

Halogen Exchange between Aluminium Halides and Phosphoryl Chloride

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LEWIS and SOWERBY have shown¹ that, in the absence of added chloride ion, no chlorine exchange is observed between solvent phosphoryl chloride and dissolved aluminium chloride. This observation has recently been used to support the view² that AlCl_4^- ions are not present in such solutions and that the aluminium chloride is most likely present as the $\text{Cl}_3\text{Al}-\text{OPCl}_3$ oxygen-bonded solvent

The Al_2Cl_6 Solution.—The principal aluminium species in a solution of Al_2Cl_6 in POCl_3 are AlCl_4^- and $\text{Al}(\text{OPCl}_3)_6^{3+}$ ions. The signal at -102.5 p.p.m. which appears in spectrum (3) for the Al_2Cl_6 - POCl_3 solution is assigned to the AlCl_4^- ion on the basis of spectral evidence from an Al_2Cl_6 - MeNO_2 solution containing added chloride ion [spectrum (4)]. The ^{27}Al chemical shifts and linewidths

TABLE

^{27}Al n.m.r. parameters^a for POCl_3 solutions of aluminium halides

Spectrum No.	Solution	Wt. % solute	^{27}Al shift ^b (p.p.m.)	Linewidth, (Hz.)	Assignment
(1)	Al_2I_6 in POCl_3	16	$+ 22.4 \pm 0.8$	77 ± 4	$\text{Al}(\text{OPCl}_3)_6^{3+}$
(2)	Al_2Br_6 in POCl_3	10	-101.3 ± 1.2	30 ± 1	AlCl_4^-
(3)	Al_2Cl_6 in POCl_3	7.3	-101.7 ± 0.5	33 ± 2	AlCl_4^-
(4)	$\text{Al}_2\text{Cl}_6 + \text{Me}_4\text{NCl}$ in MeNO_2		$+ 21.2 \pm 0.1$	55 ± 3	$\text{Al}(\text{OPCl}_3)_6^{3+}$
			-102.5 ± 0.2	10 ± 1	AlCl_4^-
			-101.5 ± 0.4	30 ± 1	AlCl_4^-

^a Measured at 15.1 MHz. with a Varian DP-60 spectrometer.

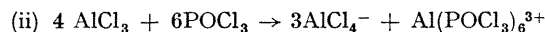
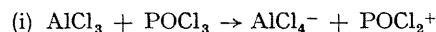
^b Chemical shifts relative to external aqueous acidic $\text{Al}(\text{H}_2\text{O})_6^{3+}$; positive shifts indicate signals on high-field side of reference.

adduct. We were surprised therefore to find the AlCl_4^- ion as the predominant solute species in phosphoryl chloride solutions of Al_2Cl_6 , Al_2Br_6 , and Al_2I_6 .

Direct observation of the ^{27}Al nucleus by n.m.r. spectroscopy is a useful technique for the identification of tetrahalogenoaluminate ions in solution,³ and both the simple AlX_4^- and the mixed $\text{AlX}_n\text{Y}_{4-n}^-$ ions can be readily identified on the basis of their ^{27}Al chemical shift. These species all give rise to n.m.r. signals which are relatively narrow† and the chemical shifts of which can be reproducibly determined with an accuracy of ± 1 p.p.m. In particular, the chemical shift for the AlCl_4^- ion, obtained by dissolving equivalent amounts of aluminium trichloride and tetramethylammonium chloride in nitromethane, is -102 p.p.m.

The ^{27}Al n.m.r. spectra which we have obtained for POCl_3 solutions of the aluminium halides are summarized in the Table.

for mixed tetrahalogenoaluminate ions³ also support this assignment. In this solution, AlCl_4^- ions can be generated in two ways, only one of which leads to chlorine exchange with solvent.

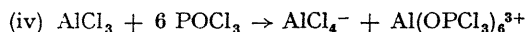
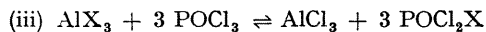


Two pieces of experimental evidence point to reaction (ii) as the source of AlCl_4^- ions. Firstly, it is consistent with Lewis and Sowerby's observation that chlorine exchange between solute and solvent does not occur.¹ Secondly, it generates a second aluminium species in solution to which can be assigned the $+22$ p.p.m. line in the ^{27}Al n.m.r. spectrum for the solution. The $+22$ p.p.m. chemical shift for this line suggests that the assignment is the octahedrally co-ordinated $\text{Al}(\text{POCl}_3)_6^{3+}$ ion, since the resonance is close to that of the reference $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ion at 0 p.p.m. Other

† In the range 10–50 Hz., depending upon the particular halogens and the symmetry about the aluminium atom. See ref. 3.

species possibly present in the solution, such as $\text{Al}(\text{OPCl}_3)_4^{3+}$ and $\text{AlCl}(\text{OPCl}_3)_3^{2+}$, are expected to have chemical shifts closer to those for $\text{Al}(\text{OH})_4^-$ (-80 p.p.m.)⁴ and AlCl_3^- (-22 p.p.m.)^{3,†} respectively.

The Al_2I_6 and Al_2Br_6 Solutions.—The resonances at -101.3 p.p.m. and -101.7 p.p.m. which occur in spectra (1) and (2) respectively indicate that the AlCl_4^- ion is the principal solute species in each. Since the only possible source of chloride ions in these solutions is the solvent, AlCl_4^- ions must arise from halogen exchange with solvent according to a reaction sequence of the type



Since no mixed tetrahaloaluminate ions of the type

† The analogy here is with the substitution of a chloride ion for an iodide in the AlI_4^- ion ($+27$ p.p.m.), which causes a paramagnetic shift in the ^{27}Al resonance of *ca.* 50 p.p.m.

$\text{AlX}_n\text{Cl}_{4-n}^-$ ($1 \leq n \leq 3$) are observed in these solutions, equilibrium (iii) must lie far to the right and halogen exchange with solvent must be virtually complete. This being the case, solutions of Al_2I_6 and Al_2Br_6 in POCl_3 are expected to yield similar solute species to those of the Al_2Cl_6 solution. Thus, spectrum (1) for the Al_2I_6 solution has an $\text{Al}(\text{OPCl}_3)_6^{3+}$ signal at $+22.4$ p.p.m. We have not, however, been able to observe a similar signal in spectrum (2) for the Al_2Br_6 solution, but this might easily be because the signal is broadened beyond recognition by chemical-exchange effects.

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¹ J. Lewis and D. B. Sowerby, *J. Chem. Soc.*, 1963, 1305.

² M. F. A. Dove and D. B. Sowerby in "Halogen Chemistry" Vol. 1, ed. V. Gutmann, Academic Press, London, 1967, p. 59.

³ R. G. Kidd and D. R. Truax, *J. Amer. Chem. Soc.*, 1968, **90**, 6867.

⁴ D. E. O'Reilly, *J. Chem. Phys.*, 1960, **32**, 1007.