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Some observations on the reaction of tris-isopropoxoaluminium(III) with limited quantities of water and with *ortho*-substituted phenols

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Abstract

Evidence from ^{27}Al NMR studies (MAS and solution) of the hydrolysis of aluminium isopropoxide suggests that the reactive intermediate in isopropanol solution is a trimeric form of the alkoxide. This form appears to be favoured in more strongly coordinating solvents. Reactions of $Al(OPr^i)_3$ with *ortho*-substituted phenols provide further support for the intermediacy of the trimer since 2,6-disubstituted phenols give products $(RO)Al(OPr^i)_2$, $(R'O)Al(OPr^i)(OH)$, $(R'O)_2Al(OH)$ (R = 2,6-dimethyl- and 2,6-di-t-butylphenyl-; R' = 2,6-diphenylphenyl-) which, like the trimer, contain four-, five- and six-coordinate aluminium. The nature of the product of the partial hydrolysis, '$AlO(OPr^i)$' depends on details of isolation but four-coordinate aluminium is the dominant species. Thermolysis of the material (to 800 °C) failed to give crystalline phases but ^{27}Al MASNMR revealed the occurrence of five-coordinate aluminium in an intermediate phase in the thermal decomposition.

Introduction

Aluminium isopropoxide (tris-isopropoxoaluminium(III), $Al(OPr^i)_3$) is an important industrial intermediate. In many applications a partial hydrolysis is involved which, probably optimistically, can be represented by the following equation:

$$Al(OPr^i)_3 + H_2O \longrightarrow \text{'}AlO(OPr^i)\text{'} + 2Pr^iOH \qquad (1)$$

Despite the commercial importance of the process, little fundamental understanding of the reaction exists. This investigation set out to obtain more data on the process by using, in particular, ^{27}Al NMR spectroscopy as an analytical tool.

The structure of $Al(OPr^i)_3$ was a matter of some debate for a number of years, but finally an X-ray single crystal analysis [1] confirmed the tetrameric structure, involving both four- and six-coordinate aluminium, originally proposed by Bradley [2]. Akitt and Duncan [3], using ^{13}C NMR spectroscopy demonstrated the existence of two isomers of the tetramer, related as mirror images. This is anticipated from the structure which could be viewed as a pseudo-tris-chelate aluminium(III) complex.

There have been persistent reports of a trimeric form of $Al(OPr^i)_3$; for example Mehrotra [4] suggested the existence of both trimeric and dimeric forms of the compound. Kleinschmidt *et al.* [5] used proton NMR, together with computer simulation of the spectra, to investigate the interconverions of the various forms of the alkoxide; a hexameric intermediate was implicated. Support for this postulate was obtained from mass spectroscopic studies of $Al(OPr^i)_3$ [6]. Integration of peak areas in the proton NMR spectrum of liquid $Al(OPr^i)_3$ [5] suggested that the trimeric component may contain five-coordinate aluminium. A vibrational spectroscopic study of a low boiling form of the alkoxide, supposed to contain the trimer, was unable to provide definitive support for five-coordination [7]. However, ^{27}Al NMR studies carried out by Kříž *et al.* [8] support the presence of five-coordinate aluminium in the trimeric species.

Experimental

Aluminium isopropoxide was supplied by Rhône-Poulenc Chemicals Ltd.

A number of methods of partial hydrolysis were attempted, the following mimic the industrial process.

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Method 1. $Al(OPr^i)_3$ (0.63 mol) and isopropanol (IPA) (2.1 mol) were heated to reflux when an IPA (1.78 mol)/water (0.6 mol) mixture was added at 2 $cm^3 min^{-1}$ via a vapouriser set to 170 °C. On completion of the addition, the vapouriser and peristaltic pump were washed through with IPA (0.1 mol). A sample of the cloudy solution was taken for ^{27}Al NMR analysis (sample A). The cloudy solution distilled at 95 °C to afford a solid product which was further treated at 90 °C under reduced pressure (28″ Hg) to give sample B.

Method 2. $Al(OPr^i)_3$ (0.30 mol) in IPA (1.2 mol) was heated to reflux. A mixture of IPA (2.5 mol) and water (0.28 mol) was prepared and added cold to the refluxing solution at a rate of 1.8 $cm^3 min^{-1}$; on completion of the addition the pump was washed with IPA (0.25 mol). The reaction mixture was treated on a rotatory evaporator (40 °C, 28″ Hg) for 1 h after which solid sample C was taken.

Method 3. $Al(OPr^i)_3$ (0.3 mol) in IPA (1 mol) was heated to and maintained at 30 °C. IPA (4.2 mol) and water (0.28 mol) were mixed and added cold at a rate of 1.4 $cm^3 min^{-1}$. On completion of the addition, the pump was washed with IPA (0.1 mol) and a sample of the precipitated solid was taken — sample D.

Method 4. $Al(OPr^i)_3$ (1.0 mol) was dissolved in IPA (1000 cm^3). Aliquots of this solution were taken and treated with water such that the mole ratios, $Al(OPr^i)_3$:H_2O, were 1:0.25, 1:0.5, 1:0.75 and 1:1. The mixtures were centrifuged and ^{27}Al NMR spectra were measured immediately. A second preparation of the 1:0.75 ($Al(OPr^i)_3$:H_2O) mixture was refluxed for 1.5 h, cooled, centrifuged, and subjected to ^{27}Al NMR analysis.

Method 5. This procedure attempts to simulate as closely as possible the industrial procedure. $Al(OPr^i)_3$ (0.73 mol) was dissolved in IPA (2.36 mol) and heated to reflux. A mixture of IPA (2.15 mol) and water (0.7 mol) was added to the refluxing solution via a vapouriser set at 180 °C, at a rate of 1.8 $cm^3 min^{-1}$. On completion of the addition, the pump was washed through with IPA (0.1 mol) and sample E was taken. The reaction mixture was distilled at 84 °C to remove the bulk of IPA (4.60 mol) — sample F was then taken. Solvent 260/290* was added and, after 10 min mixing, sample G was taken. The reaction mixture was further distilled, the temperature rising to 180 °C at which point it was held constant for 1 h.

For comparative purposes a further sample H was aquired from the industrial process.

Method 6. $Al(OPr^i)_3$ in IPA was treated directly with water (mole ratio 1:1). The resulting solid was filtered and washed. Following drying, it was examined by ^{27}Al MASNMR spectroscopy, following which samples were heated to 200, 400, 600 and 800 °C in a Carbolite furnace. The products were shown to be X-ray amorphous and were examined by ^{27}Al MASNMR.

Reaction of $Al(OPr^i)_3$ with ortho-substituted phenols

A typical procedure is as follows. $Al(OPr^i)_3$ (2.4 g, 0.012 mol) in dry toluene (30 cm^3) was heated to reflux. 2,6-Di-t-butylphenol (1.85 cm^3, 0.09 mol) in dry toluene (20 cm^3) was added dropwise; on completion of the addition, the mixture was refluxed for 2 h. IPA was distilled off, a further aliquot of dry toluene was added and reflux was continued for a further 2 h. The solvent was finally removed by distillation and the solid product was dried in a vacuum desiccator.

The products were not anhydrous. Since the objective was to mimic the industrial partial hydrolysis process, a calculated decision was taken to use the phenols to trap possible intermediates under conditions as close as possible to those of methods 1–5 above. The 'academically' preferable option of working under strictly anhydrous conditions was therefore rejected.

A similar procedure was adopted for reactions between $Al(OPr^i)_3$ and 2-t-butyl-4-methylphenol, 2,6-diphenylphenol and 2,6-dimethylphenol.

Physical measurements

NMR spectra (^{27}Al) were obtained with a Bruker AC(E) 300 MHz spectrometer at 78.206 MHz, the standard was $[Al(H_2O)_6]^{3+}$. Solid specimens were examined in Delrin rotors which were spun at 5 kHz at the 'magic angle', which was set with KBr. IR data were recorded with a Perkin-Elmer 1710 FTIR instrument. Attempts to obtain X-ray powder data were made using Philips equipment employing cobalt Kα radiation.

Results

Kříž *et al.* have reported δ (octahedral) = 3.2 ppm and (tetrahedral) = 58.5 ppm at 52.31 MHz for tetrameric $Al(OPr^i)_3$. Working at 78.206 MHz, we observed resonances in benzene solution at 0.67 (octahedral) and 60.26 (tetrahedral) ppm (see Table 2).

Methods 1–3 (experimental) were designed to add the requisite quantity of water to a solution of $Al(OPr^i)_3$ in isopropanol to produce a product mixture which was as homogeneous as possible. In practice, the final solution was, at best, cloudy. The

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*Solvent 260/290 = mixed aliphatic hydrocarbon solvent.

methods differed in the temperatures of both additive and bulk solution. The relevant NMR data are gathered into Table 1. Sample A (solution phase) shows four resolved resonances. One sharp band occurs at 0.62 ppm, close to that observed for the octahedral resonance of $[\mathrm{Al(OPr^i)_3}]_4$. A new broad band is seen in the octahedral region (5.10 ppm) together with a very broad tetrahedral resonance at 66.2 ppm, possibly arising from the overlap of two resonances, which shows a distinct shoulder at 38.2 ppm. It is probable that at least two species were present, one probably unreacted $[\mathrm{Al(OPr^i)_3}]_4$, the other a new material with three aluminium environments. The solid B, obtained by removal of solvent, also shows three aluminium environments. Method 2 was similar to method 1 but differed in the precise conditions used to isolate solid C. This material also shows three aluminium environments but absolute peak maxima differ from those observed for B. Method 3 involved adding the IPA/water mixture to a cooler solution of $\mathrm{Al(OPr^i)_3}$ in IPA. The precipitated solid D was examined in benzene solution and gave a ^{27}Al NMR spectrum with a single broad resonance in the tetrahedral region at 64.5 ppm.

Method 4 studied the effect of adding different molar quantities of water. All solutions were maintained at 70 °C (for NMR measurements also). The data are recorded in Table 2. All solutions became cloudy on addition of water, the solid phase became more apparent as the $\mathrm{Al(OPr^i)_3{:}H_2O}$ ratio approached 1:1. The data in Table 2 are largely for solution phases (at 70 °C) after centrifugation. The spectra are complex and when the $\mathrm{Al(OPr^i)_3{:}H_2O}$ ratio is >1, octahedral, penta-coordinate, and tetrahedral aluminium sites are located; reflux periods of 1.5 h (1:0.75 system) cause no significant change. When the ratio becomes 1:1, the penta-coordinate environment is lost from both solution and solid phases. Also, if the $\mathrm{Al(OPr^i)_3}$ (1 M) solution is old (4 months), only a broad tetrahedral resonance remains.

Method 5 (Table 1), although in many respects similar to methods 1–3, is closer to the actual industrial process in terms of work up following hydrolysis of the $\mathrm{Al(OPr^i)_3}$. Sample E, taken immediately following hydrolysis, showed three aluminium environments, but further work up (samples F and G) produce specimens which lack evidence of a five-coordinate aluminium site and are very similar to the spectrum of sample H obtained directly from the manufacturing process.

Method 6 (Table 1) involved the rapid addition of water to $\mathrm{Al(OPr^i)_3}$ in IPA in a 1:1 mole ratio. The solid product shows a single resonance associated with tetrahedral aluminium when dissolved in benzene solution. The product was heated successively to 200, 400, 600 and 800 °C. Changes were monitored by ^{27}Al MASNMR and XRD. Perhaps surprisingly all the specimens appeared X-ray amorphous; no evidence for crystalline aluminium oxides was obtained for specimens heated to higher temperatures. The spectra of the heated specimens were broad with many spinning side bands. The major feature of note is the steady development of a resonance located in the 36–29 ppm region which is attributable to five-coordinate aluminium; tetrahedral resonances are discernable in the specimens heated to 400 and 600 °C. The spinning side bands in the 800 °C specimen spectrum are so dominant that they may hide a resonance at $\delta \sim 0$ (octahedral) and the pos-

TABLE 1. ^{27}Al NMR data for $\mathrm{Al(OPr^i)_3}$ hydrolysis products (δ vs. $[\mathrm{Al(H_2O)_6}]^{3+}$)

Methods 1–3	δ (ppm)	Method 5	δ (ppm)	Batch hydrolysis	δ (ppm)
Sample A ($\mathrm{C_6H_6/C_6D_6}$ solution)	0.62 (sharp) 5.10 (broad) 38.2 (sh) 66.2 (broad)	Sample E	7.16 (w) 68.7 41 (sh)	Product: 1:1 = ALISO:$\mathrm{H_2O}$; in $\mathrm{C_6H_6/C_6D_6}$ solution	62.8
Sample B (MASNMR)	0.63 31.95 50.10	Sample F	5.0 (w) 67.5 (asymm.)	As above, heated to 200 °C (MASNMR)	−3.72 60.9
Sample C (MASNMR)	2.88 30.60 64.89	Sample G	5.0 (w) 67.7 (asymm.)	400 °C (MASNMR)	36 60.9
Sample D ($\mathrm{C_6H_6/C_6D_6}$ solution)	64.5 (broad)	Sample H	8.0 (vw) 71.6	600 °C (MASNMR)	36.1 61.7
				800 °C (MASNMR)	29.6 0 (overlap with SSB)

TABLE 2. Batch hydrolysis of $Al(OPr^i)_3$ – ^{27}Al NMR of solutions obtained on addition of indicated molar quantity of water to 1 M $Al(OPr^i)_3$ in n-propanol ('Experimental', method 4)

Nature of substrate	^{27}Al NMR data (vs. $[Al(H_2O)_6]^{3+}$), δ (ppm)		
	six-coordinate	five-coordinate	four-coordinate
$Al(OPr^i)_3$, 1 M in	9.52 9.17		66.7 (br)
n-propanol (A) (70 °C)			
	6.60	45.4	66.7 (br)
$Al(OPr^i)_3$, 1 M in	5.09	38.8 (br)	61.2 (br)
dmso-D_6 (70 °C)			
(A) + 0.25 mol H_2O	9.12		65.4
	6.51	43 (br)	65.4
(A) + 0.5 mol H_2O	9.10		64.8
(70 °C)	6.60	46.2	64.8
(A) + 0.75 mol H_2O	9.11		61.7
(70 °C)	6.60	42.9	61.7
(A) + 0.75 mol H_2O	9.10		69.7
1.5 h reflux (70 °C)	6.80	43.1	69.7
(A) + 1.0 mol H_2O	9.54 9.20		
(70 °C)			68 (br)
	6.62		60.6
(A) + 1.0 mol H_2O	5.40		62.1
Solid phase (MAS)			
Solution, aged 4 months (A)			72.0 (br)
$Al(OPr^i)_3$ in benzene	0.67		60.26
solution (r.t.)			

sibility that a tetrahedral resonance is still present could not be entirely dismissed.

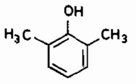
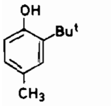
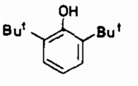
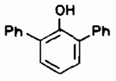
Table 3 gathers data obtained on products of reactions carried out between various *ortho*-substituted phenols and $Al(OPr^i)_3$ in a 1:1 mole ratio (2:1 and 3:1 in the case of 2,6-diphenylphenol). 2,6-Disubstituted phenols give reproducible products $(RO)Al(OPr^i)_2 \cdot xH_2O$ (R = 2,6-dimethyl- or 2,6-di-t-butylphenol) which contain four-, five- and six-coordinate aluminium, whereas the product from 2-t-butyl-4-methylphenol shows only four- and six-coordination for the metal. With 2,6-diphenylphenol the behaviour was different. Greater ratios of the phenol were necessary to obtain products and hydrolysis of Al-OPr^i linkages was a competing reaction. The products $(RO)Al(OPr^i)(OH)$ and $(RO)_2Al(OH)$ contain four-, five- and six-coordinate aluminium and also show a very sharp asymmetric band in the IR at 3517 cm^{-1}. This is assigned to a bridging hydroxyl group.

Discussion

^{27}Al is a quadrupolar nucleus ($I = 5/2$) and spinning at the 'magic angle' will not average to zero the second order quadrupole effects that will be present in a non-cubic lattice. Under these circumstances the maximum of the observed $-\frac{1}{2} \leftrightarrow \frac{1}{2}$ transition does not correspond to the isotropic chemical shift. Nor, when comparing solid state spectra, do significant differences in peak maxima necessarily imply differences in shielding [9]. Despite these problems it is fortunate that the 'apparent chemical shifts' obtained from peak maxima do reflect quite well the coordination number of aluminium. Thus resonances with maxima close to $\delta = 0$ (relative to $[Al(H_2O)_6]^{3+}$) reflect octahedral environments whereas the range 45–80 ppm implies tetrahedral coordination. Also there is evidence that the intermediate range (29–44 ppm) is attributable to five-coordination about aluminium [8, 10]. Some caution is required for MASNMR spectra since spinning side bands associated with other resonances may occur in the 'pentacoordination region'.

The attempts in methods 1–3, 4 and 5 ('Experimental') section and Tables 1 and 2) to simulate the partial hydrolysis of $Al(OPr^i)_3$ which is regularly carried out on an industrial scale have produced a complex data set. Few positive conclusions can be drawn, but there are some interesting implications arising from the data. It is clear that the final product from the plant process contains tetrahedral aluminium only; it is also true that on ageing the laboratory

TABLE 3. Solid reaction products of phenols with aluminium isopropoxide — ^{27}Al MASNMR data

Phenol	Product	Analysis (calculated)	^{27}Al MASNMR data δ^a vs. $[Al(H_2O)_6]$ (ppm)
 C_8H_9OH	$(C_8H_9O)Al(OPr^i)_2\cdot 4H_2O$	C, 49.2; H, 5.9 (C, 49.7; H, 9.1)	55.7 (four-coordinate) 28.6 (five-coordinate) 1.28 (six-coordinate)
 $C_{10}H_{15}OH$	$(C_{10}H_{15}O)Al(OPr^i)_2\cdot 3H_2O$	C, 54.9; H, 7.8 (C, 54.8; H, 10.0)	62.7 (four-coordinate) 4.7 (six-coordinate)
 $C_{14}H_{21}OH$	$(C_{14}H_{21}O)Al(OPr^i)_2\cdot H_2O$	C, 65.5; H, 9.0 (C, 65.2; H, 10.0)	65.3 (four-coordinate) 36.6 (five-coordinate) 1.04 (six-coordinate)
 $C_{18}H_{13}OH$	$(C_{18}H_{13}O)Al(OPr^i)(OH)$ (phenol:ALISO^b = 2:1) IR 3517 cm^{-1}, sharp	C, 74.8; H, 5.44 (C, 72.4; H, 6.0)	62.9 (four-coordinate) 31.1 (five-coordinate) 3.47 (six-coordinate)
	$(C_{18}H_{13}O)_2Al(OH)$ (phenol:ALISO = 3:1) IR 3517 cm^{-1}, sharp	C, 79.9; H, 5.6 (C, 80.8; H, 5.0)	58.4 (four-coordinate) 36.6 (five-coordinate) 5.09 (six-coordinate)

^{a}Resonance maxima, i.e. *not* isotropic chemical shift. ^{b}ALISO = $Al(OPr^i)_3$.

specimens (e.g. Table 2) that materials containing tetrahedral aluminium ultimately result. The other clear observation is the persistence with which resonances attributable to octahedral, five-coordinate and four-coordinate aluminium are observed simultaneously (e.g. samples B and C in Table 1 and data in Table 2). Whilst it is not possible to totally eliminate the possibility that three distinct species co-exist, the quantitative similarity of the data to those of Kříž *et al.* [8] for *trimeric* $Al(OPr^i)_3$ at 70 °C (δ = 3.2, 33.1, 61.1 ppm) strongly suggest that the initial hydrolysis product has a structure based on that of trimeric $[Al(OPr^i)_3]_3$, and that therefore it is the trimeric form of the alkoxide which is the reactive intermediate.

Heating the hydrolysis product ($H_2O:Al(OPr^i)_3$ = 1:1, Table 1) failed to produce a crystalline phase. Over the intermediate range of temperatures considered, 200–800 °C, the growth of a five-coordinate aluminium resonance was noted; this is presumably an intermediate on the path to Al_2O_3 which would be obtained on heating to higher temperatures.

If indeed the trimeric form of the alkoxide is the intermediate, reaction with a material that might arrest the process at an earlier stage would provide support for, even if not confirmation of, the hypothesis. Accordingly, the reaction between $Al(OPr^i)_3$ and various *ortho*-substituted phenols was considered. Although some products were not as well defined analytically as we would have liked, the observations made were reproducible and the persistence with which some types of ^{27}Al MASNMR spectra were seen is, we believe, further evidence of the synthesis of single compounds. Reaction of $Al(OPr^i)_3$ with 2-t-butyl-4-methylphenol (ROH) in a 1:1 mole ratio afforded a product $(RO)(Al(OPr^i)_2\cdot 3H_2O$ (Table 3) which, like some of the solids obtained from hydrolysis reaction, contains only four- and six-coordinate aluminium. However, 2,6-dimethyl- and 2,6-di-t-butylphenol give 1:1 products which show the presence of four-, five- and six-coordinate aluminium and give spectra very similar to those attributed to the trimeric alkoxide species discussed above. Thus sterically hindered phenols stabilise the trimer and, by so doing, lend support to the view that it is indeed an

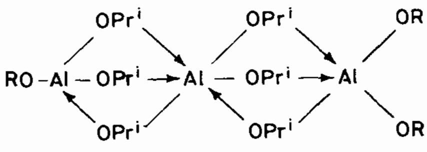


Fig. 1. Possible structure for '$(RO)Al(OPr^i)_2$'.

important intermediate in reactions of $Al(OPr^i)_3$ with both HOH and ROH. A possible structure for trimeric $(RO)Al(OPr^i)_2$ is shown schematically in Fig. 1.

Reaction with 2,6-diphenylphenol (R'OH) was slower and required a 2:1 mole ratio (phenol:alkoxide) to give a 1:1 product, $(R'O)Al(OPr^i)(OH)$; some hydrolysis also occurred, the moisture probably being of atmospheric origin. A 3:1 mole ratio of reactants afforded $(R'O)_2Al(OH)$. Sharp IR bands at 3517 cm^{-1} imply bridging OH groups [11] and given the great similarities of the ^{27}Al MASNMR spectra with those of the derivatives of other 2,6-disubstituted phenols, structures similar to Fig. 1 may be postulated. Indeed, the serendipitous ingress of moisture suggests that initial stages of hydrolysis of the alkoxide may involve replacement of (OPr^i) bridges with (OH) bridges in the trimer.

The balance of evidence in this paper suggests the reactive intermediate in the hydrolysis of $Al(OPr^i)_3$ to be a trimeric isomer, $[Al(OPr^i)_3]_3$ containing four-, five- and six-coordinate aluminium atoms when present in coordinating solvents. The final solid product has dominantly tetrahedral sites but is X-ray amorphous and fairly resistant to systematic investigation.

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