistent with the results of the present study.

Significance of Equilibrium Constants.—Although several sets of neutral mixed tetrahalide species show an equilibrium distribution approximating to the binomial or Calingaert pattern, this is rarer in tetrahalide ions. The systems $MCl_nBr_{4-n}^-$ $(0 \leqslant n \leqslant 4)$ in which M is Tl, Zn, and Fe have all been examined [6-8] and do not exhibit equilibrium mixtures containing significant amounts of all five ions. Instead, from mixtures of the appropriate composition, compounds of any individual ion can be obtained in an essentially pure state. This cannot be a kinetic effect, deriving from longer time-constants of equilibration than the 0·2 s characteristic of the halogenoaluminate ions; for in all the other cases compounds of the $MCl_2Br_2^-$ ion can rapidly be prepared by mixing in equimolar proportions solutions of MCl_4^- and MBr_4^-.

The behaviour of all the ionic systems can be understood in terms of three disproportionation equilibria of type (1), with differing values of the constants K_1, K_2, and K_3. The effect on the overall composition of varying these constants is readily explored by the mathematical treatment here employed to optimise these constants for the tetrahalogenoaluminate system. When all three constants are close to their Calingaert values, the distribution of the five ions is closely binomial. With decreasing values of K (*i.e.* disproportionation becoming less and less favourable), the distribution of the ions peaks more and more sharply at the ion whose stoicheiometry is nearest to that of the solution. With all K values equal to 10^{-4}, this favoured ion is contaminated at equilibrium by only *ca.* 1% total of the others; or if the stoicheiometry of the solution is intermediate between those of two neighbouring ions, these predominate in solution and share the halogens between them in proportion. With the three K values each equal to 10^3 so that disproportionation is strongly favoured, MCl_4^- and MBr_4^- in stoicheiometric ratio make up over 99·5% of the total metal-ion concentration, amd mixed ions are very poorly represented.

Such variations in the K values correspond to only modest differences in the heats of disproportionation. Taking the solution temperature as 299 K, and assuming any deviation from gas-phase thermodynamics (solvation effects, *etc.*) to be about the same for the very similar species on either side of the disproportionation equilibria, then $K_n = 10^{-4}$ implies a heat of disproportionation ΔH *ca.* 5 kcal mol^{-1} and $K_n = 10^3$ implies ΔH *ca.* $-4·7$ kcal mol^{-1}. The heats of disproportionation corresponding to the values of K_n in the system $AlCl_nBr_{4-n}^-$ are given in Table 2 together with their limits of error. They are all well below 1 kcal mol^{-1}; in fact only for $AlCl_2Br_2^-$ is disproportionation significantly somewhat favoured. In this respect the system is almost exactly similar to $TiCl_nBr_{4-n}$. These low energies of disproportionation implied by near-Calingaert distributions do not, however, mean that all the molecules in equilibrium have nearly identical energies, but only that adjacent members of the series differ in energy by nearly equal amounts.

I thank J. W. Akitt of the University of Newcastle upon Tyne, who ran the ^{27}Al n.m.r. spectra.

[1/1384 *Received, 6th August,* 1971]

---

[6] R. A. Walton, *Inorg. Chem.*, 1968, **7**, 640 and 1927; R. W. Matthews and R. A. Walton, *J. Chem. Soc.* (*A*), 1968, 1693.

[7] G. B. Deacon and F. B. Taylor, *J. Chem. Soc.* (*A*), 1966, 463; G. B. Deacon, J. H. S. Green, and F. B. Taylor, *Austral. J. Chem.*, 1967, **20**, 2069.

[8] C. A. Clausen and M. L. Good, *Inorg. Chem.*, 1970, **9**, 220.