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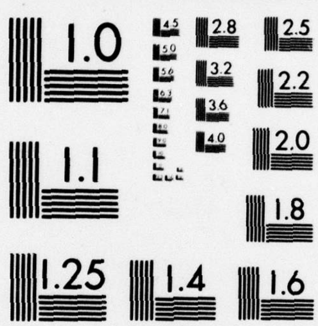

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Kinetics and Mechanism for the Elimination of Hydrogen between Dimethylaluminum Hydride and N-Methylaniline

by

O. T. Beachley, Jr. and Claire Tessier-Youngs

Prepared for Publication

in the

Inorganic Chemistry

State University of New York at Buffalo
Department of Chemistry
Buffalo, New York 14214

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→ The rate of elimination of hydrogen from dimethylaluminum hydride and N-methylaniline has been measured at -63° [deg] in toluene solution. Reaction conditions include equal concentrations of dimethylaluminum hydride and the amine, and pseudo first order conditions with excess amine. The kinetic data are consistent with a second order rate law →

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which is complicated by an equilibrium. The following steps of the mechanism determine the rate of elimination of hydrogen.

$$H(CH_3)_2Al + N(C_6H_5)(CH_3)H \overset{K_a}{\rightleftharpoons} H(CH_3)_2AlN(C_6H_5)(CH_3)H$$

$$H(CH_3)_2Al + N(C_6H_5)(CH_3)H \xrightarrow{k} H_2 + (CH_3)_2AlN(C_6H_5)(CH_3).$$

Our results are consistent with the conclusion that adduct formation is a "dead end" path for the elimination reaction. The elimination reaction is not a reaction of a performed adduct. The factors responsible for the formation of only a dimeric aluminum-nitrogen product, $[(CH_3)_2AlN(C_6H_5)(CH_3)]_2$, and the predominance of the cis isomer over the trans (80/20%) are discussed. A ${}_2\pi_s + {}_2\pi_a$ cycloaddition reaction which minimizes interactions between the bulky phenyl groups is proposed.

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by

O. T. Beachley, Jr.* and Claire Tessier-Youngs

Abstract

The rate of elimination of hydrogen from dimethylaluminum hydride and N-methylaniline has been measured at -63° in toluene solution. Reaction conditions include equal concentrations of dimethylaluminum hydride and the amine, and pseudo first order conditions with excess amine. The kinetic data are consistent with a second order rate law which is complicated by an equilibrium. The following steps of the mechanism determine the rate of elimination of hydrogen.

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Our results are consistent with the conclusion that adduct formation is a "dead end" path for the elimination reaction. The elimination reaction is not a reaction of a performed adduct. The factors responsible for the formation of only a dimeric aluminum-nitrogen product, $[(CH_3)_2AlN(C_6H_5)(CH_3)]_2$, and the predominance of the cis isomer over

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the trans (80/20%) are discussed. A $_{2}\pi_{s}$ + $_{2}\pi_{a}$ cycloaddition reaction which minimizes interactions between the bulky phenyl groups is proposed.

Introduction

The cleavage of metal carbon bonds by protic acids is a process fundamental to organometallic chemistry.[1,2] If an organometallic Lewis acid, especially of Group IIIB, reacts with a Lewis base having an acidic proton, an adduct will frequently be observed before the cleavage reaction occurs under appropriate conditions.[1,2] The species eliminated by the cleavage process is a small molecule composed of a substituent originally bound to the organometallic compound and the proton from the base. This elimination reaction finds many important applications. The semiconductor gallium arsenide[3] is synthesized from $Ga(CH_3)_3$ and AsH_3 by a series of elimination reactions which ultimately produce three moles of methane. The hydrolysis of neutral organometallic compounds[1,2] and the cations, which are the serious toxic pollutants of the aqueous environment,[4] provide more examples of the elimination reaction. Products from the elimination reaction have also been used in the formation of a variety of polymers and polymerization catalysts.[2]

Despite the significance of the elimination reaction to Group IIIB chemistry, very little is known about the mechanism of the reaction.[1,2] The common observation of the formation of a Lewis acid-base adduct prior to the elimination reaction lead researchers to conclude that the elimination reaction is a reaction of a preformed adduct.[1,5] The observed differences in reactivity of adducts for elimination were then rationalized by considering the effects of electrical strain in the adduct molecules.[5] For example, trimethylaluminum reacts more readily with methanol than dimethylamine to eliminate methane.[1,2] This observation has been attributed to the presence of a more acidic proton in methanol than dimethylamine.[1] It is regretable but none of these ideas have been supported or denied by kinetic or spectroscopic data. There has only been one report in the literature of a kinetic study of an elimination reaction of an aluminum, gallium or indium compound. Gosling and Bowen[6] attempted a kinetic study of the elimination reaction of $Cl(C_2H_5)_2AlN(CH_3)_2H$ by following the rate of formation of ethane from the pyrolysis of pure adduct in the condensed phase at 110°. Their results did not give any information about the molecularity of the reaction or a possible mechanism.

In this paper we report the kinetics of and propose a mechanism for the elimination reaction which occurs between dimethylaluminum hydride and N-methylaniline in toluene solution at -63°. The following equation describes the stoichiometry of the reaction which was studied. This

$$[(CH_3)_2AlH]_3 + 3N(C_6H_5)(CH_3)H \longrightarrow 3/2[(CH_3)_2AlN(C_6H_5)(CH_3)]_2 + 3H_2$$

reaction was chosen because the rate of reaction could be easily monitored by following the formation of hydrogen manometrically. In addition, corrections for the solubility of hydrogen in toluene would not be needed. The goal of our experiments was to determine the mechanism of the elimination reaction and the participation, if any, of a performed adduct.

Experimental

All compounds were manipulated in a vacuum line or a purified inert gas atmosphere. Toluene was dried by refluxing over sodium. The N-methylaniline was dried over KOH pellets and distilled just before use. The dimethylaluminum hydride[7] was prepared from $LiAlH_4$ and $Al_2(CH_3)_6$ by heating the mixture for an hour at 80°. The product, which was purified by a vacuum distillation, had properties identical in every respect to those previously reported for dimethylaluminum hydride.[7,8]

Nature and Stoichiometry of the Elimination Reaction. The stoichiometry of the elimination reaction between dimethylaluminum hydride and N-methylaniline was examined. When 0.1140 g (1.96 mmol) $(CH_3)_2AlH$ was combined with 0.2100 g (1.96 mmol) $N(C_6H_5)(CH_3)H$, 1.95 mmol H_2 (measured with Toepler pump and gas burette assembly) was formed. No methane was observed as a product. Additional experiments using excess N-methylaniline confirmed the identical stoichiometry. When excess dimethylaluminum hydride was used, a different aluminum-nitrogen product, probably $(CH_3)_2AlN(C_6H_5)(CH_3)Al(CH_3)_2H$, was observed.[9]

The aluminum-nitrogen product of the observed reaction is a dimer,[10] $[(CH_3)_2AlN(C_6H_5)(CH_3)]_2$, which exists as a mixture of cis and trans isomers. Our ^1H nmr measurements in toluene solution suggest that the cis isomer predominates. At room temperature the product has an 84% cis and 16% trans isomer distribution in toluene solution. A similar isomer ratio has been observed for this compound in other solvents.[10]

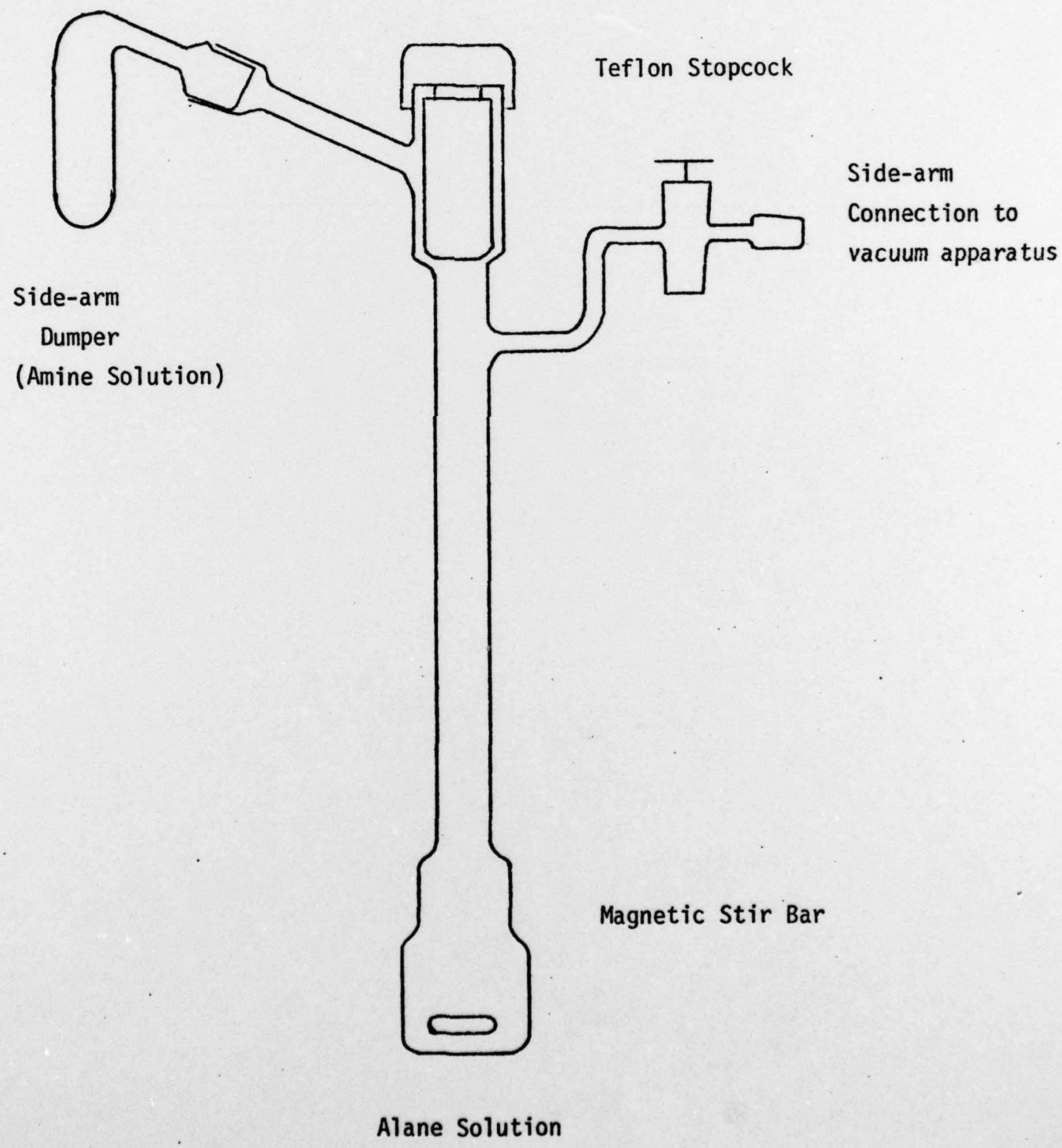
Kinetic Experiments. The apparatus for the kinetic study is shown in

Figure 1. The dimethylaluminum hydride was quantitatively transferred to the apparatus by pumping a weighed sample into the cooled (-196°) vessel. The alane was carefully dissolved in 2.00 ml toluene, measured by pipette and vacuum distilled into the apparatus. The toluene solution of N-methylaniline was prepared in a 5.00 ml volumetric flask which had been purged with argon. For the kinetic experiment, 4.00 ml of the amine solution was pipetted into the side arm dumper, attached to the kinetic apparatus, frozen to -196° and evacuated. Then, the amine and alane solutions were warmed to room temperature and finally cooled to -63° (chloroform slush bath) for thirty minutes prior to mixing. The short length of glassware between the solutions was cooled, the two solutions mixed, the timer initiated and the pressure of the evolved hydrogen measured as a function of time. A constant rate of stirring was maintained throughout the kinetic experiment by a magnetic stir bar. After the last kinetic measurement, the 63° bath was removed and the solution was warmed to room temperature to effect complete evolution of hydrogen. Then, the volatilized toluene was condensed back into the reaction vessel by cooling the latter to -196°. Finally, the -63° bath was replaced around the apparatus. After there was no pressure change, the "infinite time" hydrogen pressure was measured.

All experimental variables which might alter the pressure measurements were maintained as constant as possible. The volume of the reaction solution was 6.00 ml. in all experiments. The change in the gas volume due to the lowering of the mercury level in the manometer never exceeded 3% of the total volume.[11] It should be noted that this factor limits the maximum quantity of dimethylaluminum hydride which could

Figure 1

Kinetics Apparatus



be used. The error in the H_2 pressure measurements was $\pm$ 0.5 mm.

Results and Discussion

The kinetics of the reaction between dimethylaluminum hydride and N-methylaniline in toluene solution was investigated by following the rate of evolution of hydrogen under two sets of experimental conditions, (1) equal concentrations of alane (calculated as the concentration of the monomeric unit) and amine, (2) pseudo first order in alane (excess amine). Experiments using excess alane are prohibited because a different final product is formed.[9] Two general conclusions can be made from our experiments. The rate of formation of hydrogen is significantly faster when the concentrations of alane and amine are equal than under pseudo first order conditions. Second, the kinetic order for the formation of hydrogen changes from second to first as conditions change from equal concentrations to pseudo first order. This change in kinetic order suggests an equilibrium step in the mechanism.[12]

When the concentrations of alane and amine are equal the elimination of hydrogen follows second order kinetics as shown by the linearity of the kinetic plots,[13] $P_T/P_\infty-P_T$ vs time (Figure 2). These reactions were followed for 150 minutes, 61 to 67% completion. The kinetic data from these plots are summarized in Table I. It is apparent that the data do not fit a second order rate law based on initial concentrations. If the values of k_{obs} from the slopes of the second order kinetic plots are divided by the initial concentration of either alane or amine,[13] a constant value for the rate constant is not obtained. However, a constant value can be calculated by dividing k_{obs} by the appropriate equilibrium

Figure 2

Second Order Kinetic Plots
Equal Concentrations of Alane and Amine

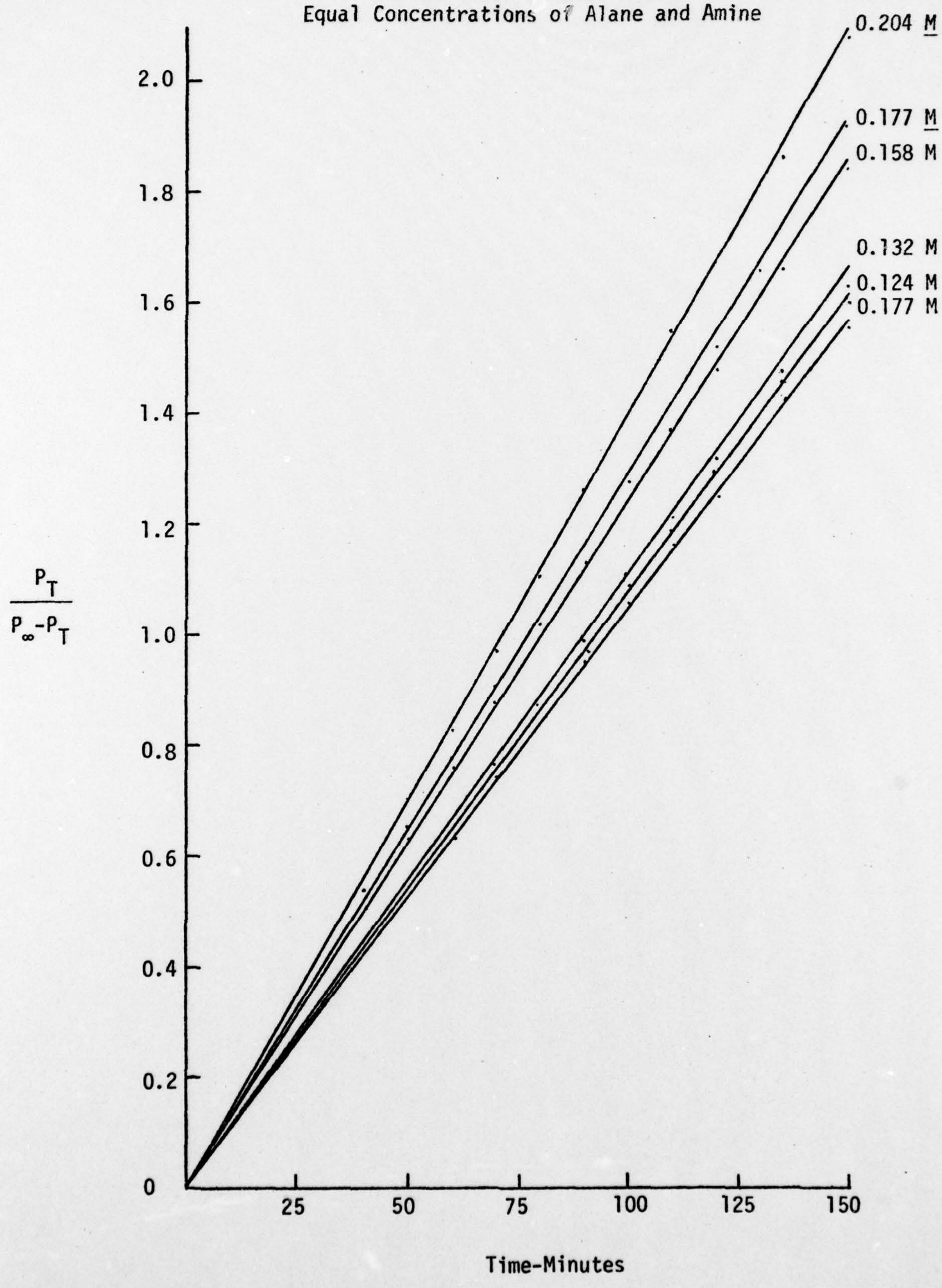


Table I. Rate Data - Equal Concentrations $(CH_3)_2AlH^a$ and $N(C_6H_5)(CH_3)H$

Initial Concentrations, [a] $\underline{M}$	$k_{obs}{}^b = k[(CH_3)_2AlH]_{eq} \times 10^4$, sec^{-1}	$[(CH_3)_2AlH]_{eq}{}^c$, $\underline{M}$	$k^d_{calcd} \times 10^3$ $M^{-1} sec^{-1}$	K^e_a, $\underline{M}$
0.204	2.33	0.0388	6.01	110
0.177	2.12	0.0353	6.01	114
0.158	2.03	0.0338	6.01	109
0.132	1.78	0.0296	6.01	116
0.124	1.77	0.0294	6.02	113
0.117	1.72	0.0286	6.01	105

a Concentrations of $(CH_3)_2AlH$ are based on the number of moles of monomeric unit.

b Value is the slope (least squares) of $P_T/P_\infty - P_T$ vs time plot. The standard deviation of the slope was 0.01×10^{-4} in all cases. All lines had a correlation factor greater than 0.999.

c Calculated using pseudo first order kinetic data, $k_{obs} = k/Ka$, and assuming a value of K_a, 110. See Results and Discussion.

d Calculated by dividing k_{obs} (Column 2) by $[(CH_3)_2AlH]_{eq}$ (Column 3).

e Calculated using the mass action expression for the equilibrium,

$$H(CH_3)_2Al + N(C_6H_5)(CH_3)H \underset{}{\overset{Ka}{\rightleftharpoons}} H(CH_3)_2AlN(C_6H_5)(CH_3)H.$$

concentration of monomeric alane or amine (See following discussion).

When the kinetics of the reaction are observed under pseudo first order conditions (excess amine), hydrogen is eliminated in a first order process. The psuedo first order kinetic plots, log $(P_\infty - P_T)$ vs time, had no deviations over a period of two half-lives, approximately 450 minutes. The kinetic data are summarized in Table II. The major conclusion from these data is the observed pseudo first order rate constants are independent of the amine concentrations in the range studied.

The following mechanism (A) can be used to explain all of our kinetic data and is consistent with the chemistry of the system. The only assumption, which must be made for this mechanism, is the initial

Mechanism A

$$[(CH_3)_2AlH]_3 \longrightarrow 3(CH_3)_2AlH \quad (1)$$

$$(CH_3)_2AlH + N(C_6H_5)(CH_3)H \underset{}{\overset{Ka}{\rightleftharpoons}} H(CH_3)_2AlN(C_6H_5)(CH_3)H \quad (2)$$

$$(CH_3)_2AlH + N(C_6H_5)(CH_3)H \xrightarrow{k} H_2 + (CH_3)_2AlN(C_6H_5)(CH_3) \quad (3)$$

$$2(CH_3)_2AlN(C_6H_5)(CH_3) \longrightarrow [(CH_3)_2AlN(C_6H_5)(CH_3)]_2 \quad (4)$$

formation of adduct is extremely rapid. This assumption is consistent with this Lewis acid-base chemistry,[1,2] other kinetic studies of aluminum hydrides[14,15] and related low temperature ^1H nmr observations.[9] The rate law for this mechanism is given by the following expression. The terms $[(CH_3)_2AlH]_T$ and $[N(C_6H_5)(CH_3)H]_T$, express the total alane and

Table II. Rate Data - Pseudo First Order Conditions, Excess $N(C_6H_5)(CH_3)H$

$[N(C_6H_5)(CH_3)H]$, M	$[(CH_3)_2AlH]$, M[a]	$k_{obs} \times 10^5$, sec^{-1}	Least Squares Correlation Factor
2.51	0.207	5.12 ± 0.01	0.999928
2.33	0.204	5.03 ± 0.01	0.999618
2.20	0.0862	5.82 ± 0.04	0.998952
2.20	0.123	5.47 ± 0.01	0.999725
1.44	0.138	5.87 ± 0.05	0.998108
1.34	0.102	5.42 ± 0.03	0.999158
	Average	5.46	

a. Concentrations of $(CH_3)_2AlH$ are based on the number of moles of monomeric unit.

$$\frac{dP_{H_2}}{dt} = \frac{-d[(CH_3)_2AlH]_T}{dt} = \left\{\frac{k}{1 + Ka\ [N(C_6H_5)(CH_3)H]_T}\right\} [(CH_3)_2AlH]_T[N(C_6H_5)(CH_3)H]_T$$

Calculated kinetic constants

$k = 6.01 \times 10^{-3}\ M^{-1}sec^{-1}$

$Ka = 110\ M^{-1}$

concentrations before elimination. Under the pseudo first order conditions, the observed rate constant (k_{obs}) is independent of the amine concentration. If Ka is sufficiently large, k_{obs} equals k/Ka, according to our rate law. However, when the concentrations of alane and amine are equal, the rate of formation of hydrogen shows second order kinetics, which is consistent with step 3 of mechanism A. The slope of the second order kinetic plot[13] is given by $k[(CH_3)_2AlH]_{eq}$ or $k[N(C_6H_5)(CH_3)H]_{eq}$, where $[(CH_3)_2AlH]_{eq}$ and $[N(C_6H_5)(CH_3)H]_{eq}$ are the equilibrium concentrations. Numerical values for both the second order rate constant, k, and the equilibrium concentrations are unknown. However, if the substitution, $k = k_{obs}Ka$ from the pseudo first order data, is made and Ka is estimated, equilibrium concentrations of alane or amine can be calculated. Knowledge of the initial and calculated equilibrium concentrations permit a recalculation of Ka using the mass action expression. After a series of successive approximations, the values of the assumed and calculated equilibrium constant, Ka, agreed (Table II). The results of these calculations support the proposed mechanism.

The other mechanism B which must be considered is given by the following two kinetically important steps. These two steps replace (2)

Mechanism B

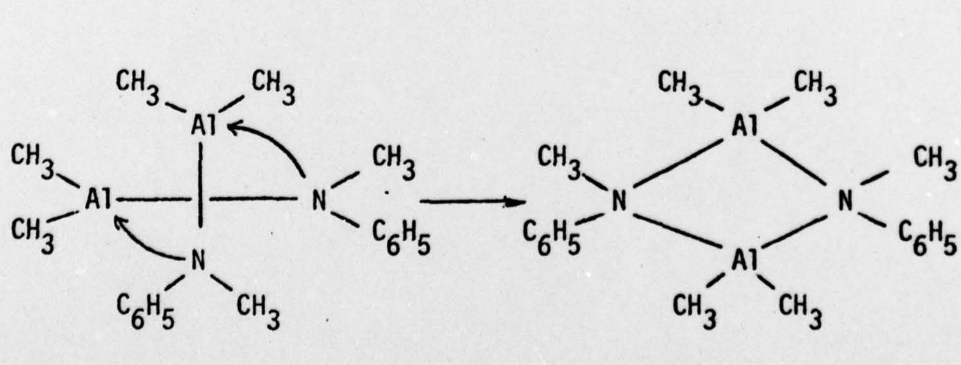
$$(CH_3)_2AlH + N(C_6H_5)(CH_3)H \underset{}{\overset{K}{\rightleftharpoons}} H(CH_3)_2AlN(C_6H_5)(CH_3)H$$

$$H(CH_3)_2AlN(C_6H_5)(CH_3)H \xrightarrow{k} H_2 + (CH_3)_2AlN(C_6H_5)(CH_3)$$

and (3) of Mechanism A. The other steps remain the same. Mechanism B is kinetically similar to the preferred Mechanism A but involves the elimination of hydrogen from the adduct. However, our data are not consistent with Mechanism B. If this mechanism was appropriate and K was large, hydrogen should be formed in a first order elimination reaction. Such observations were made under pseudo first order conditions but not when the alane and amine concentrations were equal. Furthermore, if the adduct was the species which eliminated hydrogen, the excess amine present in the pseudo first order experiments should have increased the rate of elimination, when compared to the rate observed for equal concentrations of amine and alane, rather than the observed decrease. In the preferred Mechanism A, the excess amine increases the concentration of adduct but decreases the concentration of the other reactive species, the monomeric alane.

The major conclusion from our kinetic study is that elimination is a second order reaction between a monomeric alane species and the amine. Hydrogen is not eliminated from the adduct in this particular system. Our results clearly show that adduct formation is a "dead end" path for the elimination reaction. The preferred Mechanism A suggests that the adduct dissociates into the monomeric alane and amine, probably within a solvent shell. If the alane and amine then recombine with the appropriate orientation, elimination occurs, possibly by a four-centered S_Ei process.[16] The concept of dissociation and reaction within a solvent shell is consistent with the chemistry of organoaluminum compounds in aromatic solvents,[17,18,19] but we have no specific data which support or deny it for our system.

The final product from the elimination reaction is an aluminum-nitrogen dimer $[(CH_3)_2AlN(C_6H_5)(CH_3)]_2$, which exists as a four to one mixture of cis/trans geometrical isomers. This isomer ratio is not a function of solvent polarity.[10] Since the trans isomer is most favored by thermodynamic effects, kinetic factors could be responsible for the observed predominance of the cis isomer. The product distribution might be controlled by the relative energies of the transition states for the formation of the two isomers. If the dimerization reaction is a cycloaddition reaction between two aluminum-nitrogen species with partial pi-bonding, the cis isomer can be the preferred product. The orthogonal approach of the pi-bonds of two monomeric units in the least hindered orientation, followed by a $_{2}\pi_{s} + _{2}\pi_{a}$ cycloaddition[20] could result in



Preferred Transition State   Favored cis isomer selective cis dimer formation. The favored transition state minimizes the interactions between the most bulky substituents, the phenyl groups. This cycloaddition rationale also is consistent with the observed absence of major solvent polarity effects[10] on the cis/trans ratio. A similar cycloaddition process[21] has been used to explain the selective cis olefin formation in a Wittig reaction between a phosphorus ylide and an aldehyde. It is of interest to speculate that the proposed cycloaddition reaction precludes the formation of higher polymeric aluminum-nitrogen species from the observed elimination reaction.

Our kinetic data suggest that the major factors which influence the rate of elimination will be those which alter the equilibrium constant for adduct formation, Ka, and the second order rate constant, k. More kinetic studies will be required to elucidate the mechanism of elimination for other Lewis acid-base systems and to distinguish the relative importance of the effects of Ka and k, when identical mechanisms are involved. We are also investigating the effects of substituents and the nature of the base atom on the steric course of the proposed cycloaddition reaction.

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