The Partial Hydrolysis of Ethylalane Compounds

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Abstract: The partial hydrolysis of benzene solutions of the alane compounds, $Et_{3-x}AlX_x$ (where $x = 0, 1$; $X =$ Cl, OEt), has been investigated using 2:1 molar ratios of alane to water. In each case, ethane was evolved and there formed a soluble oily product having the empirical formula $(Et_{2-x}AlX_x)_2O$ and a molecular complexity dependent upon the nature of the group X. Thus, molecular weight data indicate a higher degree of polymerization in benzene for the cases where X = Cl or OEt than for the case of $(Et_2Al)_2O$ which is trimeric. Infrared spectroscopy has shown the presence of a characteristic and very strong absorption region due to the aloxane link, Al–O–Al, in the products. The acceptor properties of these aloxanes have been investigated using trimethylamine as a donor. When Et_3Al is allowed to react with water in a 1:1 molar ratio, the hydrolysis produces mainly an insoluble amorphous material having a composition approximating EtAlO, presumably a cross-linked high polymer.

Although the violent reaction of organoalanes with water is well known,[1] little attention has been given to the possibility of the isolation and characterization of intermediate organoaloxanes, compounds having Al–O–Al bridges. Organoalane–water mixtures of various molar ratios have been found to make excellent catalysts for polymerization reactions,[2] but the nature of the catalysts themselves has not been investigated. Amdurski, *et al.*,[3] in 1961, reported the kinetic behavior of the 1:1 reaction of triethylalane and water vapor but did not isolate the aluminum-bearing products. A more recent report[4] has dealt with the reactivity of tributylalane toward water, and Sakharovskaya, *et al.*,[5] have published a paper on the reaction of trialkylalanes with water and have succeeded in isolating various isobutylaloxanes. Apart from these three reports, however, the chemistry of alkylalane–water systems has received little attention. This is in contrast to the analogous systems of the remaining nontransition members of group III where an order of reactivity, B < Tl < In < Ga, can be written for organo derivatives of these elements toward water.

Preliminary results in this laboratory indicated that the technique successful in preparing dimethylhydroxygallane[6] was not applicable to trialkylalanes because of the explosive violence of the reactions. More recent work,[7] using 1:1 ratios of triethylalane to water at very low concentrations, succeeded in moderating the reaction by employing various solvents. Up to 56% of the ethyl groups was recovered as ethane and there formed amorphous powders, insoluble in aliphatic or aromatic hydrocarbons or in donor solvents, which could not be purified.

The present paper describes the use of a novel technique in the preparation and isolation of soluble ethylaloxanes and discusses the chemistry of the systems investigated.

Experimental Section

Materials. All organoalane compounds were handled in either a drybox under an atmosphere of dry nitrogen or in a vacuum line of conventional design. Triethylalane (Texas Alkyls) was purified by distillation on a 50-cm column containing a heated nichrome spiral. The fraction distilling between 112 and 114° (27 mm) was used. Diethylmonoethoxyalane was prepared by mixing triethoxyalane and triethylalane in a 1:2 molar ratio. The mixture was heated to 170° under an atmosphere of dry nitrogen and then fractionally distilled under reduced pressure. The fraction distilling between 106 and 107° (8–9 mm) was used. Diethylmonochloroalane, prepared by the action of sodium chloride on ethylaluminum sesquichloride, was fractionally distilled before use, the fraction boiling between 106.5 and 108° (24.5 mm) being selected. The benzene solvent was rigorously dried and distilled before use. It was stored either in a glove box under nitrogen or over molecular sieves. The trimethylamine employed in this work was carefully dried and kept in a storage bulb attached to the vacuum line.

Analysis. The ethyl group content was determined gas volumetrically by solvolyzing a weighed sample with a methanol–water mixture acidified with nitric acid. The volume of the ethane evolved was measured by a Toepler pump. The resulting solution was then analyzed for aluminum by precipitating as the 8-hydroxyquinolate,[8] and for chloride (where applicable) by precipitation as silver chloride. Ethoxide determination was carried out volumetrically. A weighed sample, hydrolyzed cautiously with a small quantity of water, was added to a measured amount (excess) of chromic acid (1 *N* potassium dichromate in 12.5% H_2SO_4) in a closed vessel. After 2 hr, the unchanged dichromate was determined iodometrically. Under these conditions, ethyl alcohol is quantitatively converted into acetic acid.[9] The purity of the gases evolved during the initial hydrolysis and the analysis was checked on a mass spectrometer, Model 21-401, Consolidated Engineering Corp., Pasadena, Calif.

Molecular Weights. Molecular weights were determined cryoscopically in benzene as solvent. The apparatus was loaded in the glove box and maintained under an atmosphere of nitrogen throughout the readings.

Hydrolytic Method. A general method has been developed for treating water with organoalane derivatives which enables the reaction to proceed very slowly and minimizes the risk of precipitation of highly polymeric material from the reaction sphere. The apparatus is shown in Figure 1. In a typical experiment, the alane, weighed out accurately under nitrogen, was dissolved in benzene and introduced *via* A into the reaction vessel in the glove box.

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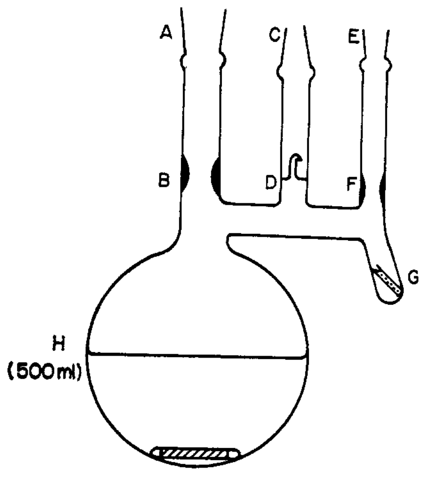

Figure 1. Hydrolysis apparatus.

The flask used in the weighing was washed with further quantities of benzene, the washings being added to the reaction vessel. The apparatus, stoppered at A and E, was removed from the glove box and attached to the vacuum line by an adapter at A. The required amount of water, weighed into a small tube, was introduced into limb G of the apparatus. First limb G and then the reaction bulb H were immersed in liquid nitrogen baths and the whole apparatus was evacuated and sealed off at the constrictions B and F. Both limbs G and H were allowed to warm to room temperature and the reaction bulb H was immersed in a cold-water bath (5°). The benzene solution was stirred magnetically while limb G was warmed to provide water vapor to the reaction bulb. The reaction was allowed to proceed until all the water had been taken up by the solution. This method ensures a decrease in rate of the reaction as the reaction proceeds since the ethane evolved slows down diffusion of the water vapor into the reaction sphere. At the completion of the reaction, bulb H was cooled in a liquid nitrogen bath, the apparatus was connected to the vacuum line *via* C, and the break-seal at D was broken. Any gases noncondensable at $-196°$ were collected and measured in a Toepler pump and checked for composition by mass spectrometry. The liquid nitrogen bath was replaced with a $-78°$ bath, and the ethane evolved was measured and checked for purity. By alternately warming the solution to room temperature and recooling to $-78°$, all the ethane could be collected. The apparatus was finally warmed to room temperature and filled with nitrogen, and the solution was filtered in the glove box. The nonvolatile soluble product remaining after removal of solvent from the filtrate was then analyzed and subjected to physical and chemical measurements. In all cases, the molar quantities are given in terms of the monomeric formulas.

Bis(diethylaluminum)oxane, $(Et_2Al)_2O$. In a typical experiment, 13.84 mmoles of triethylalane was dissolved in 100 ml of benzene, and 6.92 mmoles of water was added, as described above, to the stirred solution to give the main reaction represented by

$$2Et_3Al + H_2O \xrightarrow{\text{benzene}} (Et_2Al)_2O + 2EtH$$

A small volume of gas, noncondensable at $-196°$, was invariably evolved. This was measured as 0.276 mmole and shown by mass spectral analysis to consist of approximately equal volumes of hydrogen and methane. The ethane evolved in the reaction measured 13.75 mmoles and its purity was checked by its mass spectrum. After filtration and removal of solvent, a nonvolatile viscous liquid remained at room temperature, and this was analyzed.

Anal. Calcd for $(Et_2Al)_2O$: Al, 29.04; hydrolyzable Et, 62.3; mol wt, 186. Found: Al, 29.20; hydrolyzable Et, 61.5; mol wt, 560 ($n = 3.01$).

The viscous liquid $(Et_2Al)_2O$ was thermally stable at room temperature but, on attempted distillation under reduced pressure above 100°, it decomposed to yield a volatile, colorless, mobile liquid and a nonvolatile, slightly tacky, white solid. In a quantitative experiment, 0.8607 g of $(Et_2Al)_2O$, heated at 150° for 6 hr, yielded 0.5465 g of the volatile liquid and there remained 0.311 g of the white solid. A small amount of ethane, 3.3 ml, was evolved, but no gases noncondensable at $-196°$ were obtained.

Anal. Calcd for Et_3Al (volatile liquid): Al, 23.7; hydrolyzable Et, 76.3. Found: Al, 24.2; hydrolyzable Et, 74.4; Al:Et = 1:2.87. Calcd for EtAlO (nonvolatile solid): Al, 37.5; hydrolyzable Et, 40.3. Found: Al, 36.0; hydrolyzable Et, 43.9; Al:Et = 1:1.135.

The solid was soluble in benzene and its infrared spectrum in this solvent showed strong absorption bands around 800 cm^{-1}, characteristic of Al–O–Al linkages. An X-ray powder pattern demonstrated the absence of crystallinity in the material. The data indicate that heating causes disproportionation according to the equation

$$(Et_2Al)_2O \xrightarrow{150°} Et_3Al + EtAlO$$

Reaction of Triethylalane with Deuterium Oxide. Triethylalane, 6.08 mmoles, in 75 ml of benzene was allowed to react with 3.04 mmol of deuterium oxide in the usual way. The amount of gases noncondensable at $-196°$ was 0.116 mmole and was shown by mass spectrometry to consist chiefly of a mixture of monodeuterated methane and hydrogen deuteride, with traces of hydrogen and deuterium. The amount of monodeuterated ethane obtained was 5.99 mmoles. The aloxane, on removal of the solvent, remained as a nonvolatile, colorless, viscous liquid.

Anal. Calcd for $(Et_2Al)_2O$: Al, 29.04; hydrolyzable Et, 62.3. Found: Al, 29.12; hydrolyzable Et, 61.9.

Reaction of $(Et_2Al)_2O$ with Water. Using the method described above, 6.67 mmoles of $(Et_2Al)_2O$ was allowed to react with 6.67 mmoles of water in 100 ml of benzene. In addition to 0.259 mmole of gases noncondensable at $-196°$, 12.81 mmoles of ethane was evolved. The reaction mixture on filtering and removal of solvent yielded an insoluble white solid and a small amount of a soluble white solid.

Anal. Calcd for EtAlO: Al, 37.5; hydrolyzable Et, 40.3. Found (soluble material): Al, 31.9; hydrolyzable Et, 43.9; Al:Et = 1:1.28. Found (insoluble material): Al, 36.8; hydrolyzable Et, 34.2; Al:Et = 1:0.867.

The soluble material again showed strong infrared absorption bands in the 800-cm^{-1} region, indicating Al–O–Al bonding. The data for the reaction may be represented approximately by the net equation

$$(Et_2Al)_2O + H_2O \xrightarrow{\text{benzene}} 2EtAlO + 2EtH$$

The solubility of the solids produced decreases with loss of ethane and consequent setting up of more oxygen bridging.

Reaction of Triethylalane with Water in a 1:1 Ratio. Triethylalane, 17.52 mmoles, dissolved in 150 ml of benzene, was allowed to react with 17.52 mmoles of water. There formed 0.781 mmole of gases noncondensable at $-196°$, demonstrated to be approximately equal volumes of hydrogen and methane by mass spectrometry. The ethane evolved was 29.4 mmoles. The reaction mixture on filtering and removal of solvent yielded mainly an insoluble white solid together with a small quantity of a soluble, tacky, white solid.

Anal. Found (soluble material): Al, 31.3; hydrolyzable Et, 40.8; Al:Et = 1:124. Found (insoluble material): Al, 35.5; hydrolyzable Et, 35.3; Al:Et = 1:0.925.

The soluble material showed very strong absorption around 800 cm^{-1} in its infrared spectrum indicating an Al–O–Al linked system. The solid products, therefore, closely resembled those obtained when $(Et_2Al)_2O$ was hydrolyzed slowly with an equimolar amount of water. The net reaction is approximated by the equation

$$Et_3Al + H_2O \xrightarrow{\text{benzene}} EtAlO + 2EtH$$

Reaction of $(Et_2Al)_2O$ with Trimethylamine. Trimethylamine (3.83 mmoles) was condensed into a flask containing 1.392 mmoles of $(Et_2Al)_2O$. The flask was allowed to warm up slowly to room temperature, and after a few hours 2.495 mmoles of unreacted trimethylamine was pumped off and measured *via* the Toepler pump. Thus, 1.335 mmoles of amine was absorbed by the aloxane, suggesting the formation of a 1:1 complex, $(Et_2Al)_2O \cdot NMe_3$. After several days at room temperature no more amine was evolved from the complex, a colorless liquid; on heating, no amine was evolved below 90°. Prolonged heating at 170° gave only a slight increase in pressure in the system, indicating the relatively high thermal stability of the complex. The presence of Al–N linkages was demonstrated by obtaining the infrared spectrum of the product in benzene solution. The molecular weight of the complex in benzene solution was determined: calcd for $(Et_2Al)_2O \cdot NMe_3$, 245; found, 325 ($n = 1.325$).

Bis(ethylethoxyaluminum)oxane, $(EtAlOEt)_2O$. In a typical experiment, 12.08 mmoles of diethylethoxyalane in 100 ml of benzene

Table I. Infrared Spectra of Ethylaloxanes and Parent Ethylalanes[a]

Et_3Al[20]	$(Et_2Al)_2O$	Et_2AlCl[20]	$(EtAlCl)_2O$	Et_2AlOEt	$(EtAlOEt)_2O$	Assignments
1470 s	1465 m	1470 s	1465 m	1470 m	1465 m	$\delta_{as}(CH_3)$
1458 sh,s	1452 sh,m	1460 sh,s				
1412 s	1415 s	1410 s	1420 s	1420 m	1420 w	$\delta(CH_2\text{–}Al)$
	1405 sh,m		1405 s	1400 m	1400 m	
1401 sh,s						$\delta(CH_2\text{–}Al)$ bridge
1389 sh,m						
1379 m	1380 m	1380 m		1380 w	1380 w	$\delta_{sym}(CH_3)$
1218 m						$\gamma(CH_2)$ bridge
1230 m	1225 m	1230 m	1227 m			$\gamma\ \tau(CH_2\text{–}Al)$
1199 m	1195 m	1200 m	1205 m	1192 m	1190 m	
	1165 m		1162 m	1158 w		
				1100 s	1110 vs	$\nu(CO)$
				1054 vs	1072 vs	
					1060 sh,vs	
					1020 s	
985 vs	985 s	990 vs	990 vs	985 s	984 m	$\nu(CC)$
955 s	955 m	955 s	958 m	950 m	950 w	
921 m	924 m	925 m	930 s	921 m	920 m	
				898 vs	900 s	AlOEt mode?
	790–815 br,vs		780–812 br,vs	820 w	820 vs	$\nu(Al\text{–}O\text{–}Al)$
	755–770 br,vs		755–770 br,vs			
	735 vs		740 vs			
662 vs	654 vs	673 vs	662 s	643 vs	648 vs	$\nu(Al\text{–}C$ outer)
626 vs		628 vs	630 vs	620 sh,s		CH_2 rock
600 sh,s						
545 vs	545 m	544 s	545 w	520 w	525 w	$\nu(Al\text{–}C$ outer)
477 s	480 w	438 m				Ring vibration
			450 s			$\nu(Al\text{–}Cl)$?

[a] w, weak; m, medium; s, strong; vs, very strong; br, broad; sh, shoulder.

reacted with 6.04 mmoles of water to yield 11.94 mmoles of ethane and a completely soluble product. In this case, no gases noncondensable at −196° were observed. The reaction may be represented as

$$2Et_2AlOEt + H_2O \xrightarrow{\text{benzene}} (EtAlOEt)_2O + 2EtH$$

The aloxane, on removal of solvent, remained as a very viscous colorless liquid.

Anal. Calcd for $(EtAlOEt)_2O$: Al, 24.7; hydrolyzable Et, 26.6; OEt, 41.2; mol wt, 218. Found: Al, 24.55; hydrolyzable Et, 26.6; OEt, 40.9; mol wt, 1145 (n = 5.25).

Reaction of $(EtAlOEt)_2O$ with Trimethylamine. Trimethylamine, 4.22 mmoles, was condensed onto 1.486 mmoles of $(EtAlOEt)_2O$ and the mixture was allowed to warm to room temperature. After several hours, 4.22 mmoles of amine could be pumped off, indicating the absence of a complex stable at this temperature. The reaction was repeated at lower temperatures (−46 and −63°), but in both cases all the amine was eventually recovered even though there was indication of 1:1 complex formation, the last molar equivalent of amine being evolved very slowly.

Bis(ethylchloroaluminum)oxane, $(EtAlCl)_2O$. In this case, the reaction did not proceed as smoothly as those described above. Diethylchloroalane, 14.68 mmoles, in 100 ml of benzene was allowed to react with 7.34 mmoles of water, and 12.85 mmoles of ethane evolved. No gas noncondensable at −196° was observed.

$$2Et_2AlCl + H_2O \xrightarrow{\text{benzene}} (EtAlCl)_2O + 2EtH$$

A small amount of insoluble material collected on the sinter during filtration and the reaction flask contained a slight smear of colored resinous-looking material. On removal of solvent and volatile materials from the filtrate, the desired product remained as a colorless, viscous liquid.

Anal. Calcd for $(EtAlCl)_2O$: Al, 27.1; hydrolyzable Et, 29.1; Cl, 35.6; mol wt, 199. Found: Al, 27.1; hydrolyzable Et, 29.05; Cl, 34.0; mol wt, 975 (n = 4.9).

Reaction of $(EtAlCl)_2O$ with Trimethylamine. A mixture of 0.572 mmole of $(EtAlCl)_2O$ and 3.39 mmoles of trimethylamine was held at room temperature. After several hours, 2.83 mmoles of unreacted amine could be pumped off, 0.56 mmole being absorbed. This demonstrated the formation of a 1:1 complex, $(EtAlCl)_2O \cdot NMe_3$. The viscous liquid complex was thermally stable at room temperature and on heating to 150–200° gave only a slight pressure increase in the system. Its infrared spectrum in benzene solution afforded evidence for the presence of an Al–N linkage.

Infrared Spectra. The infrared spectra were recorded on a Perkin-Elmer Model 337 grating infrared spectrometer. Solutions in benzene and in n-hexane were used as samples, and the results, together with those for the parent compounds, are given in Table I. All solutions were prepared, and the cell filled, in the glove box under nitrogen since all the compounds are extremely moisture and oxygen sensitive. (Atmospheric oxidation of the samples can be readily demonstrated by the formation of ethoxy groups which show strong characteristic absorption bands, for example, at 910, 1110, and 1067 cm^{-1}.)[10]

Proton Magnetic Resonance Spectra. The proton magnetic resonance spectra were obtained on a Varian analytical nuclear magnetic resonance spectrometer, Model A-60, operating at 60 Mc/sec and equipped with a variable-temperature controller, Model V-6040. Because of the difficulty of using a suitable internal standard with these materials, chemical shifts are reported only as differences from the benzene signal. Table II lists the results obtained for the aloxanes and their parent compounds in benzene solution.

Table II. Proton Magnetic Resonance Spectra

	Chemical shift, ppm					
		OEt		Et		
Compound	C_6H_6	CH_2	CH_3	CH_3	CH_2	$\delta_{Et(CH_3-CH_2)}$
Et_3Al	0			6.10	6.92	0.82
$(Et_2Al)_2O$	0			6.12	6.92[3]	0.80
$EtOAlEt_2$	0	3.58[5]	6.06	6.00	7.13	1.13
$(EtOAlEt)_2O$	0	(3.33)	5.85	5.85	6.92	1.07
Et_2AlCl	0			6.04	6.91	0.87
$(EtAlCl)_2O$	0			6.04	6.92	0.88

Discussion

The infrared spectra of the aloxanes show several novel and interesting features. Table I lists tentative assignments for the absorption bands observed. The most important feature of the spectra of the aloxanes

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is the occurrence of a very intense absorption region around 750–800 cm^{-1} which is absent in the spectra of the parent compounds, even in the case of the parent ethoxy derivative, Et_2AlOEt, which is known to be dimerized through ethoxy bridges in benzene solution.[11] Accordingly, this region is assigned to Al–O–Al stretching vibrations. Additional support for this argument is gained by comparison with similar systems. Thus, Bradley and Westlake[12] in their studies of titanium oxide ethoxides attributed the absorption bands at 770 and 790 cm^{-1} in the infrared spectra to the Ti–O–Ti link, these bands being absent from the spectra of the normal ethoxide compounds which are known to contain bridging ethoxide groups. A similar behavior with the butoxy derivatives of titanium has also been observed.[13] The infrared spectra of similar tin,[14] zirconium,[15] molybdenum,[16] and sulfur[17] compounds all show M–O–M stretching vibrations in the region 750–800 cm^{-1} of their spectra. The assignment is further substantiated by the data of Nyholm, *et al.*,[18] and of Cotton and Wing,[19] who discuss the infrared spectra of metal–oxygen–metal systems of a variety of transition elements.

In the infrared spectra of the ethoxy derivatives, characteristic bands are assigned to C–O stretching vibrations in the region 1020–1110 cm^{-1}, and the intense absorption at about 900 cm^{-1} is attributed to the AlOEt group. The spectrum of the ethylchloroaloxane shows a strong absorption at 450 cm^{-1} which may be due to an Al–Cl bridge vibration,[20] although the possibility of the halogen exchange with the potassium bromide windows of the absorption cell, with consequent absorption in this region, cannot be ruled out.

It is interesting to note that the spectrum of $(Et_2Al)_2O$ below 700 cm^{-1} is considerably simplified compared with the intense absorption of the starting material, triethylalane, in this region. This is presumably due to the formation of the oxygen units in the product, replacing the bridging ethyl groups of the parent alane compound. The assignment of the remaining parts of the spectra follows directly from those of Hoffmann[20] and Mach.[10]

In the proton magnetic resonance spectra, in all cases of ethyl groups attached to aluminum, the expected "inverted ethyl signals" were observed, with the signal arising from the methylene protons at higher field than that for the methyl protons. In the case of Et_2AlOEt, two completely separate ethyl groups (see Table II) are apparent with their arrangements opposite to each other. Although the two different methyl triplets overlap, they can easily be distinguished by their relative intensities. A similar spectrum has been observed for the etherate of triethylalane, $Et_2O \cdot AlEt_3$.[21] The relatively large value of δ (δ = the separation between methyl proton and methylene proton signals of the ethyl groups attached to aluminum) in Et_2AlOEt is probably due to the inductive effect of the ethoxy group which enhances the shielding of the methylene protons in the β position. The δ values for a series of diethylmonohalogenoalanes, Et_2AlX, have recently been discussed[22] and the differences in these values attributed to the different diamagnetic anisotropies of the halogen substituents. By comparison, it is evident that the ethoxy group is much more effective in shielding the methylene protons than the halogen substituents. The proton signals from the aloxanes were all much less sharp than those of the parent compounds, perhaps because of the higher degree of polymerization of the aloxanes. In the case of $(EtAlOEt)_2O$ the two methyl proton triplets could no longer be distinguished from each other because of merging of the peaks. In general, however, the relative position of the signals and the δ values were the same for the products as for the parent compounds, with the exception of $(EtAlOEt)_2O$ where all the signals occurred at lower field.

The low-temperature nmr spectra of $(Et_2Al)_2O$ in toluene failed to show the presence of two different ethyl groups at temperatures as low as $-54°$, which indicates a structure with none of the ethyl groups bridging aluminum atoms. With decrease in temperature, the methyl triplet signals became less sharp and the methylene quartet, at higher field, eventually merged into a very broad singlet. A similar effect has been observed for solutions of triethylalane in toluene at low temperatures,[23] but in this case, at even lower temperatures it was possible to pick out signals arising from bridging ethyl groups.

The controlled reaction of ethylalane compounds with water in the mole ratio of 2:1 probably proceeds through an intermediate hydroxy molecule, which then reacts with another ethylalane molecule to yield the aloxane, by the following equations

$$Et_{3-x}AlX_x + H_2O \xrightarrow{\text{benzene}} Et_{2-x}Al(X)_xOH + EtH$$

$$Et_{2-x}Al(X)_xOH + Et_{3-x}AlX_x \xrightarrow{\text{benzene}} Et_{2-x}Al(X)_xEt_{2-x} + EtH$$

The absence of any OH absorption bands in the infrared spectra of the aloxanes prepared precludes the presence of any hydroxy derivative in the final products. The above equations, although representing the derivation of the observed final products, must be a simplified version of the actual reaction mechanism. A more elaborate scheme would have to take into account the initial dimeric nature of the parent alane compounds in the benzene solution, the possibility of condensation of two hydroxy molecules, and also the polymerization of the aloxanes. The formation of small quantities of methane and hydrogen in the reaction with triethylalane suggests a more complex mechanism in this case.

The molecular weight data show that $(Et_2Al)_2O$ is trimeric in benzene solution. A cyclic arrangement having oxygen bridging groups seems to be the most likely structure.

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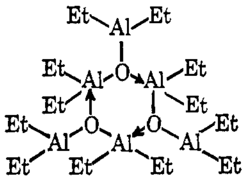

This structure has equal numbers of three- and four-coordinate aluminum atoms and, if a similar structural pattern occurs in the pure compound, could explain the uptake of only one molecule of trimethylamine per two aluminum atoms to form the complex, $(Et_2Al)_2O\cdot NMe_3$. The molecular weight data on the adduct, however, show this to be only slightly associated ($n = 1.325$) in benzene solution. This indicates a breakdown of the postulated trimeric structure of $(Et_2Al)_2O$ either on complex formation or on dissolution of the complex in benzene. The presence of an Al–N absorption mode in the infrared spectrum of the complex occurs at 516 cm^{-1} which is close to the values of previously assigned Al–N vibrations.[24]

A higher degree of polymerization in the case of $(EtAlOEt)_2$ and $(EtAlCl)_2O$ may be attributed to cross-linked structures involving ethoxy- and chloro-bridging groups, or perhaps to the formation of larger rings. The weakness of the complex formed between trimethylamine and the ethoxy derivative may be due in part to this internal satisfying of four coordinancy by the aluminum atoms, and also in part to the shielding effects of the ethoxy group. The stronger complex formed between the chloro derivative and trimethylamine may be accounted for by the electron-withdrawing effect of the halogen atoms which enhances the acceptor properties of the aluminum atoms.

The reactivity toward moist air of the compounds studied followed the expected pattern. Thus, when triethylalane is exposed to the air it immediately inflames, but $(Et_2Al)_2O$, although fuming in moist air and being readily oxidized (as evidenced by the appearance of strong C–O absorption bands in the infrared spectrum of an exposed sample), does not inflame. The substituted derivatives $(EtAlOEt)_2O$ and $(EtAlCl)_2O$ appear to be less prone to attack by moisture in the air but are again readily oxidized by atmospheric oxygen. Finally, with higher percentages of oxygen in the compounds, *e.g.*, EtAlO, the stability toward atmospheric moisture appears to be greater, although a slow oxidation of the ethyl group may still be observed in the infrared spectrum of an exposed sample.

Acknowledgments. We wish to thank the Advanced Research Projects Agency and the National Science Foundation for financial support for this research.

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Stereochemistry of Discrete Eight-Coordination. V. The Octacyanomolybdate(IV) Ion[1]

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Abstract: Accurate stereochemical parameters for the dodecahedral form of the octacyanomolybdate(IV) ion, obtained by analysis of the three-dimensional X-ray data recorded from crystalline $K_4Mo(CN)_8\cdot 2H_2O$ for $(\sin\theta)/\lambda < 0.82$, are in part as follows. The averaged Mo–C bond length is 2.163 Å, with a mean deviation of 0.005 Å and an esd of 0.007 Å; corresponding data for the C≡N distance are respectively 1.152, 0.006, and 0.009 Å, and for the Mo–N chain length, 3.314, 0.005, and 0.008 Å. Comparison of these results with analogous data for eight-coordinate oxozirconate(IV) complexes and for the octahedral $MoO_2(CN_4)^{4-}$ ion strongly suggests that the net benefits from π bonding are much larger in the d^0 Zr(IV) complexes than in the d^2 Mo(IV) species. The commonly made assumption that the D_{2d} dodecahedron is better adapted than is the D_{4d} antiprism for π bonding is highly questionable. Evidence bearing on the stereochemical form of the $Mo(CN)_8^{4-}$ ion in solution, though inconclusive, inclines toward a species having effectively D_{4d} symmetry. It is pointed out that the antiprismatic variant of the quadruply charged complex is clearly the better adapted to stabilizing short-range interactions of a specifically anisotropic nature with contiguous water molecules and/or cations in the immediate environment.

The remarkable octacyanomolybdate(IV) and octacyanotungstate(IV) complexes, known since the turn of the century, have received intensive study during recent years by a variety of modern experimental techniques. The behavior of these complexes, nevertheless, is not yet fully understood and is subject to debatable interpretations. The points at issue can be more sharply defined and, in part, resolved with the aid of accurate bond parameters for the octacyanomolybdate(IV) complex and for some other complexed species that are especially useful for comparative purposes. These data are introduced, as needed, in the general discussion; the reliability of the $Mo(CN)_8^{4-}$ data is documented in the Experimental Section of this paper.

The strong presumption that the octacyanomolybdate(IV) and octacyanotungstate(IV) complexes exist

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(1) This investigation was supported in part by National Science Foundation Grants G-23470 and GP-6710X, by Public Health Research Grant No. 5-ROI-GM09370 from the National Institutes of Health, General Medical Sciences, and by the Advanced Research Projects Agency.

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