

Aluminium-27 Nuclear Magnetic Resonance Studies of the Hydrolysis of Aluminium(III). Part 3.¹ Stopped-flow Kinetic Studies

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The decomposition of two different types of hydrolysed aluminium(III) solutions following the addition of acid has been observed using ²⁷Al n.m.r. and pH measurements. It has been possible to characterise the way in which the ion $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{OH}_2)_{12}]^{7+}$ decomposes and to suggest a mechanism to explain the observations. Decomposition is fast and seems to be controlled by the rate of exchange of water ligands on Al^{3+} . The major component of a metal-hydrolysed solution behaves similarly if an excess of acid is added, but if the acid addition is limited much more complex behaviour is observed which may indicate the formation and eventual decomposition of a different intermediate species. The high-molecular-weight material present decomposes much more slowly and so is believed to have a different type of structure to that of the above Al_{13}^{7+} cation cluster.

DILUTE hydrolysed aluminium(III) solutions have been much studied by observing how the polymeric species present break down either in the presence of a complexing agent which removes free Al^{3+} from the system²⁻¹⁰ or by the simple addition of acid.¹¹ In all cases several rates of change of the measured parameter were detected, the fastest being attributed to the initial presence of Al^{3+} and $[\text{Al}_2(\text{OH})_2]^{4+}$ (hereafter, Al_2) and the slowest to the production of Al^{3+} from colloidal or particulate material. One or two intermediate rates were also observed and these were believed to be associated with the decomposition of less highly polymerised material. An inevitable problem which arises when interpreting these results is that the composition of the solutions and the structure of their components is unknown,⁸ except that Al_2 and $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{OH}_2)_{12}]^{7+}$ (abbreviated Al_{13}) are likely to be present,¹² and there is really no way in which the rates obtained can be related to any particular component. Aluminium-27 n.m.r. spectroscopy offers the possibility of following the decomposition of different species after acid addition as well as the increase that occurs in the concentration of Al^{3+} . Unfortunately, because of the inherent insensitivity of this method, such work has to be carried out at much higher concentrations than the previous investigations so that comparison with them may not be straightforward, in particular, the rates of decomposition are expected to be much faster. That this was indeed so was found in preliminary experiments where decomposition after the addition of acid was in many cases complete by the time the sample was in position in the spectrometer probe. It was thus decided that the only way in which data were likely to be obtained was to use stopped-flow n.m.r. apparatus such as had recently been developed at Warwick.¹³

EXPERIMENTAL

The stopped-flow technique has been described previously¹³⁻¹⁷ and was adapted to ²⁷Al n.m.r. spectroscopy on the Warwick Bruker WH90 spectrometer using the ¹³C probe at 22.63 MHz and unlocked field. A short dwell time was used (25 μs) in order to accumulate data sufficiently rapidly, 20 scans taking 1 s altogether being sufficient to obtain a

good spectrum from a narrow resonance. The disc storage space available allowed 20 spectra to be accumulated in a minimum time of 30 s, and reactions were monitored over periods of 30 s up to 25 min. All free induction decays were given an exponential multiplication to minimise any variation in linewidths, and the resulting frequency-domain spectra were all given the same phase correction. It was not possible to be certain that saturation did not affect the results, although the ²⁷Al relaxation times ($T_2 \approx 0.03$ s, pulse interval 0.05 s) were sufficiently small that provided only small changes in T_2 occurred during the course of a given experiment then the results should not be significantly affected. The linewidth of Al^{3+} does vary with pH,¹⁸ but the pH changes were relatively small in a given run and the resulting changes in T_2 can probably be neglected. The width of the sharp Al_{13} resonance on the other hand has been found to vary very little. Care had also to be taken to minimise the field drift since the poor spectral definition which is a requirement for fast data accumulation (5 Hz per point) means that line intensities are very sensitive to changes in line frequency of the order of 1 or 2 Hz, although the short duration of the experiments is a considerable help here. The instant of sampling assigned to a data point has been taken as the median time of a scanning period.

Temperature control provided a major problem. Both the probe and the solutions prior to mixing were either at ambient temperature or were held at the required temperature by thermostatted gas flows. However, the mixing of concentrated acid and, effectively, base, generates heat of reaction sufficient to raise the temperature of the mixture by up to 6 °C, so that the temperature rises rapidly during mixing and then falls slowly to probe temperature over a period of ca. 5 min. This is equivalent to adding a small perturbation to the rates observed with a rate constant in the region of 0.003 s⁻¹. The pH changes which occurred during reaction were determined separately in open stirred beakers using a standard glass electrode and the result plotted on a calibrated chart recorder. The overall response time of this system was about 1 s. One slow reaction was followed entirely using standard n.m.r. techniques.

All solutions were hydrolysed to $m = 2.5$ ($m = \text{OH added/Al present}$) and either an excess of acid was added to cause decomposition entirely to Al^{3+} or the acid addition was limited so as to reduce m to 2.0 or 1.3.

RESULTS

(a) *Sodium Carbonate Hydrolysis*.—The fast hydrolysis of AlCl_3 solution using $\text{Na}_2[\text{CO}_3]$ at *ca.* 90 °C gives a solution in which about 75% of the Al occurs as Al_{13} and the remainder as a high-molecular-weight material which has an unobservably broad ^{27}Al resonance.¹ It seems certain that these solutions contain no Al^{3+} or Al_2 , the fast reacting species according to previous work. Such solutions have a ^{27}Al n.m.r. spectrum which consists of a single sharp line at 62.5 p.p.m. due to the AlO_4 group in the Al_{13} . Addition of acid causes this line to disappear and the sharp line due to Al^{3+} to appear at 0 p.p.m. so that we can in principle monitor two resonances. A variety of experimental conditions was used.

(i) *Addition of excess of acid at 300 K nominal*. Equal volumes of a hydrolysed solution 0.5 mol dm^{-3} in Al and 3.0 mol dm^{-3} HCl were used to give finally a solution containing all Al^{3+} . Twenty scans were taken per point and sets of scans were separated by 2.5-s intervals. Reaction was very fast and the Al_{13} resonance was already undetectable by the first data acquisition (*ca.* 2 s) while the Al^{3+} had reached 80% of the intensity that it was to attain in 45 s, although it continued to increase thereafter. The reaction was then followed using a longer time scale (300 scans per point separated by 60 s). The results are plotted in Figure 1. The reason for the fall in intensity towards the end of this run is not known but probably is the result of field drift which has set in at the end of the experiment. In an attempt to observe the decay of the Al_{13} signal we then carried out an experiment at reduced temperature.

(ii) *Addition of excess of acid at 273 K nominal*. Twenty scans were taken separated by 2-s intervals (Figure 2). Interestingly, the two rate constants for decay of Al_{13} and increase of Al^{3+} in this time are measurably different and the amount of Al^{3+} continues to increase well after all the Al_{13} has apparently disappeared (Figure 3). However, the signal-to-noise ratio for the Al_{13} is very poor, and it is possible to argue that the Al^{3+} signal is increasing because remaining but unobserved Al_{13} is still decomposing. We thus made a limited acid addition such that not all the Al_{13}

was destroyed and so could be monitored throughout the experiment.

(iii) *Limited acid addition at 300 K nominal*. In this case

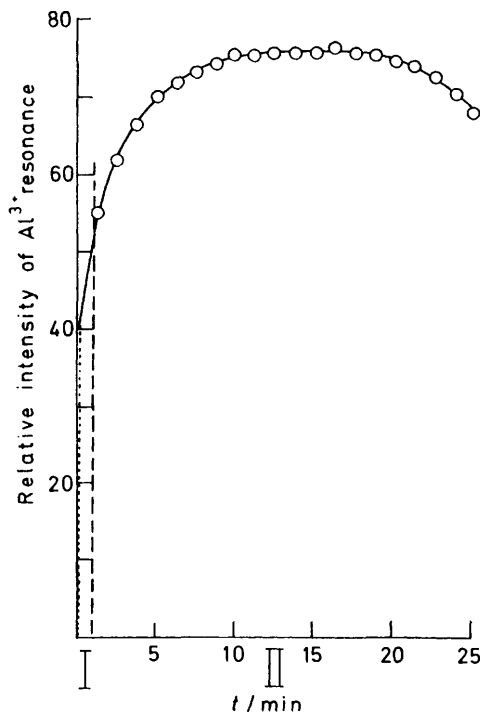


FIGURE 1 The rate of appearance of Al^{3+} after mixture of an excess of HCl with a sodium carbonate-hydrolysed solution nominally at 300 K. Region I refers to the short-period experiment and II to the long-period one. Only the points for the latter are plotted

0.6 mol dm^{-3} HCl was used which reduced the value of m from 2.5 to 1.3. The temperature rise on mixing is now only 3 °C. Twelve scans were taken separated by 1-s intervals so as to try and monitor the very fast changes

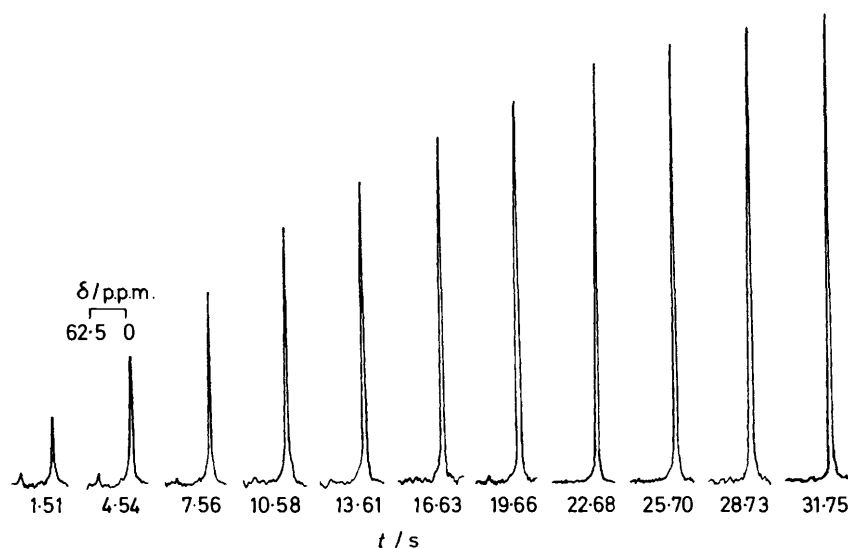


FIGURE 2 The ^{27}Al n.m.r. spectra obtained during a stopped-flow experiment nominally at 273 K. The resonance of the remaining Al_{13} is only particularly evident in the first two spectra. The times marked are the centre points of the accumulation periods. Only the first 11 spectra are shown with the p.p.m. scale marked on the second spectrum of the series

expected. Some of the spectra are shown in Figure 4 and the results are plotted in Figure 5(a). The Al_{13} decomposition is again too fast to observe and its intensity remains constant during the time of observation, whereas the Al^{3+} signal increases steadily to reach 60% of its final value by

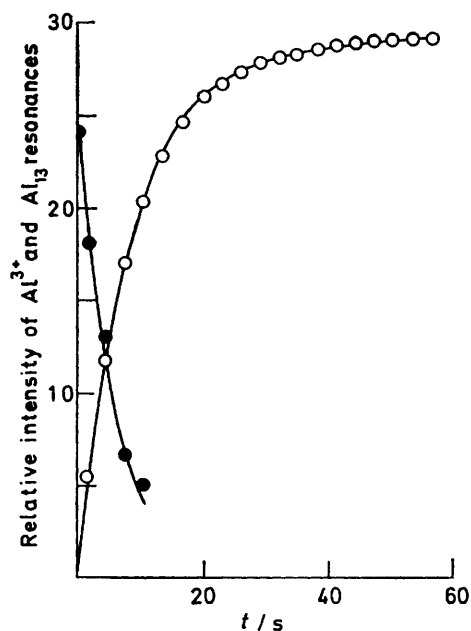


FIGURE 3 Rate of decay of the Al_{13} resonance (●) and of the appearance of Al^{3+} (○) after mixing an excess of HCl with a sodium carbonate-hydrolysed solution nominally at 273 K. The decay of Al_{13} is now slow enough for a rate constant to be extracted (the curve drawn is an exponential). Note that the Al^{3+} has attained only some 80% of its final intensity at the end of this experiment. The intensity scales for the Al_{13} and Al^{3+} are not related

30 s. A longer experiment showed that no further change occurred after 2 min.

pH changes. In run (iii) the pH fell rapidly when the acid was added and considerably overshoot its equilibrium value, to which it returned at a rate approximating the formation of Al^{3+} , although the shape of the curve is far from exponential [Figure 5(b)]. If an excess of acid is added then the pH simply falls directly to a new equilibrium value.

(b) *Metal Hydrolysis.*—The composition of solutions hydrolysed by the slow dissolution of aluminium metal in aqueous AlCl_3 is much more complex than that of the $\text{Na}_2[\text{CO}_3]$ -hydrolysed ones; the former contain Al^{3+} , Al_2 , and

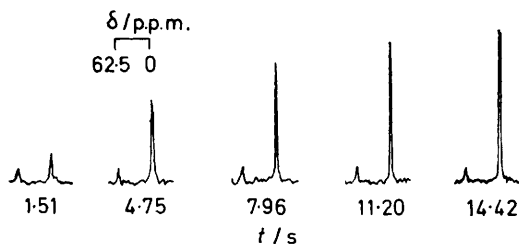


FIGURE 4 The ^{27}Al n.m.r. spectra obtained after limited acid addition to a sodium carbonate-hydrolysed solution nominally at 300 K. Alternate spectra are shown from the first nine of a run. The chemical-shift scale is indicated on the second spectrum of the series

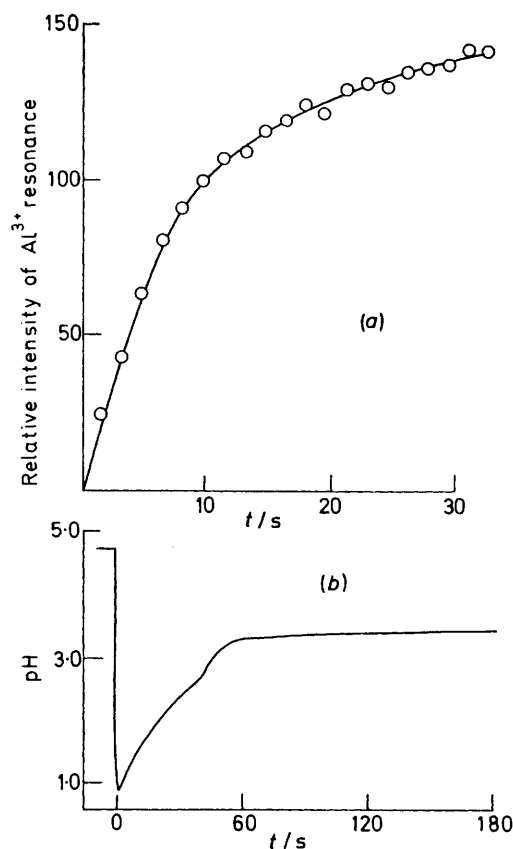


FIGURE 5 (a) Rate of appearance of Al^{3+} after a limited addition of acid to a sodium carbonate-hydrolysed solution nominally at 300 K. The peak height has attained 60% of its final intensity by 30 s. (b) pH Changes in the same solution but on a longer time scale

only a little Al_{13} . The major components are of somewhat higher molecular weight than Al_{13} and have resonances which are broad and cannot be observed in the type of experiment described here (see Part 2¹). Equally, the Al_{13} is not present in sufficient quantity for it to be observed so

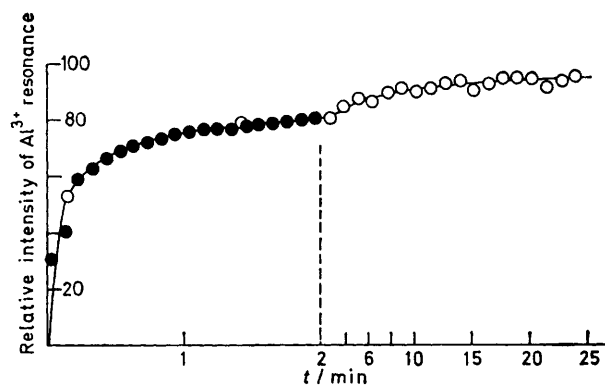


FIGURE 6 Rate of appearance of Al^{3+} after mixing an excess of HCl with a metal-hydrolysed solution nominally at 300 K. The results of two experiments on different time scales are plotted: (●), 40 scans per spectrum with 4 s between the end of one accumulation and the start of the next; (○) 300 scans per spectrum with 1 min between groups of scans

TABLE 1

Apparent rate constants obtained on addition of acid to a sodium carbonate-hydrolysed solution, 0.5 mol dm⁻³ in Al

Experiment (a) (i)	T/K	[HCl]/mol dm ⁻³	Resonance used	k/s ⁻¹	Assigned reaction
(i)	300	3.0 (excess)	Al ³⁺ (two rates)	0.006 ± 0.001	polymeric fraction <i>ca.</i> 25% aluminium content
			Al ₁₃ (one rate)	0.2 ± 0.04 > 0.5 (est.)	terminal-stage breakup of Al ₁₃ first-stage breakup of Al ₁₃
(ii)	273	3.0 (excess)	Al ³⁺ (one rate measured) *	0.12, 0.11 ± 0.03	terminal stage breakup of Al ₁₃
			Al ₁₃ (one rate)	0.17, 0.15 ± 0.03	first-stage breakup of Al ₁₃
(iii)	300	0.6 (limited)	Al ³⁺ (one rate)	0.14 ± 0.04	terminal-stage breakup of some of Al ₁₃
			Al ₁₃ (one rate)	> 0.5 (est.)	breakup of some of Al ₁₃

* Slower reaction not measured.

TABLE 2

Apparent rate constants at 300 K obtained on addition of acid to metal-hydrolysed solutions, using the Al³⁺ resonance

Experiment (b) (i)	[Al] mol dm ⁻³	[HCl] mol dm ⁻³	k/s ⁻¹	Rate arises from breakup of:
(i)	0.5	3.0 (excess)	0.13 ± 0.05	<i>ca.</i> 70% Al, Al ₁₃ -like material
			0.03 ± 0.02 0.0024 ± 0.0005	<i>ca.</i> 20% Al, not Al ₁₃ -like <i>ca.</i> 10% Al, polymeric material
(ii)	0.25	0.125 * (limited)	non-exponential increase	complex behaviour involving an intermediate

* In fact concentrated HCl was used in this case (not a stopped-flow experiment) and the concentration given has been scaled to represent admixture of equal volumes of solution so as to be comparable with the rest of the data.

that all that can be monitored for these solutions is the increase in the Al³⁺ signal after acid addition. Experiments were carried out as follows.

(i) Addition of excess of acid at 300 K nominal. Two runs

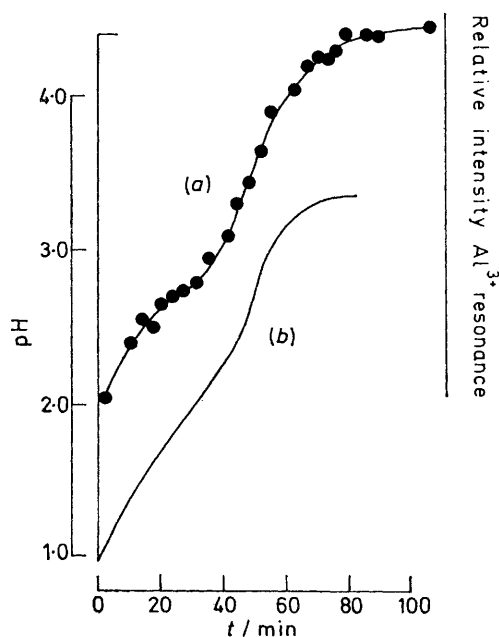


FIGURE 7 (a) Rate of appearance of Al³⁺ after a limited acid addition to a metal-hydrolysed solution nominally at 300 K. Intensities were derived from initial amplitudes of the free-induction decays (for details see J. W. Akitt and A. Farthing, *J. Chem. Soc., Dalton Trans.*, 1981, 1617). (b) The corresponding pH changes

were carried out, one at 40 scans per spectrum with 4 s between sets of scans and one with 300 scans separated by 60 s. The results differ markedly from the previous ones (Figure 6). Seventy percent of the Al³⁺ appears at a fast rate and thereafter two further slow rates of increase are detected. The pH, as before, simply falls to a new equilibrium value.

(ii) Limited acid addition at 300 K nominal. In this case the reaction was slow enough to monitor using an n.m.r. spectrometer in the standard operational mode. The changes in Al³⁺ intensity and in pH are shown in Figure 7. The pH fell and overshoot its equilibrium value and then returned slowly to equilibrium following a complex sigmoidal curve. The Al³⁺ intensity paralleled these changes, the rate of change being some four times slower than in the previous experiment. Further small additions of acid produced a pH trace which had a very similar sigmoidal shape.

Rate constants. The curves above can be quantified in terms of pseudo-first-order rate constants. We lack reliable values for the initial and final intensities of the various steps and so have used the method of Mangelsdorf to extract the constants from the curves.¹⁹⁻²¹ The resulting numbers are in Tables 1 and 2 together with an estimate of their reliability.

DISCUSSION

The previous kinetic attempts to study the composition of hydrolysed aluminium(III) solutions fall into two groups: those where the measurements have been made spectrophotometrically *in situ*, the complexing agent also causing the changes that it was desired to monitor, but in the presence of acetate buffer;²⁻¹⁰ and a second single

report where the decomposition was brought about by added acid, and the spectrophotometric method used to monitor changes in aliquots taken from the solution.¹¹ There are several differences between these two approaches. The colorimetric method probably works by removing free Al^{3+} from solution and so perturbing the equilibrium between the species present. The role of the acetate buffer is obscure although it must be present for the colorimetric assay to work. Unfortunately, no consideration seems to have been given to its possible effect on the aluminium ions present. The system Al^{3+} -acetate is an old established and now superseded method for mordanting in dyeing. Mixing the two components causes the stronger acid $[\text{Al}(\text{OH})_6]^{3+}$ to protonate the weaker acetate so that some hydrolysis takes place. Such solutions show broad ^{27}Al resonances and slowly deposit a basic aluminium acetate.²² This obviously cannot happen with a fully hydrolysed solution, but once some decomposition has occurred it seems reasonable to suppose that the acetate buffer will interact with the now hydrolysable products in a complex way so that we are then studying what may be a much perturbed hydrolysed system. Thus, although the results of this work indicate correctly the presence of a variety of a species with different rates of breakdown, we cannot be sure that these relate in any simple way to the composition of the initial solution. The addition of acid on the other hand causes the amount of Al^{3+} to increase and this may or may not interact with the other ions present. Thus the reactions involved in the two approaches will be different and there seems no reason to expect any numerical correlation between the rate constants obtained, nor indeed between the number of species.¹¹

The work reported here obviously falls into the second category.

Sodium Carbonate Hydrolysis.—In this case we have a solution which we know contains just two components. This is probably the first time that such a solution has been studied since earlier, dilute preparations all tended to be prolonged and may have contained other products. The observed behaviour is quite straightforward. Seventy-five percent of the material reacts to form Al^{3+} with $k = 0.2\text{--}0.11\text{ s}^{-1}$ depending upon temperature. This must ultimately be derived from the Al_{13} whose resonance, however, decays much faster than Al^{3+} appears. The remaining 25%, which breaks down much more slowly, is related to the high-molecular-weight fraction which must be constituted very differently to the Al_{13} .

The way in which the Al_{13} breaks down, when related to its structure, allows us to propose a quite detailed scheme as to the general mechanisms which may be involved. It is obvious that the Al_{13} and Al^{3+} resonances reflect different things. The decay of the Al_{13} is probably not associated with the breakup of the whole ion. In fact, because ^{27}Al is a quadrupolar nucleus, it is only necessary that the regular symmetry around the AlO_4 unit be destroyed for the Al_{13} resonance

to broaden and apparently disappear under the conditions of spectroscopy used here. We thus can accept a scheme of the form: $\text{Al}_{13} \longrightarrow \text{intermediate} \longrightarrow \text{Al}^{3+}$. We also note that, even though we can only provide limited figures, the indications are that the decay of the Al_{13} resonance is much more temperature sensitive than is the increase seen for Al^{3+} . If we now turn to consider a space-filling model of Al_{13} , we observe that it consists of a cluster of 40 O^{2-} ions held together by the much smaller Al^{3+} and appropriately protonated. The central AlO_4 unit does not appear to be accessible to direct attack by an H_3O^+ ion. The most obvious feature of the molecule, and the most likely point of initial attack, is the shell of 24 OH^- bridges between the Al^{3+} ions, which are fully exposed to the exterior. Protonation and breaking an OH bridge involves providing an H_2O to maintain the co-ordination of the aluminium ions, but if only one bridge is broken the molecule seems unlikely to be able to distort sufficiently to allow access to the H_2O since the whole structure is very rigid. This is presumably the reason why it is relatively stable in what are always quite highly acidic solutions. Each octahedral Al is bonded to five bridging oxygens and thus at least four bridges must be protonated before the octahedron can move much out of its normal position. Thus we need co-operative multiple protonation to occur before decomposition can be initiated.

The intensity and pH changes observed for limited acid addition suggest that the first stage of reaction involves the attachment of about 40% of the added protons to the Al_{13} cations which will have different extents of protonation. Above some level, which appears to be about 10 protons per cation, the AlO_4 unit becomes involved, perhaps by proton hops to the O^{2-} bridges and the n.m.r. signal is lost at a rate determined by this mechanism. These much loosened cations then start to break up at a rate determined by the rate of water-ligand exchange on Al^{3+} , namely 0.13 s^{-1} at 25°C ,²³ and the necessary protons are supplied by the excess of acid in solution and the less protonated cations whose n.m.r. signal remains unaffected. The figure of 10 proposed is of course very rough since we can take no account of any $[\text{Al}_2(\text{OH})_2]^{4+}$ formed and the 25% of high-molecular-weight material may act as a proton sink. The inflexion in the pH curve is sufficient to indicate that the process is not a simple one and could arise through attack on Al_2 fragments produced during the initial stages of breakdown.

Metal-hydrolysed Solutions.—In this case the majority of the Al is contained in an ion or ions of somewhat greater molecular weight than Al_{13} together with some polymeric material of much higher molecular weight. It is thus not surprising to obtain quite different behaviour upon acid addition. The major component gives rise to Al^{3+} at a rate very similar to that observed for Al_{13} if sufficient acid is added, and we can say that we are probably observing the decomposition of an Al_{13} -like material, a reasonable conclusion for a component which also possesses tetrahedrally co-ordinated Al . Two

other rates are also discernible relating to *ca.* 20 and 10% of the total Al, the latter, slower rate being presumably related to the decomposition of the high-molecular-weight material. The intermediate rate is believed to arise from the decomposition of a component which has not been separated from the Al₁₃-like material by gel chromatography and so is of similar molecular weight. The significant reduction in its rate of decomposition indicates that it does not have the same structure.

Limited acid addition gives a quite new type of response. The fast rate of Al³⁺ increase is not seen and the reaction follows a sigmoidal path which probably arises because of the slow production of a fairly fast reacting intermediate. These changes presumably involve the major component which we have suggested is related to Al₁₃ in its structure but which appears to need heavy protonation for rapid breakup to occur, whereas limited protonation seems capable of initiating the same reaction sequence several times.

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