

THE INFLUENCE OF BENZENE ON DISPROPORTIONATION OF A TERTIARY AMINE COMPLEX OF ETHYLALUMINUM DICHLORIDE

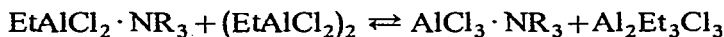
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SUMMARY

The tendency toward disproportionation of ethylaluminum dichloride complexes of tertiary amines in the presence of excess ethylaluminum dichloride



dimer has been studied in cyclohexane and benzene. With dimethylcyclohexylamine (DMCHA) the concentrations of the various possible complexes could be directly obtained via integration of the methylamino-PMR signals. The DMCHA methyl resonance exhibited a characteristic chemical shift when complexed with a specific alkyl aluminum chloride or AlCl_3 .

RESULTS AND DISCUSSION

The stability of ethylaluminum chloride complexes towards disproportionation has been the subject of several studies¹⁻³. Via PMR studies we have observed that diethylaluminum chloride complexes with dimethylcyclohexylamine (DMCHA) do not change, and do *not* disproportionate (1), either in cyclohexane or in benzene at



36° over a period of several days. Thus, for example, the *N*-methyl proton signal from $\text{Et}_2\text{AlCl} \cdot \text{DMCHA}$ in benzene remains constantly at τ 7.91, upfield from the τ 7.73 signal of this amine in an independently prepared benzene solution of $\text{AlCl}_3 \cdot \text{DMCHA}$. Likewise, we have observed that in cyclohexane, ethylaluminum dichloride complexes with DMCHA are stable at 36° for at least several days. In benzene, however, complexes of ethylaluminum dichloride with DMCHA were seen to disproportionate (2) fairly rapidly at 36°.



In excess ethylaluminum dichloride the rate of this disproportionation (2) could be easily followed by integration of the *N*-methyl signals from the two types of complexed amine; the $\text{EtAlCl}_2 \cdot \text{DMCHA}$ amine signal appears at τ 7.85. The concentration of the aluminum chloride complex, $[\text{AlCl}_3 \cdot \text{DMCHA}]$ (in moles per liter), was measured as a function of time for four runs at different initial ratios of ethylaluminum dichloride to DMCHA. After disproportionation ceased, the concentrations of the species involved were used to calculate values of the equilibrium constant, K_e ,

TABLE 1

EQUILIBRIUM DATA FOR DISPROPORTIONATION OF ETHYLALUMINUM DICHLORIDE-DMCHA IN EXCESS ETHYLALUMINUM DICHLORIDE AT 36°

[EtAlCl ₂ ·DMCHA]	[Al ₂ Et ₂ Cl ₄]	[AlCl ₃ ·DMCHA]	[Al ₂ Et ₃ Cl ₃]	K _e
0.01	1.26	0.14	0.14	2.6
0.02	1.16	0.30	0.30	3.8
0.12	0.68	0.53	0.53	3.4
0.66	0.09	0.66	0.66	4.6

for all runs at 36°. These concentrations and calculated equilibrium constants appear in Table 1. We estimate the value of K_e to be 3.6 ± 0.6.

In order to assess the kinetics of the disproportionation, the rate of appearance of the aluminum chloride complex was assumed to be a function of both the ethylaluminum dichloride complex and ethylaluminum dichloride dimer, according to the expression (3), and the reaction orders (*m* and *n*) were estimated by the method of

$$r = \frac{d[\text{AlCl}_3 \cdot \text{DMCHA}]}{dt} = k_r \cdot [\text{EtAlCl}_2 \cdot \text{DMCHA}]^m \cdot [\text{Al}_2\text{Et}_2\text{Cl}_4]^n \quad (3)$$

initial rates⁴. Plots of [AlCl₃·DMCHA] concentrations versus time at various initial concentrations of [EtAlCl₂·DMCHA] and [Al₂Et₂Cl₄] were evaluated graphically in the earlier portions to obtain initial rates directly (Fig. 1). A plot of the log of the

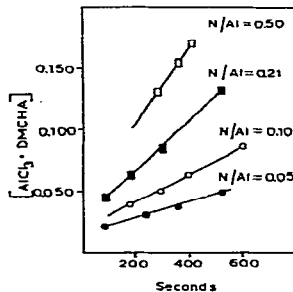


Fig. 1. Disproportionation of EtAlCl₂·DMCHA; plot of [AlCl₃·DMCHA] vs. time at four different initial ratios of [EtAlCl₂·DMCHA] to [Al₂Et₂Cl₄].

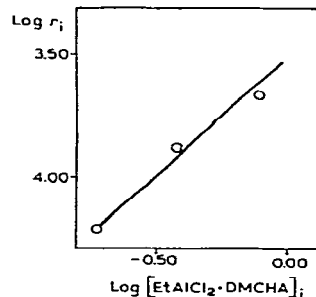


Fig. 2. Disproportionation of EtAlCl₂·DMCHA; plot of log *r_i* vs. log [EtAlCl₂·DMCHA]_{*i*}.

initial rate, log *r_i*, versus log [EtAlCl₂·DMCHA] in a region of relatively invariant dimer concentration (Fig. 2), gave a slope equal to 0.94, *i.e.*, the reaction is apparently first order with respect to [EtAlCl₂·DMCHA].

Following this, a plot of log {*r_i*/[EtAlCl₂·DMCHA]} versus log [Al₂Et₂Cl₄] was made over the region where the dimer concentration varied considerably, in order to determine an order with respect to the dimer. The slope evaluated from this plot (Fig. 3) was 0.75. Considering experimental error, this value indicated an order in dimer somewhere between one-half and one. The empirical rate constant, *k_r*, evaluated at the zero intercept of this plot, was 5 × 10⁻³ sec⁻¹.

An effort was made to distinguish a thermodynamic *vs.* a kinetic solvent effect

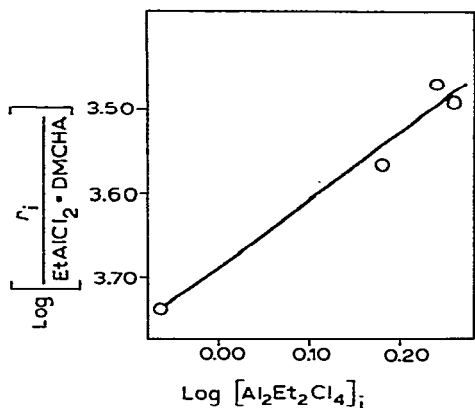


Fig. 3. Disproportionation of $\text{EtAlCl}_2 \cdot \text{DMCHA}$; plot of $\log \{r_i/[\text{EtAlCl}_2 \cdot \text{DMCHA}]\}$ vs. $\log [\text{Al}_2\text{Et}_2\text{Cl}_4]_i$.

of benzene on this disproportionation. After a cyclohexane solution of the ethylaluminum dichloride–DMCHA in excess ethylaluminum dichloride dimer was observed to undergo no change, a small quantity of benzene (ca. 10 vol. percent) was added, and disproportionation to form aluminum chloride complex was seen to occur. Several days later, when the system was assumed to be at equilibrium, the concentrations of the components were examined qualitatively; quantitative examination was impossible due to serious overlap of peaks in this solvent mixture. The position of equilibrium was adjudged to be considerably less to the right than an identical system in benzene. This suggested that benzene does play a thermodynamic role in the reaction, in addition to whatever kinetic role it obviously plays.

This kinetic role is quite interesting, for it is apparently not the usual type of “solvent effect”, *i.e.*, not due simply to a macroscopic solvent polarity change. Thus, *very little added benzene caused a reaction to occur in cyclohexane which could not be observed in cyclohexane alone.* These observations strongly suggest that the aromatic hydrocarbon forms some type of specific complex with reactants and/or intermediates. Further evidence consistent with the existence of ternary complexes composed of amine, aluminum reagent and benzene is seen in the changes in chemical shifts of

TABLE 2

CHEMICAL SHIFTS OF DIMETHYLCYCLOHEXYLAMINE (DMCHA), ALUMINUM REAGENTS AND THEIR COMPLEXES IN BENZENE AND IN CYCLOHEXANE

Reagent	Amine	τ in benzene/in cyclohexane, $\Delta\tau$		
		$\text{CH}_2\text{-Al}$	$\text{CH}_3\text{-C-Al}$	$\text{CH}_3\text{-N}$
	DMCHA			7.66/7.81, +0.15
Et_3Al		9.69/ 9.66, -0.03	8.80/8.79, -0.01	
Et_3Al	DMCHA	9.89/10.16, +0.27	8.62/8.89, +0.27	8.05/7.64, -0.41
Et_2AlCl		9.63/ 9.79, +0.16	8.80/8.89, +0.09	
Et_2AlCl	DMCHA	9.82/10.08, +0.26	8.69/8.92, +0.23	7.91/7.50, -0.41
EtAlCl_2		9.64/ 9.76, +0.12	8.85/8.92, +0.07	
EtAlCl_2	DMCHA	9.82/10.08, +0.26	8.65/8.93, +0.29	7.85/7.44, -0.41
AlCl_3	DMCHA			7.73/7.41, -0.32

protons in these components in going from cyclohexane to benzene as solvent. These changes ($\Delta\tau$, benzene \rightarrow cyclohexane) are consistently greater if the aluminum reagent is complexed by the amine, as illustrated by the data in Table 2.

While speculation about these effects in terms of specific structures of ternary complexes would be premature, the effects of benzene on the rates of exchange and the chemical shifts of various organoaluminum-amine complexes are no doubt a function of the donor character of the aromatic system⁵.

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