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$$H(CH_3)_2AlN(CH_2C_6H_5)H_2 + N(CH_2C_6H_5)H_2 \underset{}{\overset{K_1}{\rightleftharpoons}} H(CH_3)_2Al[N(CH_2C_6H_5)H_2]_2$$

$$H(CH_3)_2AlN(CH_2C_6H_5)H_2 \overset{K_2}{\rightleftharpoons} H(CH_3)_2Al + N(CH_2C_6H_5)H_2$$

$$H(CH_3)_2Al + N(CH_2C_6H_5)H_2 \xrightarrow{k} H_2 + (CH_3)_2AlN(CH_2C_6H_5)H$$

Additional equilibria which involve the aluminium-nitrogen product from the elimination reaction are proposed in order to fully describe the chemistry of the system. The large number of equilibria which complicate the kinetics of the reaction are related to the high basicity of benzylamine.

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Kinetics and Mechanism for the Elimination of Hydrogen between Dimethylaluminium Hydride and Benzylamine

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O. T. Beachley, Jr.

Abstract

The rate of elimination of hydrogen from dimethylaluminium hydride and benzlyamine has been measured at -63°C in toluene solution. All experimental data are consistent with a second-order rate law which is complicated by a series of equilibria. Initial rate data were correlated with a rate law and fitted to an appropriate mechanism. The following steps of the mechanism determine the rate of elimination of hydrogen during the early stages of the reaction.

$$H(CH_3)_2AlN(CH_2C_6H_5)H_2 + N(CH_2C_6H_5)H_2 \underset{}{\overset{K_1}{\rightleftharpoons}} H(CH_3)_2Al[N(CH_2C_6H_5)H_2]_2$$

$$H(CH_3)_2AlN(CH_2C_6H_5)H_2 \overset{K_2}{\rightleftharpoons} H(CH_3)_2Al + N(CH_2C_6H_5)H_2$$

$$H(CH_3)_2Al + N(CH_2C_6H_5)H_2 \xrightarrow{k} H_2 + (CH_3)_2AlN(CH_2C_6H_5)H$$

Additional equilibria which involve the aluminium-nitrogen product from the elimination reaction are proposed in order to fully describe the chemistry of the system. The large number of equilibria which complicate the kinetics of the reaction are related to the high basicity of benzylamine.

Introduction

The elimination reaction which occurs between an organometallic compound and a protic acid is of fundamental significance and finds many important applications. Despite the importance of this class of reaction to aluminum chemistry, only one kinetics study[1] of a reaction has lead to a proposed mechanism. However, additional kinetics studies with a variety of acid-base pairs are necessary to elucidate the general nature of the elimination step in the mechanism as well as the factors which influence the rate of the elimination reaction and the degree of polymerization of the organometallic product.

The kinetics data for the elimination reaction which occurs between dimethylaluminium hydride and N-methylaniline[1] in toluene at -63°C was consistent with a second order rate law which was complicated by an equilibrium. The following steps of the mechanism determined the rate of elimination of hydrogen. The adduct was assumed to be rapidly formed upon mixing the alane and amine. All results were consistent with the

$$H(CH_3)_2AlN(CH_3)(C_6H_5)H \underset{}{\overset{K_d}{\rightleftharpoons}} H(CH_3)_2Al + N(CH_3)(C_6H_5)H \qquad (1)$$

$$H(CH_3)_2Al + N(CH_3)(C_6H_5)H \xrightarrow{k} (CH_3)_2AlN(CH_3)(C_6H_5) + H_2 \qquad (2)$$

conclusion that adduct formation was a dead-end path for elimination. Since the elimination reaction is not a reaction of a preformed adduct, both K_d and k alter the rate of formation of hydrogen. The second pertinent conclusion derived from this kinetics study related to the observed formation of only a dimeric product, $[(CH_3)_2AlN(CH_3)(C_6H_5)]_2$,

and the predominance of the cis isomer (80%), the kinetically preferred isomer. A $_2\pi_s + {}_2\pi_a$ cycloaddition reacton which minimized interactions between bulky phenyl groups was proposed and, therefore, precluded the formation of higher aluminium-nitrogen polymers.

In this paper we report the kinetics of and propose a mechanism for the elimination reaction which occurs between dimethylaluminium hydride and benzylamine, $N(CH_2C_6H_5)H_2$ in toluene solution at -63°C. Benzylamine is a significantly stronger base with less bulky substituents than the previously studied N-methylaniline. The goals of our experiments were to determine the nature the aluminium-nitrogen product and the mechanism of the elimination reaction, and to compare the kinetic data for the two amines.

Experimental Section

All compounds were manipulated in a vacuum line or a purified argon atmosphere. The benzylamine was dried over molecular sieves and distilled just prior to use. All other reagents or solvents were prepared or purified as previously described.[1]

Reaction of $(CH_3)_2AlH$ with $N(CH_2C_6H_5)H_2$ - The stoichiometry of the elimination reaction between $(CH_3)_2AlH$ and $N(CH_2C_6H_5)H_2$ was examined and the product was fully characterized. When 0.1890 g (3.26 mmol) of $(CH_3)_2AlH$ was combined with 0.3508 g (3.27 mmol) of $N(CH_2C_6H_5)H_2$ in toluene solution, 3.24 mmol of H_2 (measured with a Toepler pump and gas buret assembly) was formed. No methane was observed as a product. Additional experiments with excess benzylamine confirmed the stoichiometry.

The aluminium-nitrogen product, $[(CH_3)_2AlN(CH_2C_6H_5)H]_2$, was fully characterized. The colorless, crystalline solid has a melting point of 65-68°C. Decomposition as evidenced by bubbling started at about 140°C. Cryoscopic molecular weight measurements in benzene solution using an apparatus similar to that described by Shriver[2] demonstrated the compound to exist as a dimer. The following experimental data were observed: $[(CH_3)_2AlNH(CH_2C_6H_5)]_2$ - formula weight - 327: [Calc. molality, (observed molecular weight)] 0.0968(327); 0.0604(318); 0.0439(317). Our ^1H NMR measurements of $[(CH_3)_2AlNH(CH_2C_6H_5)]_2$ dissolved in toluene, cyclopentane and CH_2Cl_2 suggest that the compound exists as a mixture of cis and trans isomers but the ratio of isomers has essentially no dependence on the polarity of the solvent (Table I). The infrared spectrum of $[(CH_3)_2AlNH(CH_2C_6H_5)]_2$ was recorded in the range 4000-250 cm^{-1} by means of a Perkin-Elmer Model 457 spectrometer as a Nujol mull using CsI plates. The following are the spectral data (Bands due to the Nujol have been omitted): 3262(m); 1264(m); 1192(vs); 1167(sh); 1082(sh); 1044(sh); 1017(vs); 970(m); 895(w); 842(sh); 802(s); 737(sh); 685(vs); 632(sh); 562(m); 522(w); 492(w); 452(m).

Kinetics Experiments: The kinetics of the reaction between dimethylaluminium hydride and benzylamine in toluene at -63°C was monitored by following the rate of evolution of hydrogen manometrically. The experimental procedure for adding the amine to the alane solution and following the reaction was identical to that previously described.[1] As in the earlier study all experimental variables which might alter pressure measurements were maintained as constant as possible.

Table I

^{1}H NMR Spectral Data[a] $[(CH_3)_2AlNH(CH_2C_6H_5)]_2$

Assignment		Solvent		
		$C_6H_5CH_3$	C_5H_{10}	CH_2Cl_2
$AlCH_3$	cis	10.30	10.64	10.61
	trans	10.33	10.72	10.66
	cis	10.36	10.80	10.71
N-H		8.78	b	8.64
CH_2		6.03	6.11	5.97
			6.13	6.01
		6.12	6.19	6.07
			6.21	
C_6H_5		2.73	2.82	2.43
		2.78		

[a]All data are given as τ (ppm) and are referenced to tetramethylsilane (10.00 ppm). The spectra were recorded at 90 MHz and ambient temperature with a Varian Model EM-390 spectrometer.

[b]The N-H line was not observed due to interference from cyclopentane.

Results and Discussion

The general elimination reaction which occurs between dimethylaluminium hydride and benzylamine can be summarized by the following equation. The kinetics of this reaction were investigated by following

$$[(CH_3)_2AlH]_3 + 3N(CH_2C_6H_5)H_2 \longrightarrow 3/2[(CH_3)_2AlN(CH_2C_6H_5)H]_2 + 3\ H_2 \quad (3)$$

the rates of evolution of hydrogen at -63°C in toluene solution. A variety of experimental conditions were attempted. When the amine was in excess of the alane, a clear solution was formed and hydrogen was evolved smoothly. However, when the initial concentration of the alane and amine were equal, a white precipitate was observed in the reaction vessel but no hydrogen was formed. Experiments using an excess of the alane were prohibited because a different final product would be formed.[3] Thus, all kinetics data had to be derived from experiments which employed a greater than 10-fold excess of amine.

The kinetics data are summarized in Table II. Only plots of hydrogen pressure vs. time for the early part of the reaction give data which can be correlated with a rate law and fitted to an appropriate mechanism. First, second and fractional order kinetic plots had distinct curvatures. The slope of the linear portion of pressure vs. time plots gives an observed rate which is proportional to the initial dimethylaluminium hydride concentration for a given amine concentration. Thus, the alane dependence is given by the following expression. A plot of $1/k_o$ vs.

$$\frac{\Delta P_{H_2}}{\Delta t} = k_o[(CH_3)_2AlH]_T \quad (\text{Constant } [N(CH_2C_6H_5)H_2]_T) \qquad (4)$$

Table II

Kinetic Data for $(CH_3)_2AlH$-$N(CH_2C_6H_5)H_2$ Reaction

$[(CH_3)_2AlH]_T$,[a] M	$[N(CH_2C_6H_5)H_2]_T$, M	10^3 Initial Rate mm/sec	10^5k_o[b] sec^{-1}	10^4kK_2[c] sec^{-1}
0.123	1.94	5.23	5.92	1.95
0.0891	1.68	3.83	5.99	1.82
0.0833	1.23	4.38	7.31	1.82
0.0819	1.07	4.52	7.67	1.76
0.0819	2.00	3.13	5.32	1.82
0.0776	1.44	3.42	6.12	1.68
0.0675	0.924	4.27	8.79	1.86
0.0603	1.39	2.68	6.19	1.66
0.0546	0.720	4.07	10.36	1.94
0.0575	2.03	2.08	5.03	1.74

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

b - Calculated by dividing the initial rate, converted to units of M/sec, by $[(CH_3)_2AlH]_T$. (See text).

c - Calculated from the rate law by using the calculated value of K_1 (1.21 M^{-1}), initial rate, $[(CH_3)_2AlH]_T$ and $[N(CH_2C_6H_5)H_2]_T$. (See text).

$[N(CH_2C_6H_5)H_2]_T$ is linear and demonstrates the inverse dependence of the rate of hydrogen evolution on the amine concentration. The terms $[(CH_3)_2AlH]_T$ and $[N(CH_2C_6H_5)H_2]_T$ express the total dimethylaluminium hydride and benzylamine concentrations before elimination.

Equations 5-12 can be used to explain all of the kinetic data and experimental observations, and are totally consistent with the chemistry of the system. The only assumption which must be made for this mechanism is that the initial formation of adduct is extremely rapid.[1,4,5]

$$[(CH_3)_2AlH]_3 \longrightarrow 3(CH_3)_2AlH \tag{5}$$

$$(CH_3)_2AlH + N(CH_2C_6H_5)H_2 \longrightarrow H(CH_2)_2AlN(CH_2C_6H_5)H_2 \tag{6}$$

$$H(CH_3)_2AlN(CH_2C_6H_5)H_2 + N(CH_2C_6H_5)H_2 \underset{}{\overset{K_1}{\rightleftharpoons}} H(CH_3)_2Al[N(CH_2C_6H_5)H_2]_2 \tag{7}$$

$$H(CH_3)_2AlN(CH_2C_6H_5)H_2 \overset{K_2}{\rightleftharpoons} H(CH_3)_2Al + N(CH_2C_6H_5)H_2 \tag{8}$$

$$H(CH_3)_2Al + N(CH_2C_6H_5)H_2 \xrightarrow{k} H_2 + (CH_3)_2AlN(CH_2C_6H_5)H \tag{9}$$

$$(CH_3)_2AlN(CH_2C_6H_5)H + N(CH_2C_6H_5)H_2 \overset{K_3}{\rightleftharpoons} H_2(C_6H_5CH_2)NAl(CH_3)_2\text{-}N(CH_2C_6H_5)H \tag{10}$$

$$H_2(C_6H_5CH_2)NAl(CH_3)_2N(CH_2C_6H_5)H + H(CH_3)_2Al \overset{K_4}{\rightleftharpoons} H_2(C_6H_5CH_2)NAl(CH_3)_2N(CH_2C_6H_5)HAl(CH_3)_2H \tag{11}$$

$$2(CH_3)_2AlN(CH_2C_6H_5)H \overset{K_5}{\rightleftharpoons} [(CH_3)_2AlN(CH_2C_6H_5)H]_2 \tag{12}$$

$$\frac{dP_{H_2}}{dt} = \frac{-d[(CH_3)_2AlH]_T}{dt} = \frac{k[(CH_3)_2AlH]_T[N(CH_2C_6H_5)H_2]_T}{\dfrac{K_1[N(CH_2C_6H_5)H_2]_T^2}{K_2} + \dfrac{[N(CH_2C_6H_5)H_2]_T}{K_2} + 1} \tag{13}$$

The rate law is appropriate during the early stages of a reaction which utilizes a large excess of amine. Equilibria for K_3 and K_4 (eq. 10 and 11) are included in the mechanism in order to describe the overall chemistry of the system but have been eliminated from the rate law in order to fit the observed initial rate data. If K_2 is assumed to be small, the rate law can be simplified even further to give the following expression which is consistent with the data.

$$\frac{dP_{H_2}}{dt} = \frac{kK_2[(CH_3)_2AlH]_T}{K_1[N(CH_2C_6H_5)H_2]_T + 1} \qquad (14)$$

<u>Calculated Kinetic Constants</u>

$kK_2 = 1.80 \times 10^{-4}\ sec^{-1}$

$K_1 = 1.21\ M^{-1}$

The kinetic constants kK_2 and K_1 are calculated from the slope and intercept of the $1/k_o$ vs $[N(CH_2C_6H_5)H_2]_T$ plot. Using this value of K_1, kK_2 can be recalculated from the initial concentrations and rate data for the individual experiments (Table II). The results of these calculations support the proposed mechanism and rate law. It is regrettable that it is not possible to calculate values of k and K_2 from the available data.

The proposed mechanism for the elimination reaction between dimethylaluminium hydride and benzylamine is analagous to that proposed for the N-methylaniline reaction[1] except that equilibria (K_1, K_3 and K_4) have been added. The steps of the mechanism which are required for H_2 formation (eq. 8 and 9) are identical to those proposed for the

$H(CH_3)_2Al\text{-}N(CH_3)(C_6H_5)H$ reaction.[1] The equilibrium K_1 involving the bisamine adduct, $H(CH_3)_2Al[N(CH_2C_6H_5)H_2]_2$, is necessary to explain the inverse dependence of the rate of hydrogen evolution on the amine concentration under the pseudo first order conditions (excess amine). Equilibria K_3 and K_4, which occur after H_2 has been eliminated, pertain to overall chemistry of the system. The complications of five equilibria in the mechanism are responsible for the reaction not following simple first order kinetics under pseudo first order conditions. The occurrence of these equilibria for the benzylamine reaction are consistent with its significantly high basicity due to the electronic and steric effects. For comparison purposes, equilibrium constants[6] which describe the basicity of benzylamine and N-methylaniline toward the proton in aqueous solution differ by 10^5.

The observed decreasing initial rate of hydrogen evolution with increasing benzylamine concentration at constant alane concentration is a consequence of equilibrium K_1 - eq. 7. The excess amine reduces the concentration of the adduct, $H(CH_3)_2AlN(CH_2C_6H_5)H_2$, the compound which must dissociate to form the species required for the elimination reaction, the monomeric alane and amine. Bisamine adducts which involve five-coordinate aluminium are known[7-12] but a strong base and minimium steric interactions between the acid and base are necessary. Two compounds,[13,14] $H_3Al[N(CH_3)_3]_2$ and $H_3Al[(CH_3)_2NC_2H_4N(CH_3)_2]$, have been characterized by X-ray structural studies. However, in the case of dimethylaluminium hydride-amine compounds, no bisamine adducts have been previously observed. Apparently, $N(CH_3)_3$[15] and $N(C_6H_5)(CH_3)H$[1] have too many steric interactions or are too weak a base toward $(CH_3)_2AlH$ for a

bisamine adduct to be formed even at -46°C or -63°C, respectively.

The step in the mechanism which leads to the formation of hydrogen (eq. 9) is considered to be a second order reaction between a monomeric alane and the amine. It was not possible to obtain direct kinetic data for this second order process by following the formation of hydrogen when the alane and amine concentrations were equal.[1] However, other experimental observations support our hypothesis. When the alane and benzylamine are in equal concentrations, an insoluble solid is formed upon mixing at -63°C but no hydrogen is eliminated. The insoluble solid is most likely the adduct, $H(CH_3)_2AlN(CH_2C_6H_5)H_2$, a very polar compound. The insolubility of this adduct and the equilibria which precede the actual elimination reaction (eq. 7 and 8; K_1 and K_2) must reduce the concentrations of the reactive monomeric alane and amine to effectively hinder the formation of hydrogen. If the elimination reaction was a first order reaction of the preformed adduct, hydrogen formation should have been observed even if the adduct were insoluble. Second order reactions of the adduct are inconsistent with the kinetic data.

The equilibria represented by K_3, K_4 and K_5 (eq. 10, 11 and 12) have been added to the overall mechanism of the total reaction in order to fully describe the chemistry of the system. These equilibria occur after hydrogen has been formed and involve the aluminium-nitrogen products of the reaction. Thus, they are not required to explain our kinetic observations for the initial part of the reaction. However, these complicating equilibria help to explain why the full reaction does not exhibit simple first order kinetics under pseudo first order condi-

tions. The fact that these equilibria occur in the benzylamine-alane elimination reaction but not in the corresponding N-methylaniline reaction[1] must be related to the higher basicity of benzylamine. The reaction of $(CH_3)_2AlN(CH_2C_6H_5)H$ with $N(CH_2C_6H_5)H_2$ (eq. 10, K_3) is clearly supported by ^1H NMR data (see following discussion). The subsequent reaction of $H_2(C_6H_5CH_2)NAl(CH_3)_2N(CH_2C_6H_5)H$ with $(CH_3)_2AlH$ would be a function of the increased basicity of the benzylamino group after elimination. This suggestion that the benzylamino-group can effectively compete with benzylamine for $(CH_3)_2AlH$ is based on related observations in aluminium-nitrogen chemistry.[16,17] The analogous effect is considered to be responsible for the dimerization of $(CH_3)_2AlN(CH_3)C_2H_4N(CH_3)_2$ with free $-N(CH_3)_2$ groups, rather than the formation of the chelated monomer.[17] Additional complications in the overall mechanism can be envisioned if a second elimination reaction occurred as shown in the following equation (15). A subsequent proton transfer reaction and

$$H_2(C_6H_5CH_2)NAl(CH_3)_2\ddot{N}(CH_2C_6H_5)H + (CH_3)_2AlH \longrightarrow H_2(C_6H_5CH_2)NAl(CH_3)_2\ddot{N}(CH_2C_6H_5)Al(CH_3)_2 + H_2 \qquad (15)$$

then dissociation of this product would give $(CH_3)_2AlN(CH_2C_6H_5)H$, the typical reaction product.

The comparisons of the calculated kinetic constants for the analogous benzylamine- and N-methylaniline[1]-dimethylaluminium hydride elimination reactions are of interest to determine how the amine effects the rate of elimination. Qualitatively, benzylamine reacts faster than N-methylaniline. Similarly, these observations are reflected in the calculated values of kK_2 (1.80×10^{-4} sec^{-1} $N(CH_2C_6H_5)H_2$; 5.46×10^{-5}

sec^{-1} $N(C_6H_5)(CH_3)H$). Benzylamine is a much stronger base than N-methylanailine. Thus, K_2 should be smaller for the benzylamine, probably less than 9.09×10^{-3} M, the observed value of K_2 for the $H(CH_3)_2AlN(C_6H_5)(CH_3)H$ dissociation equilibrium.[1] In order for kK_2 to be larger for the benzylamine reaction, the rate constant for its elimination reaction (k_2) must be greater than 6.01×10^{-3} M^{-1} sec^{-1}, the value calculated for the N-methylaniline reaction.[1] There are many reasons why dimethylaluminium hydride-benzylamine would eliminate hydrogen faster than N-methylaniline. There are twice as many reactive N-H bonds with less steric hindrance for the formation of the transition state for the proposed four-centered S_Ei process.[1] Our current limited data does not warrant more detailed comparisons at this time.

The final product from the elimination reaction in the absence of excess amine is an aluminium-nitrogen dimer $[(CH_3)_2AlN(CH_2C_6H_5)H]_2$, which exists as a 1:1 mixture of cis/trans geometrical isomers. This isomer ratio is not significantly affected by solvent polarity. The ^1H NMR data indicate 49.5% cis isomer in cyclopentane, 47.9% cis in toluene and 51.8% cis in methylene chloride. If a ${}_2\pi_s + {}_2\pi_a$ concerted cycloaddition reaction of two $(CH_3)_2AlN(CH_2C_6H_5)H$ monomer units is the mechanism for dimerization,[1] only small differences can exist between the relative energies of the transition states for the formation of the two isomers. The benzyl group would be expected to have small steric effects in the proposed transition state. However, if the monomer, $(CH_3)_2AlN(CH_2C_6H_5)H$, reacts with $N(CH_2C_6H_5)H_2$ as proposed in eq. 10 (K_3), subsequent sequential reactions can also be envisioned to produce the dimer. The current kinetic study does not permit us to distinguish

between these two paths but the concerted cycloaddition reaction seems more plausible, especially when the alane and amine are reacted in equal amounts. When excess benzylamine is added to a cyclopentane solution of the dimer, the unique aluminium-methyl lines of the cis/trans isomers in the ^1H NMR spectrum are lost. Only one Al-CH_3 line is observed, which is consistent with fast exchange. As previously mentioned, the equilibria represented by equations 10 and 12 (K_3 and K_5) are consistent with these observations.

The reaction between an alane and amine cannot be considered simple or straightforward. Many factors must influence the various steps of the reaction mechanism. As the basicity and steric effects of the amine change, many equilibria involving reactants and products are apparently introduced into the mechanism. More kinetics studies will be required to elucidate the relative importance of the different equilibria and the factors influencing the magnitude of the second-order rate constant for elimination.

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