Aluminium-27 Nuclear Magnetic Resonance Studies of the Hydrolysis of Aluminium(III). Part 4.[1] Hydrolysis using Sodium Carbonate

By **J. W. Akitt** * and **Alan Farthing**, School of Chemistry, University of Leeds, Leeds LS2 9JT

Hydrolysis with sodium carbonate carried out in the shortest possible time and without subsequent ageing produces solutions whose composition depends upon the degree of hydrolysis achieved and contain varying proportions of $[Al(OH_2)_6]^{3+}$, $[(H_2O)_4Al(OH)_2Al(OH_2)_4]^{4+}$, and $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$ and apparently no other species, although many new ions can form quite quickly as the solutions age. The fundamental hydrolysis reaction of Al^{3+} seems to involve only these three species and so can be described in surprisingly simple terms. As soon as any ageing is allowed then a variety of reactions can occur leading in general to the production of larger polymers, some of which may have definable structures.

THE nature of the species which are formed when solutions containing $[Al(OH_2)_6]^{3+}$, (1), are hydrolysed has been studied now for some 120 years and is still far from understood, which indicates at the same time both the intractable nature of the problem and the interest that it engenders. N.m.r. spectroscopy has recently been employed and has provided much new information about the monomeric aquo-complex (1) and the exchange rates of its ligands [2-4] although it has become evident that only ^{27}Al n.m.r. is likely to give us accessible information about the species formed during hydrolysis.[5] Earlier electrometric work had produced two conflicting viewpoints about the size of the species formed, either $[Al(OH)]^{2+}$ and $[Al_2(OH)_2]^{4+}$ or else larger polymers such as $[Al_6(OH)_{12}]^{6+}$, $[Al_{10}(OH)_{22}]^{8+}$, or $[Al_{24}(OH)_{60}]^{12+}$ being favoured, although it is now apparent that this controversy arose because different groups of workers were studying lower or higher degrees of hydrolysis respectively, where the species present are in fact different.[5] Only two such ions have had their existence confirmed *via X*-ray structural determinations of crystals of their sulphate salts, namely $[(H_2O)_4Al(OH)_2Al(OH_2)_4]^{4+}$, (2),[6] and $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$, (3),[7] a ' spherical cluster ' cation whose charge can differ from +7. The first was believed to appear at low degrees of hydrolysis with *m ca.* 1 (m = OH added/Al present) and the second at high m (approaching $m = 2.5$). The difficulty encountered in recognising electrometrically what other species might be present seems to have arisen in part from the fact that any assignment had to be based on very small voltage differences while it has always been recognised that the solutions are in some form of *quasi*-equilibrium which may lead to misleading electrometric results.[8] The first ^{27}Al n.m.r. investigation showed that both of the ions (2) and (3) can be detected in solution and that, contrary to expectation, the ion (1) is present throughout almost all the possible range of hydrolysis, decreasing in concentration almost linearly with m to zero when $m = 2.5$.[5] This result is not readily reconciled with a scheme based on the successive generation of species of increasing degree of polymerisation but points more to a fairly simple type of behaviour involving only two or three species. The behaviour is indeed very similar to that found for the hydrolysis of Be^{2+} which involves just Be^{2+}, $[Be_2(OH)]^{3+}$ and $[Be_3(OH)_3]^{3+}$.[9] However, it was thought that the system could not really be as simple as this because a proportion of the Al did not give rise to an observable n.m.r. resonance under the conditions used, so that there is at least one other species present which is either very large or has

Summary of the results of Parts 4 [a] and 5 [b]

Method of hydrolysis	Temperature/ °C	Initial ageing	Ageing temperature/ °C	Total time for preparation	Species present [c] (by ^{27}Al n.m.r.) $m = 2.5$	$m = 1.0$
(1) $Na_2[CO_3]$ solid	90	30 min	90	1 h	(3); non-visible high molecular-weight polymer	(1); (3)
(2a) $Na_2[CO_3]$ solution	100	nil		20 min	Almost all (3); with just a little non-detectable polymer	(1); (2); trace of (3)
(2b) Same as (2a). 4 months ageing			27		(3); (3)-like material with tetrahedral Al seen at 80 °C	(1); (2)
(2c) Same as (2a). 92 days ageing			100		(1) only. Polymeric species without detectable resonances also present. Precipitate forms (3), almost pure ($m = 2.4$)	
(3) Electrolysis	40	15 h				
(4) Al metal wire [Al] *ca.* 1 mol dm^{-3}	100	long prep.	100	48 h	(3); (1); (2); (3)-like polymer; non-(3)-like polymer	
(5) Al metal foil	40	long prep.	40	48 h	(3); non-visible high molecular-weight polymer [*cf.* from method (1)]	
(6) Al metal wire, high concentration	100	long prep.	100	48 h	Same as from method (4) but much Al not detectable, and a larger proportion of non-(3)-like polymer evident	

[a] Hydrolysis methods (1)—(3). [b] Results of methods (4)—(6) from Part 5 (see following paper). [c] (1) = $[Al(OH_2)_6]^{3+}$; (2) = $[(H_2O)_4Al(OH)_2Al(OH_2)_4]^{4+}$; (3) = $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$.

Al in a very distorted environment so as to cause rapid quadrupole relaxation.[10] Comparison was made at the time with Aveston's ultra-centrifugal work [11] and this led us to suggest that the unobserved material was an octamer, although we will show here that the variability of the system is such that this conclusion cannot be sustained. Indeed, our gel-permeation chromatography results [12] have shown that when $m = 2.5$ there is no evidence of species other than (3) and a *high* molecular weight material in those particular solutions, the ion (3) comprising some 75% of the total Al. We have shown recently that other observable species can be formed if the conditions of hydrolysis are varied,[12–14] in particular if the hydrolysis is slow. We will report these results in detail in Part 5 (see Table) but it is pertinent to note here that a variety of different species do exist, although not apparently in freshly prepared solutions if hydrolysed relatively rapidly with solid sodium carbonate. We report here an extensive investigation of the effects of the rate of hydrolysis and of the time and temperature history of the subsequent ageing upon the composition of these solutions, using principally the 62.5 p.p.m. resonance. We will show that initially quite simple behaviour is followed by a complex and varied series of changes.

EXPERIMENTAL

Aluminium-27 n.m.r. spectroscopy was carried out on a Bruker HFX-3 which had been modified to work in the FT mode. Samples were held in 8 mm tubes which were in turn placed in 10 mm tubes with D_2O in the annulus as lock. Spectra were taken into 2K or 4K of memory with a dwell time of 50 μs giving a sweep width of 10 kHz and a pulse repetition rate usually of 8.8 s^{-1}. Care was taken to ensure that the results were not affected by saturation effects. The number of scans used for a spectrum depended on m and increased from 300 to 3 000 with increasing m. A problem arose during phase correction of the final spectrum because we wished to be able to distinguish the Al_2 resonance underneath the sharp Al^{3+} line. It does however seem to be almost impossible to do this sufficiently well to obtain quantitative results since it becomes a matter of guesswork to decide when the remaining asymmetry is correct. Measurements were thus made of the intensities of the resonances due to (1) and (3) only. Measurements were made of the height and width at half-height to give a relative area figure. This is accurate in the case of (1), which overlaps with the signal of (2), because the intensity of the latter is negligible due to the breadth of the line. Some data were also obtained by comparing initial free-induction decay intensities with that obtained from a standard solution, a procedure which is applicable if only a single resonance is present and which allowed us to obtain an absolute measure of the amount of aluminium which was contributing to a spectrum. Aluminium salts were used as follows: $AlCl_3\cdot6H_2O$ (BDH, 97%), $Al[ClO_4]_3\cdot8H_2O$ (Koch-Light, pure crystals), $Al[NO_3]_3\cdot9H_2O$ (BDH AR), and anhydrous $AlBr_3$ (GPR). Solutions made from the perchlorate and the bromide were checked for aluminium content and the latter for bromide content in case any HBr was lost during dissolution of the anhydrous $AlBr_3$. We have substantiated the diagnostic value of the resonance of ion (3), (*a*) by using the $[AlW_{12}O_{40}]^{5-}$ anion [15] and (*b*) by examining dilute solutions of crystals of the sulphate salt of (3), which after 20 000 scans showed only the sharp resonance at 62.5 p.p.m. and a trace of (1) arising from decomposition in the dilute solution.

Anhydrous $Na_2[CO_3]$(BDH, AR) was used as hydrolysing agent either as the solid or as a 1.25 mol dm^{-3} solution. Hydrolysis was carried out in initial phases of the work (and in the earlier work [5,7]) by adding solid $Na_2[CO_3]$ to $AlCl_3$ (1.67 mol dm^{-3}) solution at 90—100 °C on a stirrer hotplate, in portions so as to maintain as clear solution as possible. If a permanent precipitate was obtained then the preparation was abandoned. The preparation was then aged with stirring while hot for 30 min. It was subsequently found necessary to attempt to minimise the time of hydrolysis so as to be able to follow the effects of ageing over short periods of time. The best way found to achieve this was to add $Na_2[CO_3]$ solution (1.25 mol dm^{-3}) to boiling $AlCl_3$ solution (1.67 mol dm^{-3}) on the stirrer hotplate as fast as possible without allowing any permanent precipitate to form, particular care having to be given to avoiding any build up of material on the stirrer bead. A solution hydrolysed to $m = 2.5$ could be obtained in this way in as little as 20 min. Ageing was avoided by cooling the solution in ice as soon as the addition of $Na_2[CO_3]$ solution was complete.

An electrolytic hydrolysis was carried out using a one-compartment cell with a platinum gauze cathode and an aluminium foil anode; $AlCl_3$ (1 mol dm^{-3}) was used as electrolyte. A current of 0.25—0.5 A was passed through 50 cm^3 of the solution with only a small portion of the anode immersed in the solution and which was lowered as dissolution proceeded. The compound $Al(OH)_3$ formed at the cathode and some of this redissolved [the method has been used to produce anion-free $Al(OH)_3$ [16]]. The final solution obtained after *ca.* 15 h had $m = 2.4$. Aluminium-27 n.m.r. indicated that it contained only ion (3) and a small proportion of (1) (*ca.* 4%).

RESULTS AND DISCUSSION

Hydrolysis with Solid $Na_2[CO_3]$.—The original ^{27}Al n.m.r. work was carried out in the continuous wave mode.[5] It is generally easier to make satisfactory phase corrections when using this technique so that the area of the resonance of (2) could be estimated with reasonable accuracy. It was also possible to demonstrate that ion (2) really was present by a differential saturation experiment. The results are presented as a plot showing how the concentrations of (1), (2), and (3) vary with m from $m = 0$ to 2.5. These resonances did not account for all the aluminium present and the way this missing material varied was obtained by difference. We attempted to reproduce these results using the Fourier transform mode, but for the reasons given above, we found it impossible to estimate accurately the area of the resonance due to (2). We thus could plot only the concentration changes for (1) and (3) and include those for (2) in the unobservable material. These results and the earlier ones [5] are compared on this same basis in Figure 1 where it will be seen that there is good although not perfect agreement, the differences demonstrating the variability which is encountered in this work. The behaviour of (2) should be noted since in the remainder of the work we will have to accept it as such, though unseen. Its concentration rises roughly linearly with m up to $m = 1$ and then falls to zero at about $m = 2.5$. Since the concentration of (1) also falls roughly linearly, then we see that the ratio [(1) : (2)] is approximately constant for $m > 1$ with a value of *ca.* 4 : 1.

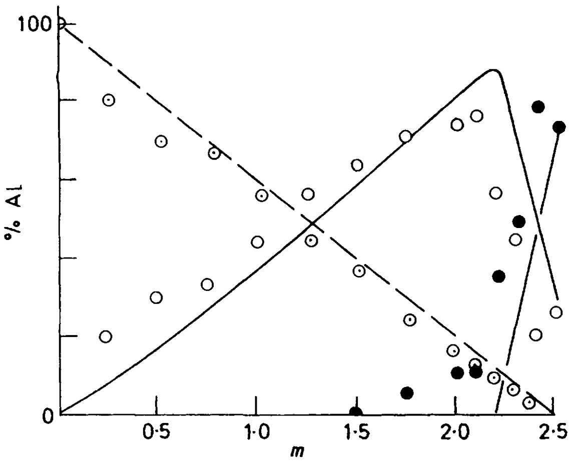

FIGURE 1 The course of hydrolysis of $AlCl_3$ solution by solid $Na_2[CO_3]$ determined by ^{27}Al n.m.r. spectroscopy. The lines (——) and (— — —) depict earlier results and the circles, data from the present work: ⊙ = $[Al(OH_2)_6]^{3+}$, (1), ○ = $[Al_2(OH)_2]^{4+}$ plus unseen material, ● = $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$, (3)

Thus, if some hydrolysis has occurred, then the presence of (1) implies also the presence of some (2). When a solution is heated to *ca.* 80 °C the aluminium ions interchange environments and the narrow resonance of (1) broadens due to the influence of the very short relaxation time of aluminium in the ion (2). This phenomenon will be noticed in many of the high-temperature spectra reported here and in Part 5 (see Table).

Anion effects. It is well known that anions co-precipitate with gelatinous aluminium hydroxide and there is a general belief in the literature that some anion specific interaction may be involved in hydrolysis. In order to test this belief some hydrolyses were carried out using solutions of $AlBr_3$, $Al[NO_3]_3$, and $Al[ClO_4]_3$ as well as $AlCl_3$. It was found that all the solutions could be hydrolysed equally easily to $m = 2.5$ and that differences were manifested only in the tendencies of the solutions to form precipitates on standing; solutions containing Br^- forming a precipitate in about 2 weeks, NO_3^- in 3 months (a gel formed), Cl^- in 4 months, while for ClO_4^- almost no precipitate had formed after one year. Thus the initial behaviour is anion-independent, whereas the behaviour on ageing is affected by the anion. Because of the time scale involved in these experiments this was not realised sufficiently early for the effect to be investigated in detail and the salt $AlCl_3$ was used for the remainder of the work principally on the grounds of cost, availability, and ease of assay of Cl^-. We cannot, however, be sure that our results apply universally although it is possible that the reactions leading to precipitation may be side reactions following the reactions observed here, and certainly Cl^- appears to interact with colloidal dispersions in these solutions.[17]

Hydrolysis with Sodium Carbonate Solution.—The changes which occur with time for hydrolysed aluminium solutions have been described by many authors [8,18-20] and the results of different methods of hydrolysis observed by us also seem to be time dependent.[13] It was decided to see whether the effects of ageing could be detected in the ^{27}Al n.m.r. spectra. In order to maximise any effect which might be observed we developed the method of rapid hydrolysis described above. The results for minimum hydrolysis time and no ageing are shown in Figure 2 and it will be seen that the differences between this and Figure 1 are most striking. Ion (3) is present at much lower m values and its concentration is increased at all higher values of m. The concentration of (1) still falls linearly to zero at $m = 2.5$ and the concentration of the unobservable fraction is much reduced and indeed must consist principally of (2) at all but the highest value of m. These results thus indicate that the short term, high-temperature ageing used previously causes ion (3) to be converted into new species with unobservably broad resonances.[12] The immediate result of hydrolysis thus appears to be that (2) and then (3) are formed in sequence in a way which is very reminiscent of the beryllium system.[9,21] The components seem to be in equilibrium involving fast reactions with (2) peaking in concentration at about $m = 1$ and (3) at $m = 2.4$; these values reflect the OH : Al ratios in the two species, 1.0 and 2.46 respectively {assuming in the latter case that the ion is $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$, although its actual charge in solution is not known}. This then probably represents the fundamental path of hydrolysis in this system and confirms unequivocally the conclusions of Aveston [11] that no species of intermediate size are formed. It is also obvious that (3) is formed rather quickly and in a solution where (1) and (2) are the major or even sole species present. It seems remarkable that (3) should be the next highest species formed after (2) and that it should be formed so easily, although the organic-phase hydrolysis [14] shows that it can form very rapidly indeed.

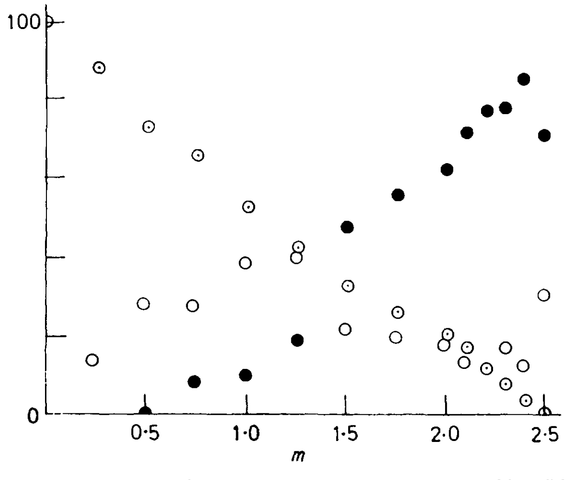

FIGURE 2 The course of hydrolysis of $AlCl_3$ solution by $Na_2[CO_3]$ solution determined by ^{27}Al n.m.r. Key as in Figure 1

Mesmer and Baes[22] have also concluded that a simple scheme as depicted here may be correct, although their results point to the possible existence of the ions $[Al_3(OH)_4]^{5+}$ and an Al_{14} species, rather than the Al_2 and Al_{13} species (2) and (3). These results are based on measurements made after equilibrium had been attained at high temperatures, where we have shown that ageing occurs quite rapidly and high molecular weight species are formed which are much larger than (3). Their conclusions are thus apparently in reasonable agreement with ours but should not be, this presumably pointing to the deficiencies of the electrometric method for these solutions.

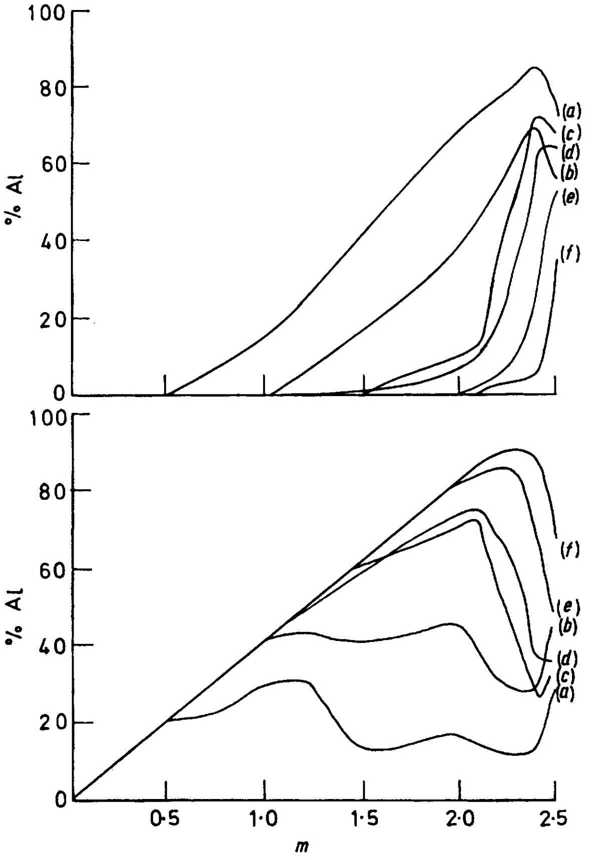

FIGURE 3 Evolution of the curves of Figure 2 with ageing. The upper set of curves show the progressive reduction in the concentration of (3) and the lower set the progressive increase in the concentration of unobservable material. The concentration of (1) remains unchanged throughout the series and as shown in Figure 2. The ageing conditions were (*a*) 4 h at ambient temperature, (*b*) two weeks at ambient, (*c*) 4 months at ambient, (*d*) as (*c*) then 1 h at 100 °C, (*e*) 5 months at ambient then 4 h at 100 °C, (*f*) as (*e*) but 8 h at 100 °C

The experiments were repeated several times and were found to be somewhat irreproducible because it was impossible to carry out the hydrolysis in a standard time especially for high *m*. The proportion of ion (3) for instance varied from 75 to 91% at $m = 2.5$.

Medium term ageing effects. A set of solutions was then allowed to age at ambient temperature over an extended period and the changes were monitored by ^{27}Al n.m.r. Very little further change occurred after 4 months and then periods of heating were used to accelerate the changes towards what might be a steady state. The results are shown in Figure 3 where the changes in proportion of (3) and the unobserved material [which includes (2)] are shown separately. The proportion of (1) remained unaltered throughout, decreasing almost linearly with *m* to zero at $m = 2.5$. The interconversion of the species is easily followed and it will be noticed that concentration of the unobserved species peaks at different *m* after different periods of ageing, increasing from *ca*. 2 to 2.4 with time. This may be related to the OH : Al ratio in the species concerned, although since the conditions are clearly non-equilibrium such a conclusion could be misleading. The short period, high-temperature ageing used in the original preparative method and the present method give similar final concentrations of species observable at 300 K. The spectra at 350 K of some room-temperature aged solutions were however found to exhibit broad ^{27}Al resonances, as shown in Figure 4. Heating a solution of low *m* value which contains only (1) and (2) causes the narrow line of the former to broaden due to exchange with the latter and this feature persists while ion (1) remains observable. No other

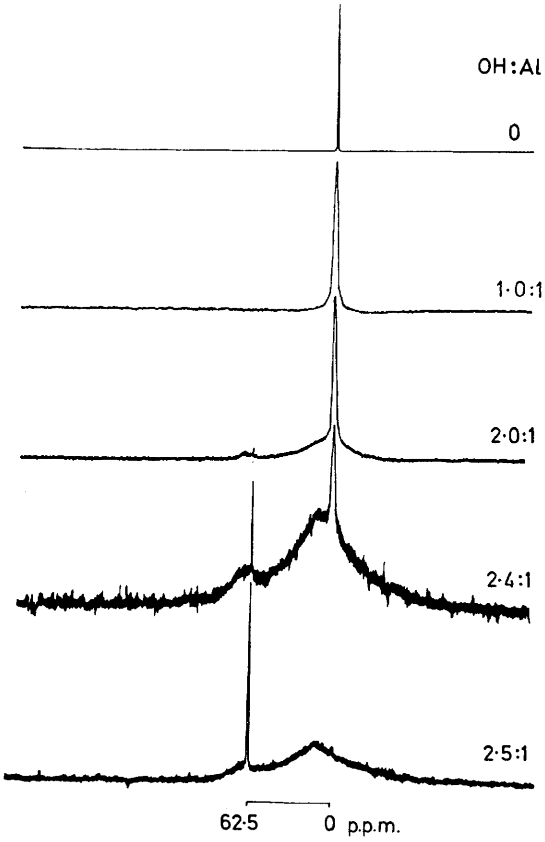

FIGURE 4 Aluminium-27 n.m.r. spectra taken at 80 °C of $Na_2[CO_3]$-hydrolysed solutions (rapid method) aged as in (*f*) in Figure 3

resonances are observed until $m > 1.75$ when two broad ones appear, in the octahedral and tetrahedral regions of the spectrum respectively. Comparison with Figure 5 shows that the high-field line is not due to the octahedral Al in ion (3). Indeed, Figure 5 demonstrates the difference which exists between the original preparative method with *high*-temperature ageing and the faster one with *low*-temperature ageing newly described here. In the former case there is a high molecular weight material present [12] which is always unobservable whereas ageing at ambient temperature produces species which must be smaller in size for their spectrum to behave in the way observed. The existence of aluminium in tetrahedral sites is of interest since this almost certainly indicates that other cluster type compounds exist with a structure related to that of (3) and this will be discussed more fully in Part 5. The previous suggestion [5] that this component might be an octamer cannot be sustained and it is now clear that in comparing the earlier n.m.r. results [5] with those of Aveston [11] there was no means of guaranteeing that like was being compared with like, such is the variability of the system.

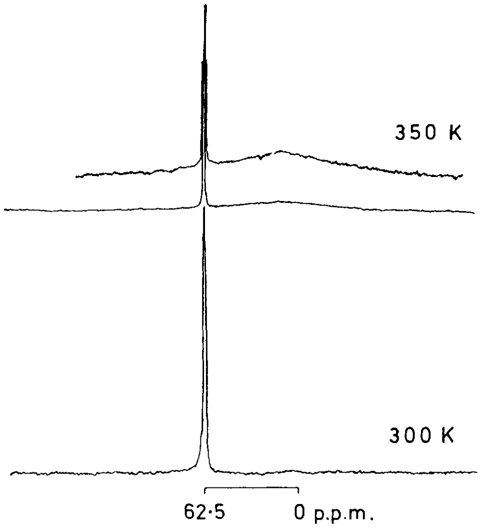

FIGURE 5 Aluminium-27 n.m.r. spectrum of a solution freshly hydrolysed with solid $Na_2[CO_3]$ taken at *ca.* 80 °C and showing the octahedral resonance of (3). Uppermost trace × 4

The only other information which we have been able to obtain about these new species is summarised in Figure 6, which gives the linewidths of the resonance of (1) in solutions aged at ambient temperature as a function of m. The viscosity of these solutions decreases with increased m so that the increase in linewidth observed must indicate the existence of some interaction in solution involving (1). The linewidth, which changes overall by a factor of five from 8 to 40 Hz, changes slowly at first but then undergoes a pronounced increase for $m \geqslant 2$ and in the region where the species formed on ageing are at their peak concentration. The change could be due to weak complexation of (1) by the species formed or to exchange of whole octahedra between polymer and solution. Unfortunately, we cannot be sure that the changes are due to a major species, or to an observable species, although we can probably accept that the species involved must be hydrolysed to an OH : Al ratio of at least 2 : 1.

Prolonged ageing. This produces a variety of effects which are not always reproducible, although a number of likely end results can be recognised. The non-reproducibility presumably arises because quite small changes in the early history of a solution can later affect profoundly the way the polymerisation reactions develop. In general, prolonged ageing of a solution with $m > 2$ causes little physical change. A precipitate may form and then (1) is detectable in the mother-liquor. The precipitate may be heavy or light, in the latter case broad ^{27}Al resonances can usually be detected in solution. In all cases the resonance of (3) will have disappeared well before the later changes set in, and in many cases no resonances will be observable. Thus we note that none of either (3) or the species giving broad resonances seems to give rise to ' alumina ' directly, an observation which agrees well with an earlier finding that rapid precipitation brought about by adding base to a freshly hydrolysed solution gives rise to a distinct type of precipitate which is not alumina-like.[20,23] An example of prolonged ageing monitored by ^{27}Al n.m.r. is shown in Figure 7 (see also Table, line 2a).

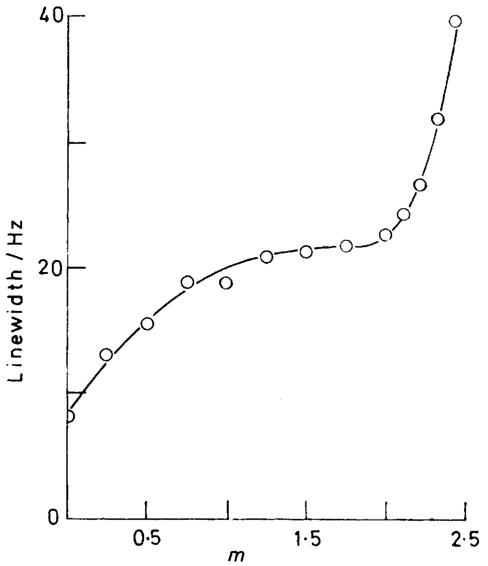

FIGURE 6 Variation of linewidth in the spectrum of (1) with m at ambient temperature

We have studied in some detail the effect of experimental conditions on the course of ageing and the decomposition of (3). Our findings can be summarised thus: (*a*) at 27 °C, $m = 2.5$, ion (3) has a half-life of about 2 years, a precipitate is produced within one year and eventually no broad resonances appear in the n.m.r. spectrum; (*b*) at 77 °C, $m = 2.5$, ion (3) is lost

1 800 times more rapidly and broad resonances are formed with only a little precipitate; (*c*) at 27 °C, $1 < m < 2.4$, (3) decomposes more rapidly than when $m = 2.5$, the broad resonances appear, very little precipitation occurs and there is no change in the concentration of (1); (*d*) at 77 °C, $m = 2.4$, the rate of decomposition of ion (3) increases just 30 times although the outcome is similar to that in the previous example. The plots for the early part of the two high-temperature runs are shown in Figure 8. The result of case (*b*) differs from that depicted in Figure 5 because the initial solution was prepared by the fast method and the high-temperature spectrum of Figure 5 was obtained in a short time.

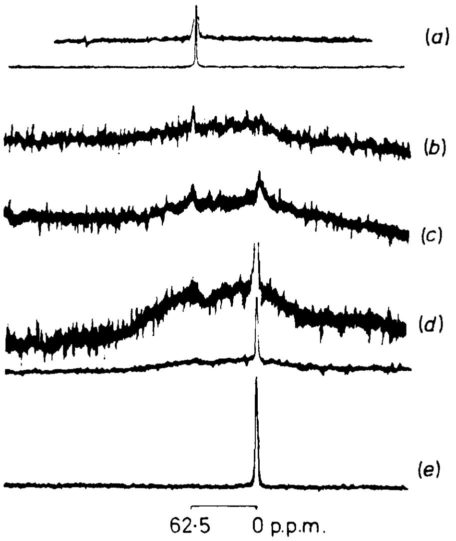

FIGURE 7 The effect of prolonged high-temperature ageing on a solution with $m = 2.5$, followed by ^{27}Al n.m.r. spectroscopy: (*a*) unchanged, (*b*) after 10 d, (*c*) 21 d, (*d*) 50 d, (*e*) 92 d

Temperature of initial preparation. With one exception, all the preparations described here were carried out at near 100 °C, at which temperature ageing is rapid. The electrolytic preparation in contrast was rather prolonged but the temperature never exceeded 40 °C. It is rather surprising to note that the product was almost entirely complex (3), there being no sign of any broad resonances in the spectrum and no unobservable Al. Thus, if the hydrolysis can be made to go at lower temperatures, the rate of reaction of the complex ion (3) produced is insufficient for any ageing effects to be observed. This result is consistent with the ambient temperature ageing effects described in Figure 3. It gives added support to our contention that (3) is the principal product of the hydrolysis of Al^{III}, although an unstable one. All the complications noted above arise because we are obliged to use higher temperatures with base hydrolyses so that the precipitates which inevitably form will redissolve before they undergo change into other less soluble material.[18,19]

Formation of $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$, (3). The way in which an AlO_4 unit is produced during hydrolysis in an acid medium is of considerable interest and the rapidity with which (3) is formed is surprising. It is first detected at *m ca.* 0.75 and when there is already an appreciable amount of ion (2) present. It only persists if $m \geqslant 1.0$, since below this point there is sufficient acidity in the system to cause decomposition by acid attack and (2) is the only stable product. As hydrolysis proceeds (3) is formed more abundantly although some must be destroyed again right through the hydrolysis process. In order for it to form at all then and especially for $m < 1.0$, it must be formed as the sodium carbonate solution is added, which is to say in the very inhomogeneous conditions which exist at the solution–basic precipitate interface. The precipitate which forms as soon as the base is added has to be encouraged to dissolve as rapidly as possible otherwise it changes into an insoluble material of which gibbsite may be a component.[18] It presumably contains many basic pockets protected from the acidic environment by the gelatinous $Al(OH)_3$ where it is quite likely that some $[Al(OH)_4]^-$ will be found. The precipitate will be attacked by the acidic $[Al(OH_2)_6]^{3+}$ ions, (1), to form the dimer (2) and this may well be in a more hydrolysed state at the interface to give $[Al_2(OH)_3]^{3+}$, $[Al_2(OH)_4]^{2+}$ *etc.* The existence of some such species is probably crucial since in order to form ion (3) from (1) the number of water molecules which are co-ordinated to aluminium has to be reduced from 78 to 40 per molecule of (3). The production of

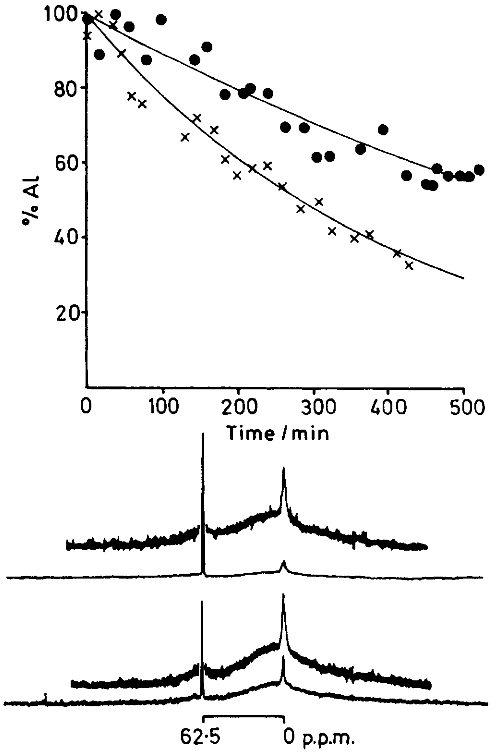

FIGURE 8 Rate of decomposition of complex (3) for solutions at 80 °C with $m = 2.5$ (●) and 2.4 (×). The spectra are from the solution with $m = 2.4$, $t = 0$ (upper) and 433 min (lower)

(2) reduces the number to be lost by 12, leaving 66, but some 4 water molecules per dimer still have to be lost. The water thus has to be labilised if ion (3) is to be formed rapidly and the increasing number of negative charges on the 'Al_2' complex should weaken the co-ordination of the water. We note that the complex ion (3) seems to be the sole product and that other large molecules are only formed at a later stage, which implies that labilisation and interconnection of dimer units occurs in a regular way. The structure of (3) can be described as being of six oxygen-sharing dimer units bridging the edges of the central tetrahedron.[24] The O–O distance in an AlO_4 unit is very similar to the separation between a pair of apical O atoms in the position normal to the plane of the $Al(OH)_2Al$ ring in (2) (310 and 290 pm respectively) and it is tempting to suggest that the Al_2 units nucleate around an $Al(OH)_4^-$ unit. Such a process would be direct and could be fast since there is no requirement for the stepwise formation of intermediate sized fragments which might then be expected to be present in solution also, especially at lower *m* values, and be detectable by n.m.r. spectroscopy. This also seems more likely than a solid-state reaction involving the $Al(OH)_3$ gel, which has the reduced number of ligands as required but which would be expected to give rise to fragments of variable size upon attack by acid. It may be significant that the fastest method of hydrolysis known, in an organic phase, where $[Al(OH)_4]^-$ seems unlikely to be present leads to the production of only a small amount of (3),[14] although the fact that it is produced at all may indicate that several mechanisms may operate.

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