Complexes of Trialkylaluminum Compounds with Polyfunctional Ethers

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Triethyl-, triisobutyl-, and tri-n-hexylaluminum form complexes with monoglyme, diglyme, and triglyme in which the alkylaluminum compounds are involved in rapid chemical exchange. The monoglyme complexes undergo little, or no, measurable dissociation as determined by ^{1}H NMR studies, whereas those of diglyme and triglyme dissociate more extensively. Low-temperature NMR studies in cyclopentane of the triethylaluminum–diglyme complex in the presence of excess triethylaluminum result in an activation energy of 6.1 kcal/mol for the exchange of complexed and free triethylaluminum. This comparatively low value suggests that exchange in this system may be occurring by a bimolecular displacement mechanism rather than a simple bond-breaking dissociation process.

Introduction

Previous studies of the complexes formed between trialkylaluminum compounds and aliphatic ethers have been limited primarily to monofunctional ethers [1]. A few papers have been concerned with the complexes formed with difunctional ethers, such as dioxane [2–4], p-dimethoxybenzene [5], or 1,2-dimethoxyethane (monoglyme) [6]. Although NMR spectroscopy has frequently been used to study the acid–base systems of boron [7–10] and gallium compounds [11, 12] with various donors, it has not been applied as extensively to similar examples involving aluminum. Much of the work that has been reported has studied the relative stabilities of various adducts by displacement reactions. Our interest in this area originated from attempts to moderate the reactivity of the alkylaluminum by forming complexes with various polyethers. Complexes of monoglyme (MG), diglyme (DG), and triglyme (TG) with triethylaluminum (TEA), triisobutylaluminum (TIBA), and tri-n-hexylaluminum (TNHA) were studied by ^{1}H NMR spectroscopy to determine their stoichiometries and the dependency of their reactivities on the size of the ether and the alkyl group attached to the aluminum. Low-temperature spectra of the TEA-DG complex have provided additional information about these systems.

Experimental

Materials

The alkylaluminum compounds were obtained from Texas Alkyls, Inc. and were used as received. The ethers (Practical Grade) and cyclopentane (Reagent Grade) were purchased from Eastman Kodak Co., distilled over sodium, and stored over 4A molecular sieves. The gaseous nitrogen was Ultrapure Carrier Grade (Air Products, Inc.) and contained less than 1 ppm each of water and oxygen.

Preparation of Samples

The various solutions were prepared using a syringe to transfer the reactants, and cyclopentane if used, into a small septum bottle containing an atmosphere of nitrogen. The quantity of each reagent was determined by accurately weighing the bottle after each addition. The NMR tubes were thoroughly dried by treatment with trimethylchlorosilane *in vacuo*; after removal of the trimethylchlorosilane, the tubes were back-filled with nitrogen. The solutions were transferred into the NMR tubes, degassed on the vacuum line, and sealed. TMS in a sealed capillary tube was used as a reference and lock signal for neat samples. This was inserted into the NMR tube and secured with Teflon spacers prior to the drying procedure. For samples that were run in solution, the cyclopentane was used as the internal lock.

Spectral Measurements

NMR spectra were run on a 90 MHz Varian Model EM390 Spectrometer equipped with a variable

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TABLE I. Change in Internal Chemical Shifts of TEA and TIBA with Concentration in Diglyme Complexes at 34 °C.

TEA (mmol)	DG (mmol)	$\Delta\delta$ (Hz)	TIBA (mmol)	DG (mmol)	$\Delta\delta$ (Hz)
4.39	0	65	1.57	0	57
16.11	2.82	83	9.16	1.91	75
14.50	4.88	99	8.63	2.10	78
11.80	4.73	106	13.02	4.48	86
12.21	5.57	107	8.10	3.26	90
13.66	7.65	106	6.57	2.94	91
12.53	9.67	108	13.19	6.44	91
15.97	14.91	108	8.59	6.07	92
			13.07	13.65	92
			9.65	12.80	92

temperature controller calibrated with a methanol sample. Chemical shifts are reported in units of δ relative to TMS. The data were plotted using a least-squares fit in the region where the internal chemical shift difference, $\Delta\delta$, varied with the mol ratio of the reactants. An average value for $\Delta\delta$ was used where it proved to be independent of the mol ratio.

Results and Discussion

Chemical shifts in the proton NMR spectra of TEA, TIBA, and TNHA in solutions with polyethers were found at higher fields than those of the neat alkylaluminum compounds. Previous workers have attributed this behavior to the increased electron density on the aluminum that results from forming a Lewis acid–base complex with the ether and have found it to be most pronounced in protons at the position α to the aluminum [13]. Only one set of resonances was observed for the alkylaluminum compounds in samples containing excess alkylaluminum, indicating that a rapid chemical exchange on the NMR time scale was occurring between the free and complexed species. Under these conditions, the observed chemical shift, δ_o, represented a weighted average of the chemical shifts of the free, δ_A, and complexed, δ_{AB}, alkylaluminum as given by the equation

$$\delta_o = \delta_A X_A + \delta_{AB} X_{AB} \qquad (1)$$

A plot of δ_o and the mol ratio of reactants has typically been used to provide information about the stoichiometry of systems such as these [7]. To minimize solvent and concentration effects on the chemical shifts, we have constructed plots for each of the alkylaluminum–ether mixtures using the internal chemical shift difference, $\Delta\delta$, between the protons in the α methylene position and those in the terminal methyl group. Table I and Fig. 1 contain data from the TEA and TIBA complexes of diglyme which are representative of the systems studied.

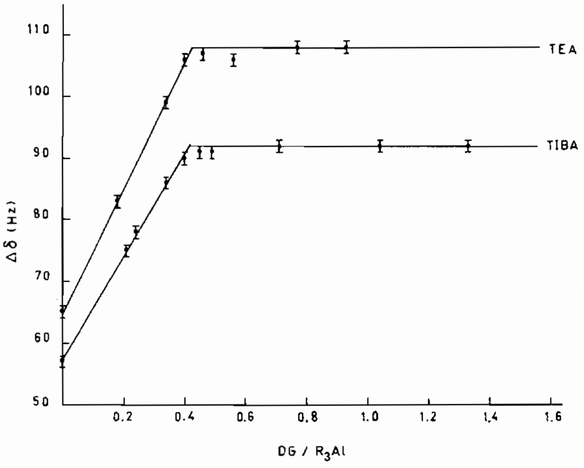

Fig. 1. Internal chemical shift of TEA and TIBA as a function of diglyme–alkylaluminum ratio.

The linear relationship found between $\Delta\delta$ and the mol ratio for solutions with an excess of alkylaluminum was consistent with a rapid chemical exchange within the system. As the amount of ether in the solution was increased, $\Delta\delta$ also increased and reached a maximum constant value which indicated that all of the alkylaluminum was complexed. Extrapolation of the two lines resulted in a point of intersection which corresponded to the stoichiometry of the complex in the presence of excess alkylaluminum. These values are given in Table II and, as expected, show that the MG complexes have a 2:1 stoichiometry. The DG and TG complexes, however, have values that are less than those expected for full coordination of the ether sites which suggests that some dissociation of the complex occurs as represented by

TABLE II. Stoichiometric Values of Ether–R_3Al Complexes.

	Ether/R_3Al[a]			
	TMA[b]	TEA	TIBA	TNHA
MG	0.49	0.49	0.48	0.50
	(2.1)	(2.1)	(2.1)	(2.0)
DG	c	0.42	0.41	0.40
	c	(2.4)	(2.4)	(2.5)
TG		0.32	0.29	0.31
		(3.1)	(3.5)	(3.1)

[a] R_3Al/ether ratios are given in parentheses. [b] Determined from chemical shift of CH_3 with respect to external TMS. [c] Neat TMA complexes of DG and TG were solids at ambient conditions and were not examined.

$$(R_3Al)_n \cdot \text{Ether} \rightleftharpoons (R_3Al)_{n-1}\ \text{Ether} + R_3Al \qquad (2)$$

To minimize effects due to dimerization of the alkylaluminum compounds or concentration changes, solutions of TEA with DG, and TIBA with DG, were examined at approximately 20 percent of their original concentration and at a constant concentration of about 1 *M* in cyclopentane; no appreciable difference in the stoichiometries was observed.

The above results can be interpreted in terms of rather simple steric arguments. Specifically, the 'outside' oxygen atoms in DG and TG would appear to be more accessible to interaction with the alkylaluminum molecules than those in the 'inside' positions. Complexation of these latter sites would not be complete, particularly in rapidly exchanging systems where incoming alkylaluminums would be hindered in their approach. The steric requirements of the branched isobutyl group appeared to be no greater in these systems than those of the longer chain n-hexyl groups in TNHA. In addition, we observed no difference in the complexing ability of the alkylaluminums with the ethers based on differences in chain lengths of the ethyl and hexyl groups attached to the aluminum as seen in earlier cryoscopic studies [14].

Information about the rate of exchange of alkylaluminum molecules in these complexes was obtained by a simplified analysis of spectral line widths in the slow exchange region of a TEA-DG mixture using the equation

$$\frac{1}{\tau} = \pi(\nu_{1/2} - \nu_{1/2}{}^{\circ}) \qquad (3)$$

where τ is the average lifetime of an exchanging nucleus, $1/\tau$ is the rate of exchange, $\nu_{1/2}$ is the measured line width, and $\nu_{1/2}{}^{\circ}$ is the line width of species undergoing no exchange. In their study of methyl group exchanges between trimethyl derivatives of Group III elements, Williams and Brown found that this method of estimating τ gave results in good agreement with those obtained from a more sophisticated approach involving computer generated spectra [15].

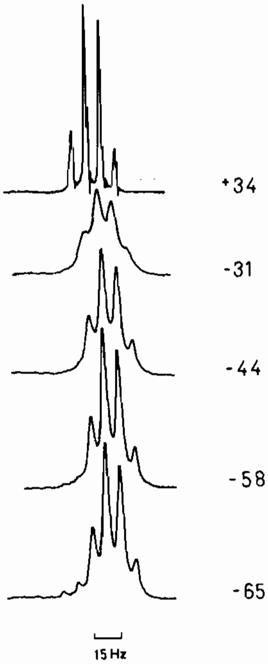

Fig. 2. Temperature dependence of TEA methylene protons in cyclopentane solution of DG.

We were able to obtain low-temperature spectra only for a cyclopentane solution of TEA and DG with a ratio of 2.9:1.0 which corresponded to an excess of TEA based on the proposed 2.4:1.0 stoichiometry discussed above. All other solutions either solidified or became too viscous at low temperatures to obtain meaningful data. At room temperature, only one methylene quartet, corresponding to an averaged resonance for the free and complexed TEA, was observed. This resonance broadened as the temperature was lowered to approximately −30 °C and then gradually became sharper below this temperature until two additional peaks believed to be part of a smaller, overlapping quartet were observed at −65 °C as shown in Fig. 2. The chemical shift of $\delta = 0.07$ for the smaller quartet was in good agreement with our measured value of 0.08, and the reported value of 0.08, for the terminal methylene group in the TEA dimer [16]. We have therefore assigned the smaller quartet to the free TEA dimer and the larger quartet to the complexed TEA species. A comparison of these spectra with those of TEA alone in cyclopentane which were run

TABLE III. Rates of Exchange of TEA with TEA-DG Complex in Cyclopentane.[a]

Temperature (°C)	$\nu_{1/2}$ (Hz)	$1/\tau$[b]
−35	10.1	28.6
−39	8.4	23.3
−44	6.7	17.8
−48	5.5	14.0
−49	5.0	12.5
−52	4.5	10.9

[a] (TEA) = 1.15 *M*, (DG) = 0.39 *M*. [b] $\nu_{1/2}°$ equals 1 Hz at these temperatures.

at the same temperature verified that this behavior was not simply the result of exchange between terminal and bridging ethyl groups.

A slow exchange is believed to be occurring between free and complexed TEA at temperatures below −30 °C. An exchange rate was calculated using eqn. 2, where $\nu_{1/2}°$, the line width of the species undergoing no exchange, was estimated from the half-height line width of cyclopentane at the temperature used, and $\nu_{1/2}$ was obtained from the most intense peak of the methylene quartet assigned to the complexed TEA. Values of $1/\tau$ at the various temperatures are listed in Table III. An Arrhenius plot of log $1/\tau$ *vs.* 1/T, as shown in Fig. 3, yielded an activation energy of 6.1 kcal/mol. Although care must be taken in determining activation energies over small temperature ranges [17], we believe this value represents at least a reasonable approximation of the correct value. It is considerably less than the enthalpies of formation reported for complexes of TEA with various ethers [1] and suggests that in the presence of excess TEA, the exchange may not be occurring *via* a simple bond-breaking dissociation process, but perhaps through a lower energy bimolecular displacement process such as

$$Et_3Al{:}DG + Et_3Al^* \rightleftharpoons Et_3Al^*{:}DG + Et_3Al \qquad (4)$$

Confirmation of this, however, will require more detailed concentration studies. Attempts to obtain similar data at different TEA/DG ratios were unsuccessful due to the existence of broad, unresolved resonances at low temperatures. Whether this resulted from a different exchange mechanism operating at these concentrations or from a physical effect in the solution (*e.g.* greater viscosity) could not be determined.

Conclusions

We have shown that the trialkylaluminum compounds TEA, TIBA, and TNHA form complexes with various polyethers in which the aluminum compounds are involved in a rapid chemical exchange. Concentration studies have shown that the complexes of monoglyme undergo little, if any, measurable dissociation, whereas those of diglyme and triglyme have been found to dissociate more extensively. This would appear to be the result of the greater steric hindrance encountered by the alkylaluminums in approaching the inner oxygen sites on the ethers. In this dissociation, little or no difference was observed in the steric requirements of the ethyl, iso-butyl and hexyl groups attached to the aluminum. Low-temperature studies of the TEA-DG complex in the presence of excess TEA in cyclopentane have provided an approximate value of 6.1 kcal/mol for the activation energy of the exchange process. The magnitude of this value in comparison to the enthalpies of formation of TEA–ether complexes suggests that the exchange may be occurring through a displacement process.

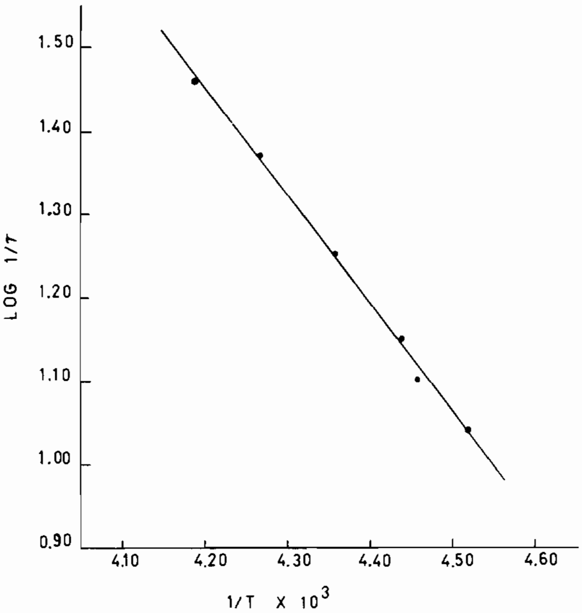

Fig. 3. Temperature dependence of exchange rate for free and complexed TEA in cyclopentane solution of DG.

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