lutions of $LiMg(s\text{-}C_4H_9)_2H$ at room temperature are apparently more stable than that of the potassium compound. When a benzene solution of $KMg(s\text{-}C_4H_9)_2H$ was added to a lithium bromide slurry in benzene, no reaction occurred even after several days of stirring. No lithium was detected in the supernatant solution which essentially retained its original composition.

There is an interesting basic difference between the reactions of $KMg(s\text{-}C_4H_9)_2H$ with lithium bromide in THF and diethyl ether. In the case of tetrahydrofuran, $LiMg(s\text{-}C_4H_9)_2H$ is formed; however, when diethyl ether is the solvent, $LiMg_2(s\text{-}C_4H_9)_4H$ is the product.

$$2KMg(s\text{-}C_4H_9)_2H + 2LiBr \xrightarrow[25°]{Et_2O} LiMg_2(s\text{-}C_4H_9)_4H + 2KBr + LiH \tag{11}$$

The solid product obtained from this reaction was analyzed and found to be a mixture of KBr and LiH formed in 2:1 ratio. It seems reasonable to suggest that $LiMg(s\text{-}C_4H_9)_2H$ is formed in the reaction and that it slowly disproportionates to $LiMg_2(s\text{-}C_4H_9)_4H$ and LiH.

On addition of sodium iodide to $KMg(s\text{-}C_4H_9)_2H$ in THF, a quantitative precipitate of KI was obtained. Analysis of

$$KMg(s\text{-}C_4H_9)_2H + NaI \xrightarrow[25°]{THF} NaMg(s\text{-}C_4H_9)_2H + KI \tag{12}$$

the resulting solution showed a Na:Mg:Bu:H ratio of 1.00:1.07:1.87:0.92 establishing the formation of $NaMg(s\text{-}C_4H_9)_2H$ in solution.

Registry No. $KMg_2(C_6H_5)_4H$, 55886-10-7; $NaMg_2(s\text{-}C_4H_9)_4H$, 55886-09-4; $KMg(s\text{-}C_4H_9)_2H$, 36426-31-0; $KMg(n\text{-}C_4H_9)_2H$, 55822-78-1; $LiMg_2(s\text{-}C_4H_9)_4H$, 55886-08-3; $LiMg(s\text{-}C_4H_9)_2H$, 55822-79-2; $NaMg(s\text{-}C_4H_9)_2H$, 44889-27-2; $[(n\text{-}C_8H_{17})_3N(n\text{-}C_3H_7)]Mg(s\text{-}C_4H_9)_2H$, 55822-81-6; $(C_6H_5)_2Mg$, 555-54-4; KH, 7693-26-7; NaH, 7646-69-7; $(s\text{-}C_4H_9)_2Mg$, 17589-14-9; $(n\text{-}C_4H_9)_2Mg$, 1191-47-5.

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Intra- and Intermolecular Exchange Reactions Involving Methyl and Tolyl Derivatives of Aluminum[1]

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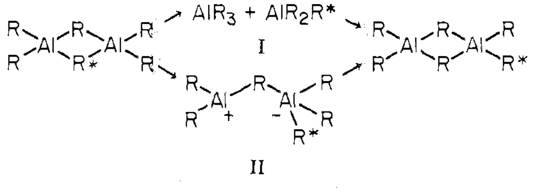
Studies of kinetic and activation parameters have been made for intramolecular bridge–terminal exchange for dimers of trimethylaluminum (TMA), tri-*p*-tolylaluminum (TPTA), and tri-*m*-tolylaluminum (TMTA). The data indicate that the first of these reactions proceeds via a dissociative mechanism as proposed earlier but the latter two most likely proceed via a mechanism involving only a partial dissociation of the electron-deficient bridge. This conclusion is supported by the unusually low activation energies of 9.7 ± 1.0 and 8.0 ± 1.0 kcal/mol, respectively, for TPTA and TMTA as well as negative entropies of activation, −9 eu for TPTA and −13 eu for TMTA. The reaction which occurs between trimethylaluminum and tetramethyldi-*p*-tolylaluminum to form pentamethyl-*p*-tolylaluminum appears to proceed via a similar mechanism with a partial dissociation of the tolyl bridges in tetramethyldi-*p*-tolylaluminum. The activation parameters for this reaction are $E_a = 11.1 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = -11$ eu.

Introduction

The exchange reaction which takes place between bridging and terminal methyl groups in the dimer of trimethylaluminum (TMA) has been studied by many workers including Brown and coworkers[2,3] and Jeffery and Mole.[4,5] While these workers differ concerning the precise details of the exchange mechanism, they substantially agree that exchange occurs with a dissociation of the dimer into monomers (path I, eq 1) and



(1)

have ruled out the earlier suggested mechanism[6,7] involving the breaking of only one of the three-center bridges followed by rotation and re-formation of the second bridge (path II, eq 1). Principal support for a dissociative mechanism has been a rather large positive entropy of activation,[7] which is consistent with such a mechanism, and the fact that kinetic parameters for intermolecular exchange are quite similar to those for intramolecular exchange.[2] It has been generally assumed that intermolecular exchange would not result from an activation of the dimer by a single bridge opening (path II, eq 1), although it has been pointed out that this alternative pathway cannot be ruled out completely.[4] The major drawback to the dissociative mechanism has been the seeming discrepancy between the activation energy for the exchange process and the gas-phase dissociation energy of the TMA dimer. The activation energy for bridge–terminal exchange has been determined as 16.0 kcal/mol in cyclopentane[7] and 15.4 ± 2 kcal/mol in toluene.[2] The gas-phase dissociation energy of the TMA dimer has been determined as 20.2 ± 1 kcal/mol.[8] More recent studies have shown that the dissociation energy for the dimer in solution is less than that in the gas phase. Smith has estimated the dissociation energy of trimethylaluminum to be 15.6 ± 1.4 kcal/mol in toluene[9] and 19.4 kcal/mol in cyclopentane.[10]

These data have been used to speculate[9,11] that a dissociative mechanism is operative for bridge–terminal exchange in toluene with some other mechanism being responsible for exchange in cyclopentane, e.g., a single-bridged intermediate or possibly some type of monomer pair formation instead of complete dissociation. Similar inconsistencies were pointed out for triethylaluminum in cyclopentane and toluene solutions.[11] It should be noted that the entropies of activation for bridge–terminal exchange in all the systems just mentioned as well as those for tripropylaluminum in cyclopentane are very similar, ranging from +13 to +16 eu.[11]

In light of the large amount of data available for alkylaluminum systems it is surprising that no quantitative kinetic studies have been made on the intra- and/or intermolecular exchange reactions of arylaluminum compounds. Several spectroscopic studies have indicated that unsaturated groups are better bridging groups than alkyls. NMR evidence has been obtained showing that in the dimers of dialkylvinylaluminum,[12] dimethylphenylaluminum,[13] dimethyl-*p*-tolylaluminum,[13] dimethyl(phenylethynyl)aluminum,[13] and dimethylvinylgallium[14] the unsaturated moieties are without exception the preferred bridging groups. Structural evidence also exists that indicates that the π systems of unsaturated organic ligands can interact with the molecular orbitals of the three-center bridge framework to give rise to a bridge of somewhat greater stability than exhibited for aliphatic hydrocarbons. The crystal structure of triphenylaluminum[15] shows the plane of the bridging phenyl groups to be roughly perpendicular to the plane of the Al–C–Al bridge allowing for interaction of the π systems with the nonbonding orbitals of the bridge framework. The C–C bond distances in the bridging phenyl groups seem to indicate that such an interaction does exist, but this is not conclusive since similar distortions are found[16] in other phenyl–metal compounds which do not have three-center bridges. These distortions persist in the dimer of dimethylphenylaluminum.[17] In addition, evidence for this type of interaction has been given by Sanders and Oliver[18] for the dimer of tricyclopropylaluminum in which the bridge–terminal exchange occurs very slowly, presumably because of interactions between p orbitals on the bridgehead carbon atoms and the electron-deficient framework.

The present study involves a kinetic investigation of intra- and intermolecular exchange reactions involving tri-*p*-tolylaluminum (TPTA), tri-*m*-tolylaluminum (TMTA), and mixtures of tri-*p*-tolylaluminum and trimethylaluminum. In addition some kinetic parameters for intramolecular exchange in trimethylaluminum have been redetermined in various solvents in an effort to clarify some of the inconsistencies in the literature mentioned earlier.

Experimental Section

Handling of Air-Sensitive Materials. All alkyl- and arylaluminum compounds were handled either in a high-vacuum system or in an inert-atmosphere box containing dry, oxygen-free nitrogen. Solid substances or those of low volatility were introduced into sample tubes in a drybox in which the atmosphere was continually passed over liquid sodium–potassium alloy (NaK) to ensure against small amounts of oxygen and/or water. Detailed procedures for handling air-sensitive substances have been described by Shriver[19] and will not be elaborated on here. All hydrocarbon solvents used were dried over NaK and stored in a vacuum line prior to use. Dichloromethane was dried by refluxing over anhydrous barium oxide and stored on the vacuum line.

Materials. Di-*p*-tolyl- and di-*m*-tolylmercury were prepared by the method of Gilman and Brown[20] and were isolated in 65% and 62% yields, respectively. The melting points of 238 and 102°, respectively, correspond to those given in the literature.[21]

Tri-*p*-tolyl- and tri-*m*-tolylaluminum were prepared according to the method originated by Krause and Dittmar[22] and modified by Eisch and Kaska[23] by the reaction of aluminum metal and the correct diarylmercury compound. The only modifications were to use aluminum powder and to carry out the entire reaction in a small inert-atmosphere box filled with dry nitrogen. The *p*-tolyl derivative was formed in 88% yield. The *m*-tolyl derivative was formed in 80% yield; mp 168° (lit.[24] mp 168–70°).

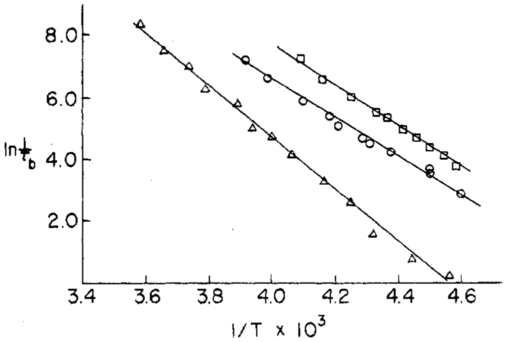


Figure 1. Arrhenius plots for trimethylaluminum intramolecular exchange in cyclopentane (△), toluene (○), and dichloromethane (□).

Trimethylaluminum was purchased from Ethyl Corp. and used without further purification.

NMR Measurements. NMR samples were prepared (in the drybox) by loading solid or nonvolatile substances into a sample tube fitted with a standard taper joint. This tube was then connected to a stopcock via standard tapered joints. The apparatus was then moved to a vacuum line where the appropriate solvent and reference standard were added using normal high-vacuum techniques.[19] Concentrations of solutions were determined by weighing solid materials in preweighed NMR tubes or by adding measured amounts of liquid materials inside the drybox. Solvents were added in known volumes by condensing them into the sample tube (from a pipet sealed onto the vacuum line).

A Varian A-60A NMR spectrometer equipped with variable-temperature accessories was used for all experiments. Temperatures were measured using the temperature dependence of the internal chemical shift of methanol as described by VanGeet.[25] This method measures the temperature at the center of the receiver coil and helps to eliminate the problem of a temperature gradient as discussed by Mole.[4]

Interpretation of NMR Data. Lifetimes for the exchanging groups were determined by using the Bloch equations as modified by McConnell.[26] The calculated spectra were fitted to the experimental by a method of iteration over the lifetimes. This method has been described in detail elsewhere.[27]

Results

Trimethylaluminum. In an attempt to clarify some of the confusion in the literature concerning the kinetic parameters and mechanisms for bridge–terminal exchange of the trimethylaluminum dimer,[2-5,9,11] we have reexamined this system in three solvents: toluene, cyclopentane, and dichloromethane. We have found, as have all previous workers, that the lifetimes for methyl groups involved in bridge–terminal exchange is independent of the concentration of the trimethylaluminum dimer. This is true for all three solvents studied.

The Arrhenius plots of ln τ_b^{-1} vs. T^{-1} for each of the solvents are shown in Figure 1. A least-squares fit of the curves gives rise to the activation energies and other activation parameters in Table I. Results of other workers are given where appropriate.

Tritolylaluminum Intramolecular Exchange. The dimers of both tri-*p*-tolyl- and tri-*m*-tolylaluminum provide convenient aromatic aluminum systems for study in that the methyl groups give rise to sharp uncoupled NMR signals for either the bridging or terminal tolyl methyl groups and a two-site exchange program may be used to obtain the preexchange lifetimes of these groups. The temperature-dependent NMR spectra of the tolyl methyl region for the TPTA system are given in Figure 2. The two resonances which appear at lower temperatures integrate in a 1:2 ratio and are assigned to the bridge and terminal methyl groups, respectively. Since the

Table I. Activation Parameters for Intramolecular Bridge-Terminal Exchange Reactions (Calculated at 225°K)

Compd	Solvent	E_a, kcal/mol	$\Delta H^{\ddagger}$,[a] kcal/mol	k, sec^{-1}	$\Delta S^{\ddagger}$,[b] eu
Trimethylaluminum	Toluene	15.4 ± 2[c]			
		13.6 ± 1	13.2	65.0	+9
	Cyclopentane	16.0[d]	15.6[d]	4.4[d]	+20[d]
		16.3 ± 0.6	15.8	6.6	+16
	Dichloromethane	13.6 ± 0.8	13.1	224	+11
Tri-*p*-tolylaluminum	Dichloromethane	9.7 ± 1.0	9.2	60.1	−9
Tri-*m*-tolylaluminum	Dichloromethane	8.0 ± 1	7.6	290	−13

[a] $\Delta H^{\ddagger} = E_a - RT$. [b] $\Delta S^{\ddagger}/R = \Delta H^{\ddagger}/RT + \ln(K/h) + \ln k$. K is Boltzmann's constant, h is Planck's constant, and k is the first-order rate constant. [c] Cf. ref 2. [d] Cf. ref 7.

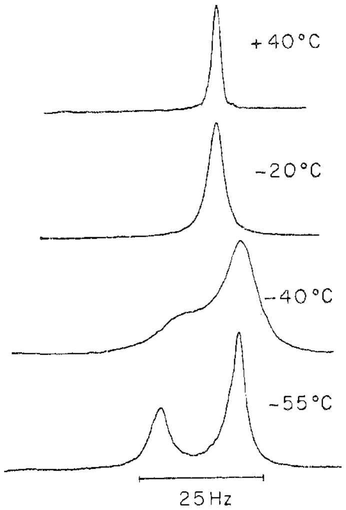


Figure 2. Variable-temperature 60-MHz ^{1}H NMR spectra of the ring methyl protons in the dimer of tri-*p*-tolyaluminum.

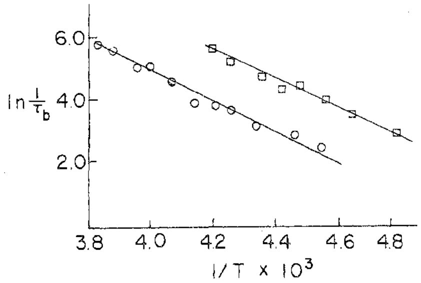


Figure 3. Arrhenius plots for tri-*p*-tolyaluminum (○), and tri-*m*-tolyaluminum (□) intramolecular exchange in dichloromethane.

aromatic region of the spectrum is quite complex, all kinetic parameters have been obtained from the tolyl region.

The lifetimes of the bridging groups and, therefore, the terminal groups as well, are concentration independent. An Arrhenius plot of ln ($1/\tau_b$ vs. $1/T$ (°K) is shown in Figure 3. The activation parameters are given in Table I. For the purpose of calculating $\Delta S^{\ddagger}$, we have used the relationship $k_1 = 3(1/\tau_b)$. This will be explained in the Discussion.

TMTA exhibited similar behavior, except that the first-order rate constants for the meta system are approximately 5 times faster than those of the para at comparable temperatures. An Arrhenius plot for the meta system is shown in Figure 3 and the activation parameters are given in Table I. Again, $k_1 = 3(1/\tau_b)$.

Mixtures of TPTA and TMA. When TMA and TPTA were mixed in a 2:1 ratio, only two resonance lines were observed in the methyl region at all temperatures, one in the tolyl methyl region and one in the Al methyl region. Mole[13] has assigned these absorptions to the tolyl methyl and the methyl groups of the dimer of dimethyl-*p*-tolylaluminum. The tolyl groups were presumed to be in the bridge position. When trimethylaluminum is present in a ratio greater than 2:1, the Al methyl region, in the low-temperature spectrum as reported by Mole,[13] becomes quite complex showing methyl resonances for the dimer of TMA (bridge and terminal), the dimer of dimethyl-*p*-tolylaluminum (terminal only), and pentamethyl-*p*-tolylaluminum (bridge and terminal). The latter substance represents a bridged species containing two different bridging groups, methyl and tolyl. The tolyl methyl region of a 5:1 mixture of TMA and TPTA has been heretofore unreported and is shown in Figure 4. Peak A (0.19 ppm upfield from toluene) corresponds to the observed spectrum for the dimer of dimethyl-*p*-tolylaluminum and, therefore, peak B (0.27 ppm upfield from toluene) is assigned to the bridging tolyl group in pentamethyl-*p*-tolylaluminum. As the temperature dependence of the spectra show, the equilibrium represented by eq 2 is dynamic and can be studied using conventional line shape analysis of the tolyl methyl region.

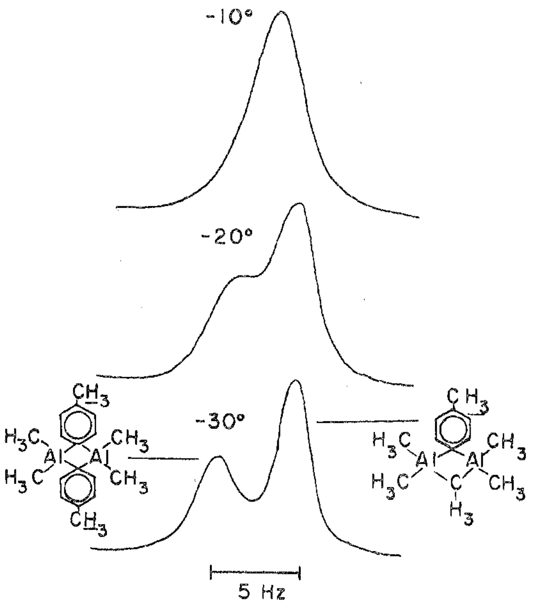
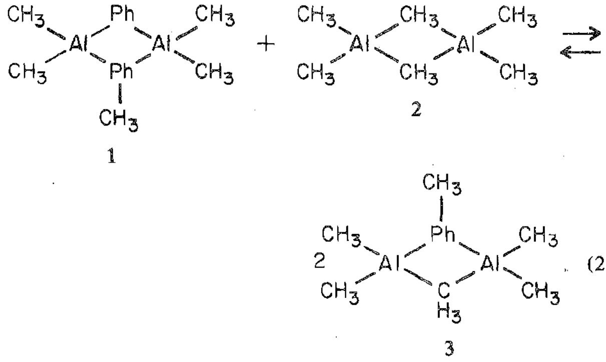


Figure 4. Variable-temperature 60-MHz ^{1}H NMR spectra of the ring methyl protons of the tolyl group in tetramethyldi-*p*-tolyldialuminum and pentamethyl-*p*-tolyldialuminum.



(2)

Table II. Calculations of Equilibrium Constants from Eq 3

Temp, °C	[1], *M*	[2], *M*	[3], *M*	*K*
−24.5	1.08	1.52	3.04	5.63
	0.194	0.390	0.678	6.08
	0.105	0.187	0.336	5.75
	0.260	0.322	0.716	6.12
	0.155	0.277	0.506	5.96
			Av	5.9 ± 0.2
−22.6	1.10	1.53	3.02	5.42
	0.268	0.152	0.461	5.22
	0.193	0.389	0.680	6.16
			Av	5.6 ± 0.5
−16.5	0.553	.770	1.50	5.28
	0.093	.191	0.347	6.78
	0.059	.100	0.156	4.12
	0.144	.175	0.330	4.32
	0.278	1.28	1.26	4.46
			Av	5.0 ± 1

Table III. Concentration Dependence of $1/\tau$ for Groups in **1**

[1]	[2]	[3]	$1/\tau$
		−24.5°	
0.542	0.794	1.52	5.79
0.133	0.074	0.251	4.52
0.097	0.194	0.339	4.42
0.052	0.093	0.168	3.32
0.130	0.161	0.358	4.18
0.773	0.138	0.253	3.63
		Av	4.3 ± 0.8
		−16.5°	
0.553	0.770	1.50	8.10
0.093	0.191	0.347	8.33
0.059	0.100	0.156	6.18
0.144	0.175	0.329	7.20
0.278	1.28	1.26	9.58
		Av	7.9 ± 1.3

The equilibrium constant for eq 2 can be determined from the expression

$$K = [3]^2/[1][2] \qquad (3)$$

The relative concentrations of the substances were determined at each temperature by integration of the ^{1}H NMR signals and by an iterative fit of the calculated line shape data to the observed spectra. The results for several samples at three temperatures are given in Table II. While these numbers are rough, the variation of K with temperature can give an estimate of ΔH for the reaction in eq 2. A plot of ln K vs. $1/T$(°K) yields a value for ΔH of −2.6 kcal.

Results of the line shape analysis on several samples at two different temperatures are given in Table III. The scatter in these data is not unusually large for NMR line shape measurements, particularly when the relatively small chemical shift separation and the difficulty in measuring the concentration of each of the species in solution at each of the temperatures is taken into account. This latter point could well lead to much of the scatter since the mole fractions of the tolyl-containing moieties are necessary for computing the lifetimes. Even considering the scatter, however, no perceptible relationship between the lifetimes of the tolyl groups and the concentration of any of the species can be found. A plot of ln $(1/\tau)$ vs. $1/T$ is shown in Figure 5. The activation energy abstracted from the slope of this line is 11.1 ± 1.0 kcal/mol. $\Delta H^‡$ and $\Delta S^‡$ are 10.6 kcal/mol and −11 eu, respectively. The first-order rate constant at 225°K is 1.1 sec^{-1}.

Discussion

Trimethylaluminum. The lifetimes of methyl groups in the bridge and terminal positions of the TMA dimer are found to be independent of concentration. The prior conclusion of a first-order rate law for the exchange appears, therefore, to be correct as is the assignment that $1/\tau_b = {}^2/_3k$ and $1/\tau_t = {}^1/_3k$[4] where $1/\tau_b$ and $1/\tau_t$ are the reciprocal lifetimes for the bridge and terminal positions and k is the first-order rate constant for the dissociation process.

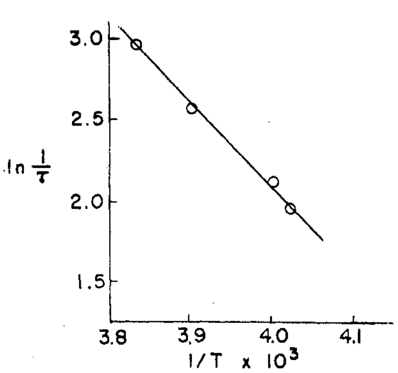


Figure 5. Arrhenius plot for the exchange of tolyl groups between tetramethyldi-*p*-tolyldialuminum and pentamethyl-*p*-tolyldialuminum.

The mechanism currently accepted for intramolecular exchange in the dimer of TMA requires complete dissociation of the dimer into monomer units. The activation energy for the exchange process should therefore be equal to or greater than the heat of dissociation of the dimer. As noted earlier several authors have pointed out that the measured activation energy is somewhat less than the thermochemically determined heat of dissociation. However, this apparent difference may very well be the result of the difficulty in making such measurements on air-sensitive materials, as well as the many approximations that must be made in performing the calculations themselves. Nonetheless, it does seem apparent that the heat of dissociation of the trimethylaluminum dimer is less in solution than the value of 20.2 kcal/mol reported for the gas phase, and Smith's estimated value of 15.4 ± 1.4 kcal/mol[9] for the dissociation in toluene is not in bad agreement with the value of E_a = 13.6 ± 1.0 kcal/mol obtained in our study. Therefore it seems reasonable to accept the complete dissociation of the dimer as the rate-determining step for this process because (1) the exchange process is first order, (2) the measured entropy of activation is positive, and (3) the energy of activation is close to the solution-phase heat of dissociation.

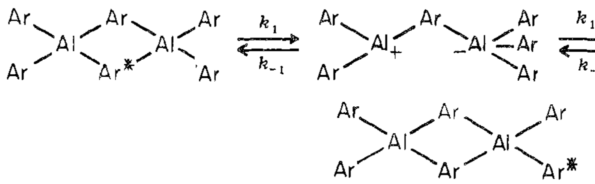
Williams and Brown[2] discussed the bridge–terminal exchange process for TMA in terms of the formation of solvent-caged monomers as the intermediate step in an attempt to explain the marked differences in rate observed when toluene and cyclopentane are used as solvents. We have observed the same difference in rate as shown in Table I. The cage effect explanation seems unsatisfactory to some authors,[5] and we suggest that the observed difference in rates may be explained in terms of a solvent effect in which the toluene stabilizes the transition state in the dissociation process relative to the dimer resulting in a somewhat lower activation energy. This seems plausible in that the developing monomers should be stabilized by electron-donating solvents and the probability of monomer formation should be greater. Assuming completely random recombination, then, the rate of bridge–terminal exchange in toluene should be expected to be faster than in cyclopentane. Dichloromethane may also be described as an electron-donating solvent and the activation parameters for the exchange process in dichloromethane are quite similar to those found for toluene (see Table I).

Tri-*p*- and Tri-*m*-tolylaluminum Intramolecular Exchange. As a result of the concentration independence of the lifetimes of tolyl groups observed for the tritolylaluminum intramolecular exchanges, the rate expression for the exchange reaction may be written as

$$\text{rate of exchange} = k_1\,[\mathrm{Al_2(C_6H_4CH_3)_6}] \qquad (4)$$

in which the rate-determining step is the unimolecular activation of the tritolylaluminum dimer. In comparing the activation energies found in Table I with that obtained for the TMA intramolecular exchange, one sees that the activation of an organoaluminum dimer which contains all aromatic groups appears to require considerably less energy than that necessary to activate a dimer in which all ligands are saturated. If the same mechanism is assumed, this completely contradicts all the evidence that shows aromatic and other unsaturated ligands to be the better bridging groups (cf. the Introduction).

To account for this significant difference in activation energy, we propose mechanism 5 for the bridge–terminal exchange



(5)

reaction for the tritolylaluminum dimers, where Ar is the *p*-tolyl or *m*-tolyl group. In this mechanism only one of the electron-deficient bridge bonds ruptures followed by rotation about the remaining aluminum–carbon bridge bond and subsequent re-formation of the dimer. Since each single-bridge opening of this dimer can result in the exchange of only one bridging group from a bridge to a terminal position and since there is a two-thirds probability of such a group ending up in a terminal position, the rate of exchange of tolyl groups out of the bridge site is given by

$$\text{rate} = {}^2/_3k_1\,[\mathrm{Al_2(C_6H_4CH_3)_6}] \qquad (6)$$

and

$$\tau_b^{-1} = \frac{{}^2/_3k_1\,[\mathrm{Al_2(C_6H_4CH_3)_6}]}{2\,[\mathrm{Al_2(C_6H_4CH_3)_6}]} = {}^1/_3k_1 \qquad (7)$$

Similarly

$$\tau_t^{-1} = {}^1/_6k_1 \qquad (8)$$

Using these relationships the data found in Table I were obtained.

We suggest that the stabilization of the electron-deficient bridge bond by interaction with the relatively electron-rich π system of the aromatic group occurs to such an extent that only one such bridge bond is easily ruptured in the exchange process as opposed to the rather facile rupture of both bridge bonds observed in the exchange reaction of the trimethylaluminum dimer.

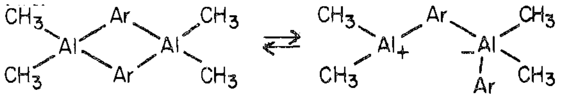
The negative values for the entropies of activation also support this mechanism. By simply considering the change in the number of degrees of freedom, one might expect that the partial dissociation of the dimer should result in an increase in entropy. However, the role of the solvent cannot be neglected, particularly when the reaction sequence involves a charged species such as the single-bridged activated complex. Calculations have been made for the influence of the medium on the entropy of activation for processes which involve the formation of more polar species from less polar species for molecules of intermediate size and dipole moment.[28] These calculations show that $\Delta S^\ddagger$ is negative for aromatic as well as nonpolar solvents. It seems possible, therefore, to explain the negative entropy of activation observed for these intramolecular exchange processes in terms of an interaction of the charged activated complex with the solvent.

The differences in kinetic and activation parameters between the *p*-tolyl and *m*-tolyl systems are small but subtly consistent with the proposed mechanism. The meta derivative undergoes more rapid exchange with a lower activation energy as seen in Table I. These observed differences can be understood in terms of hyperconjugative effects involving the tolyl groups. In the case of the TPTA, the methyl group in the para position allows for the stabilization of the bridge bond in the dimer by π donation of electron density to the electron-deficient bridge framework.

Mixtures of Tri-*p*-tolylaluminum and Trimethylaluminum. As pointed out in the Results, mixtures of TMA and TPTA in a ratio of 2:1 result in the formation of species **1** exclusively, while those with a ratio of TMA to TPTA of greater than 2:1 result in a mixture of **1**, **2**, and **3**. The exchange process under study here is the interchange of *p*-tolyl groups between **1** and **3**. As the data in Table III indicate, the lifetimes of the tolyl groups in **1** are independent of the concentration of all species and the rate of the forward reaction in eq 2 is first order with respect to the concentration of **1**, i.e.

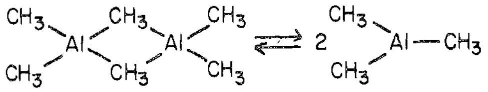
$$\text{rate} = k_1\,[\mathrm{(CH_3)_4Al_2(C_6H_4CH_3)_2}] \qquad (9)$$

Again it seems likely that the rate-determining step for this reaction is the unimolecular activation of the diaryl-bridged dimer, **1**. The energy of activation for this process is 11.1 ± 1.0 kcal/mol and its similarity to the activation energy for the intramolecular exchange in TPTA leads to the conclusion that activation of **1** involves only reversible single-bridge opening of the electron-deficient bridge. The resulting intermediate species, **4**, similar to that proposed for the case of tritolylaluminum, can react with a monomer of TMA to give a complex which readily dissociates resulting in the formation of **3**. This series of steps is illustrated in eq 10–12.

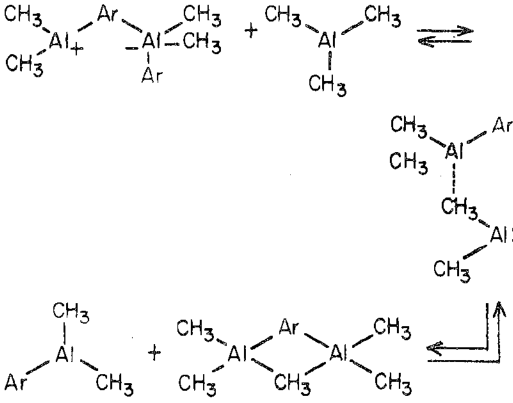


(10)

1 4



(11)



(12)

5 3

The reactive monomer, **5**, could react with a TMA monomer to give **3** or with another molecule of **5** to give **1**. Using this mechanism, treatment of eq 9 yields the relationship

$$1/\tau = k_1$$

where $1/\tau$ refers to the inverse lifetime for the tolyl groups in **1**. It is found for this system that E_a, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ are 11.1 ± 1.0 kcal/mol, 10.6 kcal/mol, and −11 eu at 250°K in toluene solvent.

The rate of exchange between **1** and **3** is approximately two orders of magnitude slower than the self-exchange in TPTA (notice that the solvent is different and an exact comparison cannot be made). This difference could result from the degree of opening required in the two intermediates. The intermediate shown in eq 5 requires very little opening of the unbroken Al–C–Al bond angle to facilitate rotation. However, in **4**, the bond angle must be opened further to allow attack by a TMA monomer. This is consistent with the slightly higher activation energy and the more negative entropy of activation found for the exchange between **1** and **3** and compared to the exchange in TPTA.

Registry No. TPTA dimer, 17439-80-4; TMTA dimer, 56030-41-2; TMA dimer, 15632-54-9; tetramethyldi-*p*-tolylaluminum, 17439-75-7; pentamethyl-*p*-tolylaluminum, 17439-77-9.

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Raman Spectra of Trifluoromethylsulfinyl Fluoride, Trifluoromethylsulfinyl Chloride, and Sulfinyl Chloride Fluoride

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Gas-phase infrared (2000–400 cm^{-1}) and liquid-phase Raman spectra (2000–100 cm^{-1}) for $CF_3S(O)F$, $CF_3S(O)Cl$, and FS(O)Cl are reported, and vibrational analyses are made for the three molecules. Depolarization ratio measurements indicate that the compounds belong to symmetry species C_1 and thus are pyramidal in agreement with lone-pair repulsion considerations.

Introduction

A relatively large number of sulfinyl halides have been synthesized and characterized by vibrational spectral analyses.[1-7] We report here the infrared and Raman spectra and vibrational assignments for the unsymmetrical sulfinyl halides $CF_3S(O)F$, $CF_3S(O)Cl$, and FS(O)Cl.

Although the assignments for FS(O)Cl are tentative due to the impurity of the sample, comparative analyses of the spectra for all three compounds gave rise to consistent results. The structures of the three compounds have not been determined; however, a pyramidal geometry is predicted from lone-pair repulsions. The three molecules may belong to point group C_s (planar) or to point group C_1 (pyramidal). Related sulfinyl compounds $S(O)F_2$,[8] $(CF_3)_2SO$,[9] and $S(O)Cl_2$[10] have been shown to be pyramidal.

Experimental Section

Bis(trifluoromethyl)disulfane (PCR, Inc.) was allowed to react with AgF_2 at 0° for 12 hr to give good yields of CF_3SF_3.[11] The CF_3SF_3 was then carefully hydrolyzed to give quantitative yields of $CF_3S(O)F$. Pure $CF_3S(O)F$ was obtained by gas chromatography using a column constructed of 0.25-in. o.d. copper tubing packed with 25% FS 1265 on Chromosorb P. When HCl was allowed to react with $CF_3S(O)F$ for 1 hr at 25°, good yields of $CF_3S(O)Cl$[12] were obtained. It was also purified by gas chromatography using the same column.

FS(O)Cl was obtained from the reaction between equimolar quantities of ClF (Ozark-Mahoning) and $SOCl_2$ at −78° over a period of 12 hr. Yields of FS(O)Cl approached 50%. The FS(O)Cl was purified somewhat by low-temperature distillation.

Infrared spectra were recorded on a Perkin-Elmer Model 621 grating spectrometer. Gas-phase infrared spectra were obtained by using a 7-cm glass cell equipped with KBr windows (pressures from 5 to 35 Torr). A Jarrell-Ash Model 25-300 Raman spectrometer equipped with a Coherent Radiation Model CR-MG krypton–argon laser (4880 Å for $CF_3S(O)F$ and $CF_3S(O)Cl$ and 5308 Å for FS(O)Cl) was used to record the Raman spectra. Samples for liquid-phase Raman spectra were sealed in 0.4-cm o.d. Pyrex tubes. Rotation of a half-wave plate by 45° turned the direction of the electric vector of the incident light through 90°, allowing the measurement of depolarization ratios.

Discussion and Results

For both $CF_3S(O)F$ and $CF_3S(O)Cl$, 14 of the expected 15 fundamentals are observed in the Raman spectrum, while all six fundamentals are observed in the case of FS(O)Cl. For C_1 symmetry, all bands in the Raman spectrum are expected to be polarized, and this is observed. All bands are both infrared and Raman active. In Figure 1 are the Raman spectra of $CF_3S(O)F$ and $CF_3S(O)Cl$. The Raman and infrared spectral data and the assignments for $CF_3S(O)F$ and $CF_3S(O)Cl$ are given in Table I. The Raman and infrared spectra and band assignments for FS(O)Cl are found in Table II. The small number of bands observed in the infrared spectrum is a result of complete absorption by the KBr windows below 400 cm^{-1}.

Although mixing of some of the fundamentals may occur, group theory provided a basis for at least first approximations of band assignments. It was most convenient in this study to