# Notes

## Hydrolysis of Hexa-aqua-aluminium(III) in Organic Media

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An unusual method is described for the hydrolysis of the aqua-aluminium cation in organic solvents. Hydrolysis occurs very much more rapidly than is normal and a mechanism is suggested which is based upon the formation of mixed solvates.

WE have shown[1] that the nature of the products of the hydrolysis of $[Al(OH_2)_6]^{3+}$ depends markedly upon the method used for hydrolysis. Hydrolysis of any aluminium salt solution to $m = 2.5$ ($m$ = OH added/Al present) with sodium carbonate leads principally to the formation of the spherical $Al_{13}$ polycation $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$. Hydrolysis by dissolution of aluminium metal in an aqueous solution of an aluminium halide or perchlorate to the equivalent of $m = 2.5$ gives a $^{27}Al$ n.m.r. spectrum showing that only a small proportion of the $Al_{13}$ polymeric ion is present. Only partial hydrolysis is possible with aluminium nitrate solutions however, for it is found that a permanent precipitate forms after only part of the metal has dissolved and we can only reach an $m$ value of about 1.5.

An early report[2] indicated that a basic gallium salt $[Ga_2(OH)_5][NO_3]\cdot 2H_2O$ may be obtained by adding an ethanolic solution of $Ga[NO_3]_3\cdot 9H_2O$ to an excess of hot diethyl ether. Thus the preparation appears to have produced a fully hydrolysed nitrate with $m = 2.5$. It was of obvious interest to find out whether the method would work for aluminium nitrate also, and to observe what products might be formed. The method was found to work well and a number of variants were tried with the results detailed below.

### EXPERIMENTAL AND RESULTS

AnalaR $Al[NO_3]_3\cdot 9H_2O$ was used throughout and solvents which were dry to GPR standard. The other salts used were GPR. The original method for Ga when adapted for Al gave a wet and coloured product. We tried a variety of alcohols and ethers to see if the method could be improved and found that the best conditions appeared to be the use of methanol as solvent and of acetone to bring about reaction. Diphenyl ether or di-n-butyl ether gave no precipitate, while higher alcohols usually gave gelatinous precipitates before any other solvent could be added. The optimum procedure was to dissolve the aluminium nitrate in warm dry methanol to give a 20% (*ca.* 0.5 mol dm$^{-3}$) solution and add this to five volumes of refluxing dry acetone. A precipitate formed immediately and was a pure white, powdery material which was easily filtered off, washed with dry acetone, and dried in air. The product was infinitely soluble in water. It accounted for *ca.* 98% of the total aluminium and assayed as 17.15% Al, 5.60% N, 3.55% H, and 0.55% C, leading to the formulation $Al_2(OH)_{4.8}(NO_3)_{1.2}(OCMe_2)_{0.05}\cdot xH_2O$, with $x$ = 2—4. The remaining acetone could only be removed by dissolution in water and evaporation to dryness.

Hydrolysis was always found to proceed to $m = 2.4$ however the method was varied. Use of more acetone than stated did not lead to more highly hydrolysed solutions, and the use of less acetone merely gave less material of the same degree of hydrolysis. The $^{27}Al$ n.m.r. spectra, which were obtained as described previously,[1] indicated that a solution of the product contained $[Al(OH_2)_6]^{3+}$, $[Al_2(OH)_2]^{4+}$, and a little of the $Al_{13}^{7+}$ polymeric cation. No other resonances could be seen, although a comparison of the initial free induction decay of the sample with that of a standard aluminium salt solution showed that only 9% of the total aluminium present was being observed, the remainder, which includes the octahedral Al of the $Al_{13}^{7+}$, giving broad undetectable resonances. The composition of the solutions and so presumably of the solid can be calculated approximately from these spectra and we obtain 9.5% $Al_{13}^{7+}$, 4.4% $[Al_2(OH)_2]^{4+}$, 3.9% $Al^{3+}$, and 82.2% unknown. The average value of $m$ for the species which are observed is 1.6 and this leads us to believe that the unknown component is highly hydrolysed to *ca.* $m = 2.6$.

The method was also used in attempts to hydrolyse a number of other aluminium salts. It would not work at all for the chloride and perchlorate, with which essentially no precipitate was obtained, while the bromide could not be made in a sufficiently dry form for a precipitate to be expected. In the case of the sulphate, almost all the aluminium precipitated but this was only partially hydrolysed to $m = 0.6$, and appeared to be a mixture of $[Al(OH_2)_6]^{3+}$ and $[Al_2(OH)_2]^{4+}$.

Finally, it should be noted that a mixture of an acidic nitrate with organic solvents is potentially hazardous.

### DISCUSSION

A curious feature of these results is the occurrence of almost instantaneous hydrolysis which is in startling contrast to all other methods which have been used and which take between 15 min and 15 d. We observe that the presence of $NO_3^-$ seems essential for organic-phase hydrolysis to work and that higher alcohols cause spontaneous hydrolysis. In this medium we can assume that $HNO_3$ is a weak acid and associates, so withdrawing protons from the system and allowing OH bridges to form. These do not appear to form in methanol where mixed complexes containing $H_2O$, MeOH, and perhaps $NO_3^-$ almost certainly exist.[3-8] The association of $HNO_3$ seems then to occur when the acetone is added. Ligand-MeOH exchange rates should increase as the coordinated OH leads to effective reduction in the charge of the ion and so polymerisation can proceed rapidly *via* the vacant co-ordination sites to give a range of products, as is observed. We thus realize that the idea, implicit in past formulations, that this type of product is a single phase is quite incorrect and that it is in fact a complex mixture, only partially resolvable at present, although often with a fixed and reproducible overall stoicheiometry.

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