on the idea that the problem of activity coefficients for the reactants can continue to be avoided even while recognizing that the rates of many acid-catalyzed reactions fit neither $h_0$ nor $C_{H^+}$. The proposal is to introduce the activity of water as a rather fundamental variable and to diagnose a reaction by consideration of one or the other of two empirical parameters $w$ and $w^*$. These are, respectively, the slopes of plots of log $(k_{H^+}/h_0)$ vs. log $(a_{H_2O})$ and of log $(k_{H^+}/C_{H^+})$ vs. log $(a_{H_2O})$, the idea being that for any given reaction one or the other of these log–log plots will be reasonably linear. (In the event that neither plot is sensibly linear one can of course still look for acidity ranges where one or the other of the slopes is approximately constant.) In an approximate sense, ignoring the problem of non-linear plots, $w$ is close to zero when the slope of log $k_{H^+}$ vs. $-H_0$ is about unity, is negative when the slope is greater than unity and is positive when the slope is less than unity. Similarly, $w^*$ is close to zero when the slope of log $k_{H^+}$ vs. log $C_{H^+}$ is about unity.[36] These additional parameters clearly permit a more detailed classification of acid-catalyzed reactions than do the functions $h_0$ and $C_{H^-}$ alone. Classification by itself is, however, not a very exciting occupation and the much more interesting question is, does a consideration of $w$ and $w^*$ values give significant new insight into the problem of mechanism? Bunnett considers this question in detail and reaches the somewhat qualified conclusion that $w$ and $w^*$ values are frequently useful for mechanism considerations but that they occasionally lead to inconsistencies.

The data for the cyclohexanedione system cover a wide enough acidity range to permit analysis in terms of $w$ and $w^*$. The characteristics of the relevant plots are listed in Table IV. Two of the most obvious features of the results are: (a) there is a significant variation of slope with catalyst; (b) for a given catalyst when one of the plots, say for $w$ is straight, that for the other is likely to be curved. Both of these features are frequently indicated by Bunnett in his extensive tabulation of data.

We now turn to the mechanistic implications of these results. The first question is, what is the expected behavior for ketones and enols? Bunnett's Table I-1 lists data for several reactions of ketones to form enols.

(36) Bunnett actually introduces a third, related parameter, $w_a$, but for the present brief recapitulation we shall avoid consideration of this.

TABLE IV
SLOPES OF BUNNETT-TYPE PLOTS

| Catalyst | w plot | | w* plot | |
|---|---|---|---|---|
| | Type | w | Type | w* |
| For reaction of ketone, $k_f$ | | | | |
| HCl | Straight | 0.0 | Curve | $\sim -5$ |
| HClO₄ | Straight | 1.8 | Curve | $\sim -3$ |
| H₂SO₄ | Sl. curve | $\sim 0$ | | |
| For reaction of enol, $k_f$ | | | | |
| HCl | Curved | $\sim 5$ | Str. | $-3.7$ |
| HClO₄ | Curved | $\sim 8$ | Str. | $-1.1$ |
| H₂SO₄ | Curved | $\sim 3$ | | |

The $w$ plots are apparently usually linear with slope ranging from roughly 2 to 7; the $w^*$ plots are only occasionally linear with slopes in the order of $-1.5$. Bunnett does not list slopes for ketonization of enols, but if one were to assume approximate independence of keto–enol equilibrium with electrolyte concentration then the same slopes as above might be expected for the enol reaction. The results for ketones play a large role in the development of Bunnett's Chart I which lists his conclusions on correlation of $w$ and $w^*$ values with mechanisms. The relevant conclusions are that a larger $w$ than 3.3 and a larger $w^*$ than $-2$ indicate that water is acting as a proton transfer agent in the slow step.

Since from other considerations it has been concluded that the keto–enol transformation of cyclohexanedione involves a monohydrated ketone and probably also a monohydrated transition state, there is no strong reason to expect this reaction to behave exactly like those of other ketones. In fact, the results are rather different from that expected from Bunnett's Chart I. For the ketone reaction the $w$ plots are straight but $w$ is low and is in the expected range for "water acting as a nucleophile." Furthermore the slopes for the forward and reverse reactions are so different as formally to lead one to say that water was a nucleophile for one of the directions but a "proton transfer agent" for the reverse. This is, of course, an unreasonable conclusion. We do not wish to generalize from these results at the present time and will only indicate our belief that, relative to a consideration of the mechanistic implications of the hydration equilibrium and the Arrhenius parameters, a consideration of $w$ and $w^*$ values does not appear to add significantly to our understanding.

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# The Structures of Some Aluminum Alkoxides

BY V. J. SHINER, JR., D. WHITTAKER AND V. P. FERNANDEZ

Molecular weight and nuclear magnetic resonance spectral measurements indicate that aluminum $t$-butoxide exists in solution in a number of organic solvents over a temperature range from $-14$ to $74°$ as a cyclic dimer. There was obtained no evidence for dissociation of the dimer at higher temperature or by such basic solvents as dioxane or $t$-butyl alcohol. Similar evidence indicates that solid aluminum isopropoxide, dissolved in organic solvents, has the tetrameric structure proposed by Bradley.[8] It has also been shown that at higher temperatures, either on melting or in solution, this material is converted into a cyclic trimer which only slowly reverts to the tetramer at lower temperatures in the supercooled melt or in solution. The nuclear magnetic resonance spectra also allow some interesting conclusions concerning the mechanism of intramolecular alkoxide exchange.

## Introduction

The structures of aluminum alkoxides have been investigated by measurement of their molecular weights[1-5] and other physical properties such as dipole moment.[1] The available data have recently been summarized by Bradley.[6,7] Ulich and Nespital[1] suggested structure I for tetrameric aluminum alkoxides, such as the isopropoxide, by comparison with the structure of tetrameric thallium alkoxides suggested by Sidgwick and Sutton.[8] Mehrotra[4] suggested structure II (R =

(1) H. Ulich and W. Nespital, Z. physik. Chem., 165, 294 (1933).

(2) R. A. Robinson and D. A. Peak, J. Phys. Chem., 39, 1125 (1935).

(3) S. M. McElvain and W. R. Davie, J. Am. Chem. Soc., 73, 1400 (1951).

(4) R. C. Mehrotra, J. Indian Chem. Soc., 30, 585 (1953).

(5) G. Rudakoff, Kolloid-Z., 170, 62 (1960).

(6) D. C. Bradley, "Metal Alkoxides," Advances in Chem. Series, Vol. 23, American Chemical Society, Washington, D. C., 1959, p. 10.

(7) D. C. Bradley, "Progress in Inorganic Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1960, p. 303.

(8) N. V. Sidgwick and L. E. Sutton, J. Chem. Soc., 1461 (1930).

*t*-butyl) for dimeric aluminum *t*-butoxide, similar to the bridged structure of the dimeric aluminum halides, which Palmer and Elliott[9] confirmed by electron diffraction studies.



I　　　　　　　　II
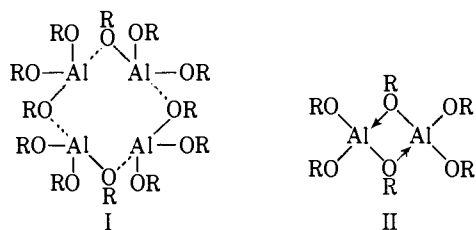
The work of Wardlaw[10] on the structures of alkoxides of other metals showed that the degree of polymerization of the alkoxide depended on the branching of the alkyl group. Bradley[11] has further suggested that an alkoxide undergoes the minimum degree of polymerization consistent with the attainment of the maximum covalency of the metal. These conditions lead to structure II for dimeric aluminum alkoxides, but for tetrameric alkoxides Bradley[6] proposed structure III.



III
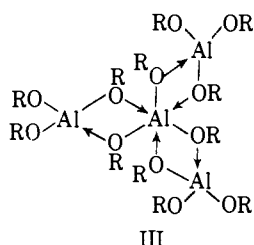
The structure of aluminum *t*-butoxide has been briefly examined by Bains,[12] using nuclear magnetic resonance spectroscopy. He has shown that the structure contains two different types of *t*-butyl groups, which he suggests may correspond to bridging and non-bridging *t*-butoxide groups. O'Reilly[13] has measured the aluminum resonance spectrum of aluminum isobutoxide, and concludes that the environment of the aluminum atom displays approximately cubic (*i.e.*, tetrahedral or octahedral) symmetry.

## Results

**Aluminum *t*-Butoxide.**—Measurements of the molecular weight of aluminum *t*-butoxide in carbon tetrachloride solution and in *t*-butyl alcohol solution show that it is dimeric, in agreement with the results of the majority of earlier workers. Detailed results are given in the Experimental section.

Details of the nuclear magnetic resonance spectra of solutions of aluminum *t*-butoxide in a number of solvents are given in Table I.

The spectrum of the solution in toluene was unchanged on cooling to −14.0°, except for very slight broadening of the peaks; the spectrum of the carbon tetrachloride solution was unchanged on heating to 74.0°. The spectra confirm the report of Bains[12] that two distinguishable *t*-butyl groups exist in aluminum *t*-butoxide. Measurements of peak areas show that they are in the ratio 1:2, as would be expected from structure II (R = *t*-butyl), peak A resulting from the protons of the bridging *t*-butoxide groups, and peak B resulting from the protons of the non-bridging groups. The position of peak A varies only slightly with solvent, as does the peak resulting from the *t*-butyl protons of *t*-butyl alcohol, while peak B moves downfield in aromatic solvents relative to its position in non-aromatic solvents. The downfield shift relative to tetramethylsilane in aromatic solvents might be correlated with the partial negative charge on the non-bridging oxygen atoms, since it does not occur with the bridging groups or with *t*-butyl alcohol itself. Some form of association with the aromatic solvent may be involved, but our results are not extensive enough to elucidate further this question.

**Aluminum Isopropoxide (Solid).**—Measurements of the molecular weight of solid aluminum isopropoxide in benzene solution show that it is tetrameric, in agreement with the results of the majority of earlier workers. Detailed results are given in Table V.

Details of the nuclear magnetic resonance spectra of solutions of aluminum isopropoxide in a number of solvents are given in Table II.

### TABLE I
### N.M.R. SPECTRA OF ALUMINUM *t*-BUTOXIDE

| Solvent | Position of methyl proton peaks[a] | | Integration, | Position of methyl proton peak of *t*-butyl alcohol[a] |
|---|---|---|---|---|
| | A | B | B/A | |
| Carbon tetrachloride | 90 | 74 | 2.01 | 72 |
| Benzene | 91 | 84 | 2.05 | 70 |
| Carbon disulfide | 88 | 72 | 2.04 | 70 |
| Toluene | 91 | 83 | 1.97 | 69 |
| Dioxane | 92 | 76 | 2.14 | 70 |
| Mesitylene | 91 | 82 | .. | 71 |
| *t*-Butyl alcohol | 93 | .. | .. | 74 |

[a] In cycles per second (at 60 Mc.) from internal tetramethylsilane.

### TABLE II
### N.M.R. SPECTRA OF SOLID ALUMINUM ISOPROPOXIDE DISSOLVED IN VARIOUS SOLVENTS

| Solvent | Position of methyl proton peaks[a] | | | | | | Position of methyl proton peaks of isopropyl alcohol[a] |
|---|---|---|---|---|---|---|---|
| | C | D | E | F | G | H | |
| Carbon tetrachloride | 92 | 85 | 80 | 74 | 70 | 64 | 71, 65 |
| Benzene | 102 | 96 | 86 | ..[b] | 80 | 74 | 68, 62 |
| Carbon disulfide | 91 | 84 | 80 | 74 | 70 | 64 | 70, 64 |
| Toluene | 102 | 96 | 86 | ..[b] | 80 | 74 | 71, 65 |
| Dioxane | 95 | 89 | 83 | 77 | 72 | 66 | 69, 63 |
| Mesitylene | 101 | 95 | 87 | 81 | 79 | 73 | 71, 65 |
| Isopropyl alcohol | 96 | 90 | 84 | .. | .. | .. | 73, 67 |

[a] In cycles per second (at 60 Mc.) from internal tetramethylsilane. [b] Peak F was obscured by peak G.

The separation of peaks C and D from the other methyl proton peaks in the spectrum of the benzene solution permits accurate measurement of the ratio of peak areas, (E + F + G + H)/(C + D), which has been found to be 3.00. Integrations of the complete spectra are given in Table III.

### TABLE III
### RELATIVE PEAK AREAS OF SPECTRA OF SOLID ALUMINUM ISOPROPOXIDE DISSOLVED IN VARIOUS SOLVENTS

| Solvent | Relative peak areas | | | | | |
|---|---|---|---|---|---|---|
| | C | D | E | F | G | H |
| Carbon tetrachloride | 1.00 | 0.91 | 0.92 | 3.23 | | 1.88 |
| Dioxane | 1.00 | 1.04 | 1.06 | 0.93 | 1.89 | 1.87 |
| Carbon disulfide | 1.00 | 1.03 | 0.99 | 3.06 | | 1.79 |

The results show that the ratio C:D:E:F:G:H approximates 1:1:1:1:2:2. Measurement of the spectrum of the carbon tetrachloride solution with the methyl protons decoupled from the single proton of the isopropyl group gives a spectrum containing three

(9) K. J. Palmer and N. Elliott, *J. Am. Chem. Soc.*, **60**, 1852 (1938).
(10) W. Wardlaw, *J. Chem. Soc.*, 3569 (1955).
(11) D. C. Bradley, *Nature*, **182**, 1211 (1958).
(12) M. S. Bains, *Can. J. Chem.*, **40**, 381 (1962).
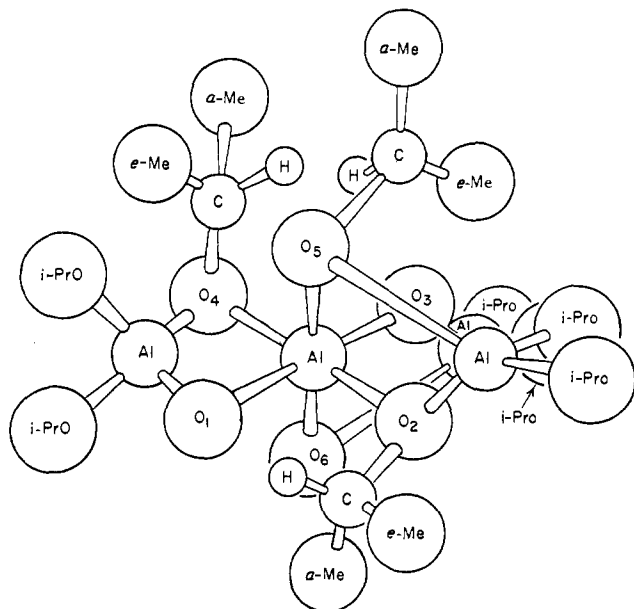(13) D. E. O'Reilly, *J. Chem. Phys.*, **32**, 1007 (1960).

Fig. 1.—Partial structure for aluminum isopropoxide tetramer showing the four aluminum atoms and the twelve oxygen atoms. Only three of the six isopropyl groups attached to bridging oxygen atoms and none of the six attached to non-bridging oxygen atoms are shown.

methyl proton peaks only, at 90, 78 and 68 c.p.s., but the loss of resolution resulting from use of this technique is too great to allow any gain in the accuracy of integration.

The spectrum of the solution in toluene was unchanged on cooling the sample to $-13.0°$, except for very slight broadening of the peaks. On heating solutions of aluminum isopropoxide, a small extra peak appeared, detectable at $49.0°$ and increasing in intensity with increasing temperature. This peak is at 84 c.p.s. in benzene solution, and at 77 c.p.s. in carbon tetrachloride. The peak appeared rapidly as the temperature of the solution was raised, and disappeared rapidly on cooling. Other peaks in the spectrum were not affected by heating for a short time, but on prolonged heating a slow rearrangement of the alkoxide took place, the spectrum changing to that of the melt form (see later). This rearrangement is complete in 4 hours at $110°$. It is partly reversible on cooling, the spectrum reverting to that of a mixture of the two forms over a period of several weeks at room temperature.

The spectrum of structure I (R = isopropyl) should, by comparison with the spectrum of aluminum $t$-butoxide, show four methyl proton peaks, with areas in the ratio 1:1:2:2. The measured spectra clearly rule out this structure. In structure III (R = isopropyl), the isopropoxide groups attached to the central aluminum atom would be expected to become spectroscopically identical, giving a structure with only two distinguishable types of isopropyl groups. A model of the structure, however, indicates that the isopropoxide groups attached to the central aluminum atom cannot rotate freely on account of steric hindrance; this is consistent with the fact that aluminum $t$-butoxide does not exist in any structure involving six $t$-butoxide groups surrounding one aluminum atom. Consequently, the methyl groups of the isopropoxide groups attached to the central aluminum atom have fixed orientations. They are approximately equatorial or axial to the plane of the aluminum atoms, and hence are spectroscopically distinguishable, giving rise to two pairs of peaks in the methyl proton region. The spectrum of the methyl protons in this structure would thus be expected to show

six peaks, with areas in the ratio 1:1:1:1:2:2, as observed.

This structure is further supported by the spectra of the single protons of the isopropoxide group. A model of the structure indicates that the single protons of the isopropoxide group attached to the central aluminum atom are identical, so that structure III (R = isopropyl) contains two distinguishable types of single protons, present in equal numbers. The spectrum obtained by decoupling the single protons from the protons of the methyl groups consists, as expected, of two peaks, at 269 and 252 c.p.s., but in the ratio of approximately 2:3, probably because the decoupling technique used is inadequate to give complete decoupling in these circumstances.

Peaks G and H show solvent shifts similar to those associated with the non-bridging $t$-butoxy groups in aluminum $t$-butoxide. This is consistent with their being assigned to the six non-bridging isopropoxide groups in the aluminum isopropoxide tetramer. However, peaks C, D, E and F assigned to the six bridging isopropoxy groups also show solvent shifts very near to those associated with non-bridging $t$-butoxy groups. This might be explained by extending the argument given above that the solvent shift is related to the extent of negative charge on the oxygen atoms. Bridging to a six-coördinated aluminum, as in the present case, would not be nearly as effective in reducing this charge as bridging to the four-coördinated aluminum in the $t$-butoxide dimer. Thus the solvent shift correlates qualitatively with the extent of negative charge expected on the oxygen. The solvent shifts for peaks E and F are less than those for C and D. One of these sets represents the "axial" methyl groups of the six bridging isopropoxy groups and the other the "equatorial" methyl groups. The difference in these solvent shifts between methyl groups attached to equivalent carbon atoms must be related to different steric hindrances to solvent approach to the two different positions.

The observed spectra are thus consistent in detail with tetrameric aluminum isopropoxide having structure III (R = isopropyl).

**Aluminum Isopropoxide (Melt).**—The tendency of molten aluminum isopropoxide to supercool, giving a sirupy liquid which is stable for several days at room temperature before undergoing slow crystallization, has been recorded previously,[2] but the properties of this melt have not been investigated.

Measurements of the molecular weight of aluminum isopropoxide melt dissolved in benzene show that the average degree of polymerization is 2.83, suggesting that it is mainly trimeric. This is in good agreement with the observation of Mehrotra[4] that freshly distilled aluminum isopropoxide is trimeric, but slowly rearranges to the tetramer on standing. The results do not, however, prove that other polymers do not exist in the melt. The dimer has been shown to exist, though observed only in the vapor phase,[14] and the experiments of Wilhoit[15] on the vapor pressure of aluminum isopropoxide suggest that the melt may be a mixture of polymers at higher temperatures.

The nuclear magnetic resonance spectrum of molten aluminum isopropoxide at $198.0°$ consists of a pair of peaks upfield from a much smaller septet, similar to the spectrum of isopropyl alcohol-$d$. The positions of the peaks were not measured. On cooling the melt to room temperature, it was too viscous to give a good spectrum, the measured spectrum showing only two broad peaks. Masdupuy and Gallais[16] report that molten aluminum ethoxide has a very low specific elec-

(14) R. C. Mehrotra, *J. Indian Chem. Soc.*, **31**, 85 (1954).
(15) R. C. Wilhoit, *J. Phys. Chem.*, **61**, 114 (1957).
(16) E. Masdupuy and F. Gallais, *Compt. rend.*, **225**, 128 (1947).

| Solvent | Position of methyl proton peaks[a] |
|---|---|
| Carbon tetrachloride | 70,[b] 64 |
| Benzene | 84, 78 |
| Carbon disulfide | 69,[b] 63 |
| Toluene | 83, 77 |
| Dioxane | 72,[b] 66 |
| Mesitylene | 83, 77 |

[a] In cycles per second (at 60 Mc.) from internal tetramethyl-silane.    [b] A broad, unresolved shoulder stretches from approximately 90 c.p.s. to the downfield peak of the pair.

trical conductance, so that by comparison an ionic structure for molten aluminum isopropoxide appears unlikely. It is probable that all the isopropyl groups of the melt structure have become equivalent through rapid exchange at this temperature, resulting in a simple spectrum.

Details of the nuclear magnetic resonance spectra of solutions of supercooled molten aluminum isopropoxide are given in Table IV. All the spectra show the presence of a small quantity (approximately 5%) of the tetramer in the solution, probably as a result of rearrangement while cooling the melt to room temperature. These extra peaks are not listed in Table IV.

On cooling the toluene solution, the spectrum shows rapid broadening of the peaks, a single broad peak appearing at $-13.5°$. On further cooling, this peak was again split, the resolution improving with decreasing temperature, until the spectrum at $-39.0°$ showed three peaks at 88, 83 and 77 c.p.s. On further cooling, the spectrum was unchanged except for a slight decrease in the resolution. The resolution was insufficient at any temperature to permit integration of the peak areas. On cooling the carbon disulfide solution to $-28.5°$, the shoulder on the peak at 69 c.p.s. was split into two peaks, so that the total spectrum consisted of four peaks, at 82, 76, 67 and 61 c.p.s. The resolution was not sufficient to permit integration of the peak areas, but peak heights suggest an approximate ratio of peak areas of 1:1:2:2.

These results are characteristic of a compound in which two or more groups of identical structure exchange positions rapidly at room temperature, so giving a simplified spectrum, which can be resolved only by cooling to a temperature at which the exchange is slow. The experiment does not distinguish between intermolecular and intramolecular exchange; however, on adding isopropyl alcohol to a solution of aluminum isopropoxide melt in toluene at room temperature, the nuclear magnetic resonance spectrum of the mixture showed separate methyl proton peaks due to the alkoxide (at 83 and 77 c.p.s.) and the alcohol (at 72 and 66 c.p.s.), indicating that the exchange is intramolecular.

The molecular weight measurements and spectroscopic data indicate that the melt has structure IV (R = isopropyl).



IV
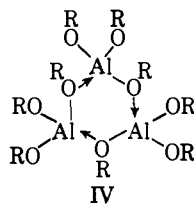
The spectra of solutions of the melt at room temperature show solvent shifts consistent with a time average structure in which all the isopropoxide groups show mixed bridging and non-bridging character.

Solutions of the melt rearrange to the tetramer considerably more slowly than the pure melt. The rate of rearrangement of the pure melt has therefore been measured by dissolving samples in benzene at intervals and observing the spectra. The rearrangement of the melt has a half-life of approximately 50 hours at 22°. The nuclear magnetic resonance spectrum of a benzene solution of the melt, prepared 48 hours after melting, has peaks characteristic of the tetramer and trimer, and two small extra peaks at 79 and 73 c.p.s. These peaks probably indicate a third form of aluminum isopropoxide, present in proportions too small to provide any indication of the size or type of structure.

## Discussion

The results reported above confirm the structures of aluminum isopropoxide and aluminum $t$-butoxide predicted by Bradley,[6,7] but extension of his rules to consider the structure of the melt of aluminum isopropoxide suggests a dimeric structure rather than the trimeric structure observed. This is, however, an exceptional case, since this structure predominates only at high temperatures. The results also confirm Bradley's suggestion that the slow increase in molecular weight of freshly distilled aluminum isopropoxide is caused by the tendency of aluminum to increase its coördination number from four to six.

The data obtained on the intramolecular exchange of alkoxide groups provides information on the mechanism of this reaction. The reaction may be expected to proceed either by preliminary fission of a bridging aluminum–oxygen bond to give the intermediate structure V, followed by formation of another aluminum–oxygen bond, or by formation of another alkoxide bridge, giving an intermediate structure similar to VI, followed by fission of one of the bridging aluminum–oxygen bonds.



V                    VI
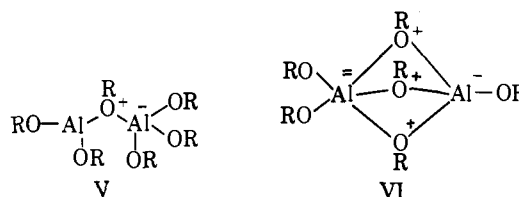
The results clearly favor the second mechanism. Aluminum $t$-butoxide exchange does not occur rapidly enough to be detected by the nuclear magnetic resonance method at 74.0°, while trimeric aluminum isopropoxide, which has a comparable cyclic structure, exchanges alkoxide groups at a detectable rate at $-13°$. This suggests that aluminum may readily achieve a state with five isopropoxy, but not five $t$-butoxy, coördinating groups.

It is a condition of exchange of the bridging and nonbridging alkoxide groups on an aluminum atom by this mechanism that one aluminum atom to which an alkoxy group is bridged must be capable of expanding its coördination and the other must carry a non-bridging alkoxy group. This condition is not satisfied in the proposed tetrameric aluminum isopropoxide structure, consistent with the fact that exchange between bridging and nonbridging isopropoxide groups is not observed.

## Experimental

**Measurement of Molecular Weight.**—Results of cryoscopic determinations of molecular weights are given in Table V. Freezing point depressions were measured by using either a Beckmann thermometer or a five-junction copper–constantan thermocouple. The molecular weight of aluminum $t$-butoxide in carbon tetrachloride solution was also determined by the Signer method using the technique described by Clark,[17] with

(17) E. P. Clark, Ind. Eng. Chem., Anal. Ed., 13, 820 (1941).

TABLE V

CRYOSCOPIC MOLECULAR WEIGHT DETERMINATIONS

| Compound | State | Solvent | Wt. of compd., g. | Wt. of solvent, g. | F.p. depression, °C. | Molecular weight | Av. mol. wt. | Degree of polymn. |
|---|---|---|---|---|---|---|---|---|
| Aluminum | Solid | t-Butyl | 0.8733 | 19.72 | 0.698 | 523 | | |
| t-butoxide | | alcohol | .7209 | 19.72 | .605 | 506 | 524 | 2.14 |
| | | | .7695 | 19.72 | .60 | 544 | | |
| Aluminum | Solid | Benzene | 1.9737 | 21.96 | .56 | 823 | 820 | 4.20 |
| isopropoxide | | | 1.3505 | 21.70 | .39 | 817 | | |
| Aluminum | Melt | Benzene | 0.7007 | 8.039 | .767 | 582 | 578 | 2.83 |
| isopropoxide | | | 0.6719 | 8.094 | .741 | 574 | | |

Cryoscopic constant of t-butyl alcohol = 8.37; cryoscopic constant of benzene = 5.12.

azobenzene as standard. Values of 477 and 483 were obtained, the average corresponding to a degree of polymerization of 1.95.

To prepare the supercooled melt solution, approximately 1 g. of aluminum isopropoxide was sealed in a Pyrex tube, heated to 200° for 5 minutes in an oil-bath, then removed, opened, and the contents immediately dissolved in benzene. In this way, rearrangement of the melt was kept to a minimum.

**Preparation of Materials.**—Commercial samples of aluminum isopropoxide were purified by distillation under reduced pressure; aluminum t-butoxide was prepared as described by Wayne and Adkins,[18] and purified by recrystallization from benzene.

**Nuclear Magnetic Resonance Spectroscopy.**—All nuclear magnetic resonance spectra were measured on either a Varian A-60 or a Varian DP-60 nuclear magnetic resonance spectrometer. Measurements involving temperature effects, spin decoupling or integration of aluminum isopropoxide spectra were carried out on the DP-60 spectrometer, others on the A-60.

All samples, except melt solutions, were made up in a drybox, and used either tetramethylsilane or hexamethylbenzene as internal references for measurement of peak positions. Saturated solutions of aluminum t-butoxide in t-butyl alcohol and of tetrameric aluminum isopropoxide in dioxane and isopropyl alcohol were used. Other solutions contained 15–20% of the alkoxide. All peak positions are in cycles per second (at 60 Mc.) from internal tetramethylsilane reference. Peak positions quoted are considered accurate to ±1 cycle per second, except for peaks of spin decoupled spectra.

Spin decoupling of the methyl protons from the single proton of the isopropoxide group in aluminum isopropoxide dissolved in carbon tetrachloride was achieved by generating a side band at 185 cycles per second from the main band, then scanning the methyl frequencies with the side-band generator on. Decoupling the single proton of the isopropoxide group from the methyl protons was achieved in the same way, but because of the difficulty of saturating six protons with a side band generated on the signal from one proton, decoupling was not quite complete,

and the results are less accurate. Peak positions of spin decoupled peaks were measured by extrapolation from the known positions of other peaks in the spectrum, since the side band generator, normally used for measuring peak positions, was already in use. Peak positions quoted for spin decoupled peaks are probably accurate to ±3 c.p.s.

Solutions of the supercooled melt of aluminum isopropoxide were prepared as described above. Supercooled molten aluminum isopropoxide is considerably more soluble than the tetramer in all solvents used in this work and is readily soluble in a good many solvents such as pyridine in which the tetramer is almost insoluble.

The solubilities of the two forms in a number of solvents were determined by removal of solvent from a weighed quantity of the saturated solution, and are given in Table VI.

TABLE VI

SOLUBILITIES OF TRIMERIC AND TETRAMERIC ALUMINUM ISOPROPOXIDE AT 22°

| Solvent | Solubility, g. per 100 g. of solv. Trimer | Tetramer |
|---|---|---|
| Carbon tetrachloride | Miscible | 65.3 |
| Benzene | Miscible | 66.8 |
| Cyclohexane | Miscible | 109.7 |
| Dioxane | Miscible | 2.52 |
| Isopropyl alcohol | Miscible | 4.92 |

(18) W. Wayne and H. Adkins, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 48.

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# COMMUNICATIONS TO THE EDITOR

## Rates of Ethanolysis of Camphene Hydrochloride and Related Alpha Methyl Substituted 1-Chloro-1-methylcyclopentanes—the Question of a Non-classical Camphenylyl Cation

*Sir:*

We wish to report that the rate of ethanolysis of camphene hydrochloride is comparable in magnitude to those exhibited by representative model compounds derived from 1-chloro-1-methylcyclopentane. Consequently, the fast rate of solvolysis of the bicyclic chloride cannot be utilized as an argument for the formation of a stabilized synartetic (mesomeric, non-classical) ion in its solvolysis.[1]

It was originally suggested by Wilson and his co-workers that the camphene hydrochloride–isobornyl chloride rearrangement might involve a mesomeric

cation[2] instead of the classical ions considered by Meerwein.[3] The very fast rate of ethanolysis of camphene hydrochloride (6000 times greater than that of t-butyl chloride[1]) was considered to provide strong support for its ionization to such a stabilized mesomeric intermediate.[1]

It would be of considerable interest to possess an estimate of the driving force afforded by the formation of the stabilized mesomeric intermediate. Such an estimate could be realized by comparing the observed rate of ionization with that of a comparable model compound which does not ionize to form a mesomeric species. It is evident that acyclic derivatives, such as t-butyl chloride, with their ability to minimize non-bonded interactions, cannot be satisfactory model systems. It would appear that 1-chloro-1-methyl-cyclopentane and its methyl derivatives, with bond

(1) F. Brown, E. D. Hughes, C. K. Ingold and J. F. Smith, *Nature*, **168**, 65 (1951).

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