

## Interconversion Reactions of Aluminum Isopropoxide Polymers

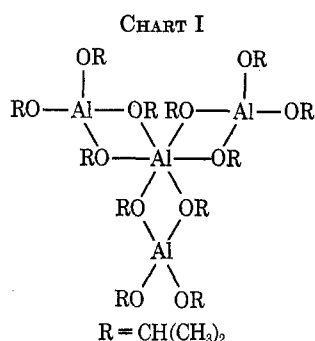
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The interconversion reactions of the dimeric, trimeric, and tetrameric forms of aluminum isopropoxide have been studied by cryoscopic and nuclear magnetic resonance techniques. Starting from pure dimer, the first reaction is rapid equilibration with trimer, after which the tetramer is formed very much more slowly; starting from pure tetramer, a mixture of all three species is slowly formed. Rate coefficients for individual steps of the interconversion process are suggested on the basis of the fit of the overall kinetic results to a computer simulation of the reaction scheme.

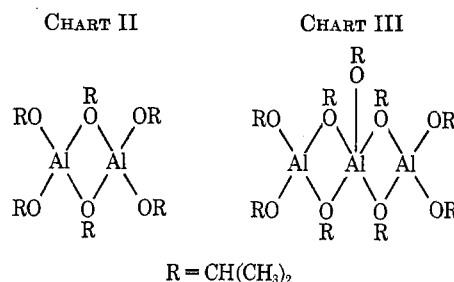
It has long been known from cryoscopic studies that solid aluminum isopropoxide dissolves in benzene to give a solution in which the alkoxide is tetrameric.<sup>1</sup> The structure, shown in Chart I, was first put forward



by Bradley,<sup>2</sup> who deduced it on the basis of his general principle of alkoxide chemistry<sup>3</sup> that an alkoxide undergoes the minimum degree of polymerization consistent with the maximum covalency of the metal. This structure was later confirmed by proton magnetic resonance studies of the alkoxide.<sup>4</sup> On melting, solid aluminum isopropoxide gives a liquid which is stable over a period of days at room temperature, the solid crystallizing out slowly. The liquid form, known as the melt, was shown to be approximately trimeric in benzene solution by cryoscopic measurements,<sup>5</sup> and proton magnetic resonance studies<sup>4</sup> showed that it had a different structure from the tetramer; the alkoxide groups of the trimer were undergoing exchange at room temperature sufficiently fast for them to be indistinguishable by nmr spectroscopy. On cooling to  $-39^\circ$ , the methyl proton region showed two doublets, in approximately the ratio of 1:2, though the resolution obtained was insufficient to permit accurate integration of the spectrum.

A more recent investigation of the melt<sup>6</sup> has shown that at high temperatures it consists largely of the dimer and that, by rapid cooling of a hot solution of the melt, a solution of dimeric aluminum isopropoxide can be obtained. Studies of the dimer by proton magnetic resonance spectroscopy<sup>6</sup> are consistent with it having a bridged structure, similar to that of aluminum halides

in the gas phase<sup>7</sup> and aluminum *tert*-butoxide in solution<sup>4,5</sup> which is shown in Chart II.



However, studies of the trimer by aluminum magnetic resonance spectroscopy<sup>6</sup> have led to the suggestion that the trimer has the structure shown in Chart III, in which two aluminum atoms are 4-coordinate and one is 5-coordinate. Although penta-coordinate aluminum is relatively uncommon, it has been postulated to exist in complexes of aluminum isopropoxide with ethylenediamine<sup>8</sup> and with  $\beta$ -dicarbonyl compounds,<sup>9</sup> and in complexes of trialkylaluminum with diamines<sup>10</sup> and tetramethyltetrazene.<sup>11</sup>

## Experimental Section

**Preparation of Materials.**—Purification of aluminum isopropoxide was by distillation at  $108.5\text{--}109.5^\circ$  (0.4 mm), then the melt was allowed to crystallize slowly at room temperature;<sup>12</sup> solutions of the pure tetramer in dry benzene were made up and sealed in nmr tubes. Reactions were carried out in the nmr tubes, which were thermostated at appropriate temperatures between points. The tetramer remained stable in benzene solution, frozen at  $0^\circ$ , but the melt form could not be stabilized; so the contents of a tube were converted to melt before each run, using the heating and rapid cooling technique outlined earlier.<sup>12</sup>

**Kinetics.**—The reaction was followed by integration of the methyl proton region of the nmr spectrum recorded on a Varian A-60 spectrometer, at least 12 integrals of each spectrum being recorded and averaged. The integral of the two peaks at 102 and 96 cps from TMS, which have been shown to constitute 25% of the methyl protons of the tetramer,<sup>4</sup> were compared with the integral of the rest of the methyl proton peaks, which constitute 75% of the methyl proton peaks of the tetramer, and all the methyl proton peaks of the melt.<sup>4</sup> In this way, the amount of tetramer in the solution could be calculated. Results obtained in this way were reproducible to  $\pm 2\%$ .

**Calculation of Results.**—In order to test possible mechanisms,

- (1) H. Ulich and W. Nespital, *Z. Physik. Chem.*, **165**, 294 (1933).
- (2) D. C. Bradley, "Metal Alkoxides," *Advances in Chemistry Series*, 23, American Chemical Society, Washington, D. C., 1959, p 10.
- (3) D. C. Bradley, *Nature (London)*, **182**, 1211 (1958).
- (4) V. J. Shiner, Jr., D. Whittaker, and V. P. Fernandez, *J. Amer. Chem. Soc.*, **85**, 2318 (1963).
- (5) R. C. Mehrotra, *J. Indian Chem. Soc.*, **30**, 585 (1953).
- (6) D. C. Kleinschmidt and V. J. Shiner, Jr., unpublished work.

- (7) K. J. Palmer and N. Elliott, *J. Amer. Chem. Soc.*, **60**, 1852 (1938).
- (8) V. J. Shiner, Jr., and D. Whittaker, *J. Amer. Chem. Soc.*, **87**, 843 (1965).
- (9) R. K. Mehrotra and R. C. Mehrotra, *Can. J. Chem.*, **39**, 795 (1961).
- (10) N. R. Fetter, B. Bartocha, F. E. Brinckman, Jr., and D. W. Moore, *Can. J. Chem.*, **41**, 1359 (1963).
- (11) N. R. Fetter, F. E. Brinckman, Jr., and D. W. Moore, *Can. J. Chem.*, **40**, 2184 (1962).
- (12) V. J. Shiner, Jr., and D. Whittaker, *J. Amer. Chem. Soc.*, **91**, 394 (1969).

details of the reaction schemes were programmed onto an E. A. I. TR-10 analog computer, and rate constants were adjusted to give the best fit with observed data. The data given in Table I were

TABLE I<sup>a</sup>  
FORMATION AND DECOMPOSITION OF ALUMINUM ISOPROPOXIDE  
TETRAMER IN BENZENE SOLUTION AT 45.00°

Reaction starting from tetramer Time, hr	Tetramer, <i>M</i>	Reaction starting from melt Time, hr	Tetramer, <i>M</i>
0	0.1482	0	0.0000
23	0.1424	23	0.0179
46	0.1353	46	0.0258
93	0.1248	69	0.0328
116	0.1211	92	0.0391
163	0.1152	116	0.0425
186	0.1085	162	0.0476
209	0.1065	185	0.0485
256	0.1012	Infinity	0.0536
327	0.0916		
374	0.0872		
421	0.0844		
492	0.0777		
539	0.0753		
Infinity	0.0561		

<sup>a</sup> Alkoxide concentration was 0.607 *M* (calculated as monomer).

used for this purpose, since the rates of reaction in both directions were slow enough to permit accurate measurement of data, but fast enough to permit the reaction to be easily followed over two half-lives.

### Results and Discussion

**Dimer to Trimer Interconversion.**—Heating a solution of aluminum isopropoxide in toluene to 110° for 6 hr, followed by rapid cooling to the temperature of the nmr probe, gave a solution whose spectrum, measured 4 min after completion of heating, was a sharp doublet at 79 and 73 cps from TMS, together with a smaller, much broader doublet at 84 and 78 cps. On standing, the upfield doublet decayed and the downfield doublet increased in size, until an equilibrium was reached in which the latter predominated. We have already shown this solution to have a molecular weight of 587, suggesting it to be a mixture of dimer and trimer, in which the latter predominates;<sup>4</sup> in order to confirm that the upfield doublet results from the dimer and the downfield doublet from the trimer, changes in nmr spectrum and molecular weight were followed on samples of the same solution of aluminum isopropoxide in benzene. On the basis of the nmr data, measured at the melting point of benzene, the degree of polymerization of the solution was calculated as a function of time; these results are given in Table II.

TABLE II<sup>a</sup>  
NMR STUDY OF ALUMINUM ISOPROPOXIDE MELT IN BENZENE

Time, <sup>b</sup> min	Integral <sup>c</sup>		Calculated degree of polymerization
	Downfield doublet	Upfield doublet	
21	17.1	18.8	2.48
43	19.1	17.6	2.52
68	18.9	18.8	2.53
93	18.9	18.8	2.53
134	24.0	14.0	2.63
344	22.7	10.0	2.69

<sup>a</sup> The solution used was identical with that used to obtain the data recorded in Table III. In all cases, the integrals were the average of upfield and downfield sweeps. <sup>b</sup> Measured from removal of tube from oven. <sup>c</sup> In arbitrary units.

The molecular weight was measured as a function of time at the temperature of freezing benzene by observing changes in the freezing point depression; the results obtained, given in Table III, confirm the assignment

TABLE III<sup>a</sup>  
CRYOSCOPIC STUDY OF ALUMINUM  
ISOPROPOXIDE MELT IN BENZENE

Time, <sup>b</sup> min	Mol wt	Degree of polymerization
18	526	2.58
43	501	2.46
66	536	2.63
90	566	2.78
156	566	2.78
2520	566	2.78

<sup>a</sup> The solution used contained 0.153 *M* alkoxide, calculated as monomer. It was heated to 110° for 6 hr before use, then cooled rapidly in a Dry Ice-acetone bath. <sup>b</sup> Measured from removal of the tube from the oven.

of the upfield doublet to the dimer and the downfield doublet to the trimer.

The data show that, at the temperature of freezing benzene, the half-life for the conversion of dimer to the dimer-trimer equilibrium mixture is *ca.* 15 min; the equilibrium mixture has a degree of polymerization of 2.7, lower than that observed earlier<sup>4</sup> for the melt form of the alkoxide, 2.83, consistent with the latter containing some tetramer.

On account of the speed of the interconversion, compared to the rather slow method of studying it, an accurate kinetic study has not been attempted.

**Tetramer to Melt Interconversion.**—The term "melt" is used to describe the equilibrium mixture of dimer and trimer which was used in the experiments described below. Preliminary experiments showed that the rate of interconversion of the tetramer and melt forms of aluminum isopropoxide was very much slower than the rate of the dimer to trimer interconversion, and could conveniently be followed by nmr analysis of the reaction mixtures; the assignments of the nmr spectrum of the tetramer are given in an earlier paper.<sup>4</sup>

Using this method, the kinetics of formation of tetramer from melt and of formation of melt from tetramer were measured. The reactions are complex ones in which several equilibria are involved; so they would not be expected to show any simple kinetic form. Surprisingly, the data at each alkoxide concentration were found to fit a first-order rate plot over 2 half-lives. The reaction is clearly much more complex than a simple first-order reaction, but the fortuitous balance of rates and equilibria apparently combine to give "deceptively simple kinetics."

We have used this phenomenon to simplify presentation of our data, reducing them to "first-order" rate coefficients. These are quoted in Tables IV and V.

The equilibrium concentrations of the tetramer under different conditions of temperature and alkoxide concentration are listed in Table VI. These values are the average of those obtained by approaching the equilibrium from either side.

Attempts to calculate equilibrium constants on the assumption that the melt, at this stage, contained only trimer were not successful. If, however, the equilibrium mixture was assumed to contain dimer, trimer, and

TABLE IV  
FIRST-ORDER RATE COEFFICIENTS FOR THE FORMATION OF  
TETRAMERIC ALUMINUM ISOPROPOXIDE FROM THE MELT FORM  
IN BENZENE SOLUTION<sup>a</sup>

Concn of aluminum isopropoxide, mol of monomer	10 <sup>6</sup> k <sub>1</sub> , sec <sup>-1</sup>		
	25.00°	35.00°	45.00°
0.607	1.00	1.57	3.75
1.030	1.48	2.00	4.15
1.789	1.61	3.16	6.32

<sup>a</sup> Mean energy of activation was 12.0 kcal mol<sup>-1</sup>.

TABLE V  
FIRST-ORDER RATE COEFFICIENTS FOR THE CONVERSION OF  
TETRAMERIC ALUMINUM ISOPROPOXIDE TO THE MELT FORM IN  
BENZENE SOLUTION<sup>a</sup>

Concn of aluminum isopropoxide, mol of monomer	10 <sup>6</sup> k <sub>1</sub> , sec <sup>-1</sup>		
	35.00°	45.00°	65.00°
0.607	0.292	0.810	3.69
1.030	0.438	1.008	3.92
1.789	0.544	1.354	4.90

<sup>a</sup> Mean energy of activation was 15.2 kcal mol<sup>-1</sup>.

TABLE VI  
EQUILIBRIUM CONCENTRATIONS OF TETRAMERIC ALUMINUM  
ISOPROPOXIDE IN BENZENE SOLUTION<sup>a</sup>

Concn of aluminum isopropoxide, mol of monomer	Tetramer at equilibrium, %			
	25.00°	35.00°	45.00°	65.00°
0.607	53.1	41.9	36.2	20.2
1.030	58.4	48.2	41.7	24.6
1.789	63.3	53.7	46.9	28.5

<sup>a</sup> The values are quoted as per cent of monomeric alkoxide existing as the tetramer.

tetramer simultaneously, then the equilibria [tetramer]/[trimer] =  $k_A$  and [tetramer]/[dimer] =  $k_B$  exist simultaneously. The values of  $k_A$  and  $k_B$  calculated on this basis were found to be self-consistent, and are listed in Table VII. From these, the equilibrium con-

TABLE VII  
VALUES OF THE EQUILIBRIUM CONSTANTS,  $k_A$  AND  $k_B$ , FOR THE  
EQUILIBRIUM BETWEEN THE DIMERIC, TRIMERIC, AND  
TETRAMERIC FORMS OF ALUMINUM ISOPROPOXIDE  
IN BENZENE SOLUTION

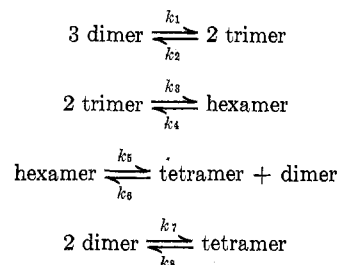
Equilib- rium constant	Value, l. mol <sup>-1</sup>			
	25.00°	35.00°	45.00°	65.00°
$k_A$	182	27.9	4.39	0.323
$k_B$	26.3	6.65	8.77	3.46

centrations of each species can be calculated over the range of concentrations and temperatures covered by the kinetic studies.

The kinetic data are inconsistent with decomposition to monomer, followed by recombination of the monomer to different polymeric species. The overall reaction consists of a fast interconversion of dimer and trimer, followed by a much slower interconversion involving all three species. All possible reaction mechanisms involve at least four separate steps; so, in order to test possible mechanisms, each was programmed onto an

analog computer, and then tested against the data given in Table I.

A number of mechanisms were tested in this way. Those which involved formation of a monomeric species were fairly easy to fit to the data by suitable choice of rate coefficients; in all cases, however, they predicted an equilibrium mixture containing a large concentration of monomer, which is contrary to the data in Tables VI and VII. The only mechanism tested which fitted both kinetic and equilibrium data is that given below.

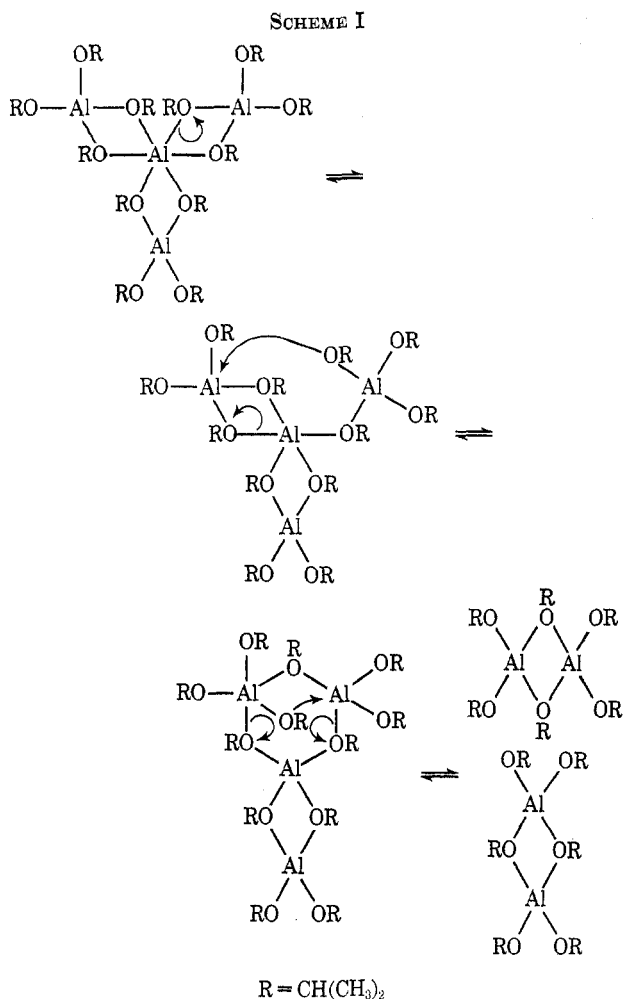


One set of rate constants which fits this to the observed data follows:  $k_1$  is fast;  $k_2$  is fast;  $k_3 = 0.267 \times 10^{-6}$  l. mol<sup>-1</sup> sec<sup>-1</sup>;  $k_4 = 5.6 \times 10^{-4}$  sec<sup>-1</sup>;  $k_5 = 5.6 \times 10^{-4}$  sec<sup>-1</sup>;  $k_6 = 2.82 \times 10^{-6}$  l. mol<sup>-1</sup> sec<sup>-1</sup>;  $k_7 = 0.098 \times 10^{-6}$  l. mol<sup>-1</sup> sec<sup>-1</sup>;  $k_8 = 0.528 \times 10^{-6}$  sec<sup>-1</sup>.

The values of the other rate constants required to obtain a fit are only affected by the ratio of  $k_1$  to  $k_2$  and not by their absolute magnitude. Therefore  $k_1$  and  $k_2$  were set at large values and their ratio was adjusted so that the rate of approach to overall equilibrium was fitted by the same set of constants starting with either "melt" or tetramer. The values for  $k_4$  and  $k_5$  were the largest the program could use. Within wide limits there is no restriction on their magnitude if they are set significantly larger than  $k_3$  and  $k_6$ , consistent with there being no detectable concentration of hexameric alkoxide. Further,  $k_4$  and  $k_5$  were arbitrarily set equal; a different ratio would require a corresponding change in the relative values of  $k_4$  and  $k_5$ .

This mechanism predicts that, starting from a solution of 0.607 *M* aluminum isopropoxide (calculated as monomer), the equilibrium concentration of each species at 45° would be, for dimer, 0.077 *M*; trimer, 0.072 *M*; tetramer, 0.059 *M*. These are in reasonably good agreement with the values obtained experimentally: dimer, 0.079 *M*; trimer, 0.078 *M*; tetramer, 0.055 *M*. The mechanism involves assumptions that aluminum isopropoxide does not exist as a monomer, and that it can exist fleetingly as a hexamer. The first of these assumptions was expected, since monomeric aluminum isopropoxide has not been observed; it is dimeric in the vapor phase,<sup>13</sup> even at high temperatures. Since trivalent aluminum is an excellent electron acceptor, and the oxygen of the alkoxide group a good electron donor, it seems likely that it would be at best a transient species with a very high energy barrier to its formation, and consequently playing no part in reactions in solution. The existence of a hexameric form of aluminum isopropoxide has been predicted by Bradley,<sup>3</sup> and, although this form has not been isolated, our mechanism requires its existence only in a very low concentration. It is not even necessary for the hexamer to exist in the structural form predicted by Bradley; a temporary

(13) R. C. Mehrotra, *J. Indian Chem. Soc.*, **31**, 85 (1954).



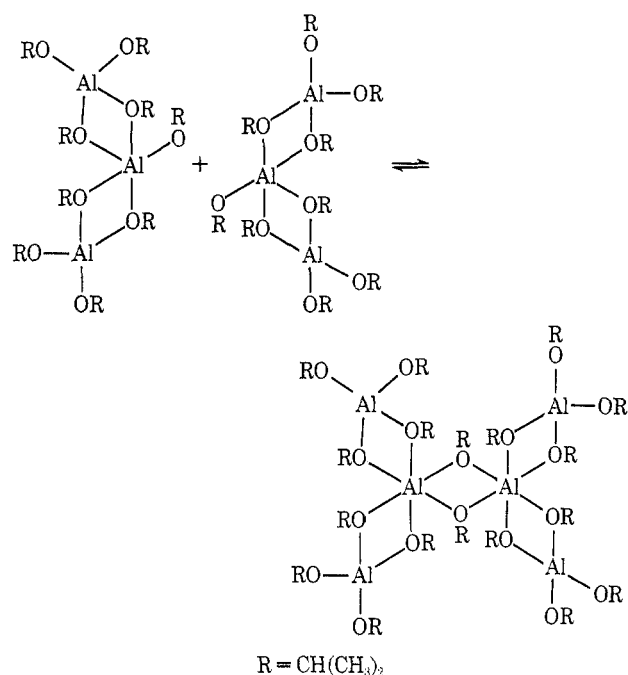
association of the reacting species would satisfy kinetic requirements.

Although the interpretation of our kinetic data described above is not necessarily unique, it provides one possible outline of the sequence of reactions involved in interconversion of the aluminum isopropoxide polymers. It is further consistent with the only information available about any individual step of the reaction, which is the observation that the rate of the tetramer to melt reaction is greatly increased by added alcohol.<sup>12</sup> In benzene at 25°, the formation of melt from tetramer shows first-order kinetic behavior, with  $k_1 = 0.11 \times 10^{-6} \text{ sec}^{-1}$  for an initial concentration of 0.61 *M* alkoxide (measured as monomer). However, repeating the reaction at 25° in a solution containing 0.741 *M* alkoxide (measured as monomer) and 1.274 *M* isopropyl alcohol gave a first-order reaction with  $k_1 = 2.5 \times 10^{-6}$ , a rate increase by a factor of almost 25. The most probable interpretation of this observation is that the first step of reaction of the tetramer is fission of a bridging aluminum-oxygen bond, the alcohol serving to stabilize the intermediate thus produced, preventing its immediate return to tetramer. This is consistent with observations that the exchange of aluminum isopropoxide and deuterated isopropyl alcohol is zero order in alcohol over the range of concentrations 0.6–2.5 *M*.<sup>12</sup> The alcohol merely serves to block the fast return to tetramer. The requirement

that aluminum-oxygen bond fission in the tetramer is fast and reversible is consistent with the exchange of deuterated acetone with aluminum isopropoxide giving an alkoxide in which all isopropyl groups are equally labeled.<sup>12</sup>

This alkoxy scrambling reaction in the tetramer must involve preliminary aluminum-oxygen bond fission, as any alternative mechanism would involve formation of 7-coordinate aluminum.<sup>4,12</sup> Taking fission of a bridging aluminum-oxygen bond as the probable first step, then a possible mechanism of the tetramer-dimer interconversion may be written (Scheme I).

The reaction of two molecules of trimer to give a molecule of hexamer almost certainly involves the pentacoordinated aluminum atoms, since these are less stable than the four or six coordinated aluminum atoms, so that a possible mechanism is that shown below.



The loss of the dimeric aluminum isopropoxide unit from the hexamer structure suggested above can be visualized as occurring through a sequence of bonding changes similar to that indicated for loss of a similar unit from the tetramer.

Thus, although there is necessarily a large speculative element in the mechanistic details proposed, and alternative possibilities can be suggested, these mechanisms provide a concise rationalization of the observed structural changes, and involve intermediates containing a minimum of novel structural features.

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**Registry No.**—Aluminum isopropoxide tetramer, 25443-56-5; aluminum isopropoxide dimer, 32572-47-7; aluminum isopropoxide trimer, 33570-44-4.