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THE MONOMER–DIMER EQUILIBRIA OF LIQUID ALUMINUM ALKYLS

IV. TRIETHYLALUMINUM IN MESITYLENE

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SUMMARY

The monomer–dimer equilibrium of triethylaluminum (TEA) in mesitylene solution has been studied by measuring heats of dilution. The value obtained for the heat of dissociation of one mole of TEA dimer in mesitylene, 13.3_1 kcal, is significantly smaller than the corresponding value in n-hexadecane (16.9_3 kcal). The difference is ascribed primarily to the (exothermic) complexation of mesitylene with TEA monomer. Degrees of dissociation of TEA in mesitylene at various mole fractions are tabulated over a wide temperature range and compared with corresponding values in aliphatic (saturated) hydrocarbons. The results indicate that TEA is about eight times as dissociated in mesitylene as in an aliphatic hydrocarbon at −50°C. The ratio decreases with rising temperature and becomes unity at about 170° C. The results have been extended to trimethylaluminum (TMA) and to other aromatic solvents. The estimated value for the heat of dissociation of TMA in toluene (15.6 ± 1.4 kcal · (mole of dimer)$^{-1}$) is consistent with the literature value (15.4 ± 2.0 kcal · mole^{-1}) for the activation energy for the bridge–terminal exchange of methyl groups. This supports the literature contention that the exchange in toluene solution occurs via dissociation of dimeric molecules to monomers as the rate determining step. Since the literature value for the activation energy for exchange in cyclopentane solution (15.6 ± 0.2 kcal · mole^{-1}) is well below the heat of dissociation of TMA in cyclopentane (19.4 kcal · mole^{-1}), there is a distinct possibility that the exchange mechanism is different in the two solvents.

INTRODUCTION

Parts I, II and III of this series dealt with triethylaluminum (TEA)[1], triisobutylaluminium (TiBA)[2] and trimethylaluminum (TMA)[3] in straight-chain saturated hydrocarbon solvents. Whereas such solvents would be expected to show little, if any, interaction with aluminum alkyls, aromatic solvents might be expected to interact or complex appreciably with the monomeric species. To determine the effect of such interaction on the monomer–dimer equilibria, the heat of dilution experiments on TEA were repeated in the present study with mesitylene as the solvent.

EQUATIONS

Consider the addition of f_0 gfw (gram formula weights) of TEA to a solution of f_1 gfw of TEA dissolved in n_h moles of mesitylene. Let $f_2 = f_0 + f_1$ = gfw of TEA in final solution; $r_1 = n_h/f_1$; $r_2 = n_h/f_2$; β = weight fraction of alkyl dissociated; β_0 = apparent* β for pure alkyl; $\beta_1 = \beta$ for initial solution; $\beta_2 = \beta$ for final solution; ΔH_d^0 = heat of dissociation, cal·(mole of dimer dissociated)$^{-1}$; Q_T = total (experimental) heat absorbed on dilution, cal·(gfw of alkyl added)$^{-1}$; Q_d = portion of Q_T due to dissociation; and Q_p = portion of Q_T due to physical mixing.

As derived in part I, the following equations apply:

$$Q_T = Q_d + Q_p \tag{1}$$

$$K_d = X^2_{\text{monomer}}/X_{\text{dimer}} = 4\beta_0^2/(1-\beta_0^2) \tag{2}$$

$$\beta/\beta_0 = \sqrt{\beta_0^2 \cdot r^2 + 2r + 1} - \beta_0 \cdot r \tag{3}$$

$$Q_d = (\beta_0 \cdot \Delta H_d^0/2) \cdot [G_2 - (f_1/f_0) \cdot (G_1 - G_2)] \tag{4}$$

where

$$G_i = \sqrt{\beta_0^2 \cdot r_i^2 + 2\,r_i + 1} - \beta_0 \cdot r_i - 1$$

$$\ln K_d = \frac{\Delta S_d^0}{R} - \frac{\Delta H_d^0}{R \cdot T} \tag{5}$$

$$Q_p = \left(\frac{A}{2} + \frac{B \cdot t}{2}\right) \cdot \bar{X}_h^2 \tag{6}$$

where A and B are constants, t is temperature (°C), and $\bar{X}_h$ is the average mole fraction of hydrocarbon before and after the alkyl addition.

RESULTS AND DISCUSSION

The experimental results are listed in the first seven columns of Table 1. At each temperature the total heat absorbed (Q_T) is roughly half as great for a "B" experiment (in which the initial solution contained about 10 ml of TEA) as it is for an "A" experiment (in which the initial solution contained about 2 ml of TEA). This reflects the inhibiting effect of monomeric molecules present in the initial solution on the dissociation of added TEA. Within either the "A" series or the "B" series, the value of Q_T, and therefore the net amount of dissociation occurring on dilution, increases exponentially with temperature.

Values of the parameters ΔH_d^0, ΔS_d^0, A, and B were determined using a non-linear least-squares computer program based on eqns. (1), (2–5) and (6). This routine solves for the values of the parameters for which the sum of the squares of the differences between calculated and observed heats of dilution (Q_T) is a minimum. The values obtained using an IBM 1130 computer are listed in Table 2 with their estimated

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* Since mesitylene is a complexing solvent, a value of β_0 developed by the computer program refers, not to the pure alkyl, but to solutions containing complexed monomers and dimers "extrapolated to zero concentration of excess solvent".

TABLE 1

HEATS OF DILUTION OF LIQUID TRIETHYLALUMINUM WITH MESITYLENE

Expt. No.	*Temp. (°C)*	*Initial solution*		*TEA added (g)*	$-\Delta t$ *(°C)*	Q_T *(cal·gfw^{-1})*		Q_p	Q_d
		Mesitylene (g)	*TEA (g)*			*Exptl.*	*Calcd.*		
40A1	40.446	158.48	1.8025	3.4323	0.0437	148	141.2	17.4	123.8
40A2	40.408	158.27	1.8122	3.6341	0.0433	139	138.9	17.4	121.5
40B1	40.547	159.72	8.6734	3.6549	0.0219	73	75.7	16.6	59.1
40B2	40.472	159.07	8.5845	3.5217	0.0215	74	76.0	16.6	59.4
60A1	60.983	158.95	1.8202	3.4746	0.0723	252	249.6	12.3	237.3
60A2	60.272	158.47	1.8818	3.3667	0.0672	241	243.4	12.5	230.9
60B1	59.781	158.37	8.6806	3.5495	0.0335	118	121.2	12.1	109.1
60B2	59.923	158.74	8.6179	3.5818	0.0356	124	122.2	12.1	110.1
80A1	79.990	158.55	1.7913	3.4411	0.1135	412	416.2	7.7	408.5
80A2	79.875	157.76	1.9165	3.5316	0.1140	402	401.5	7.7	393.8
80B1	79.535	159.86	8.5446	3.4476	0.0545	205	202.5	7.5	195.1
80B2	79.716	159.27	8.5846	3.4923	0.0537	199	202.2	7.4	194.8
100A1	99.879	159.58	1.7887	3.4529	0.1819	683	677.8	2.8	675.0
100A2	99.719	158.97	1.7892	3.5209	0.1813	666	670.4	2.8	667.6
100B1	99.371	159.77	8.5655	3.5933	0.0878	328	323.4	2.8	320.6
100B2	99.589	159.78	8.6257	3.4966	0.0838	322	324.7	2.8	321.9

TABLE 2

VALUES OF PARAMETERS DERIVED BY COMPUTER PROGRAM

ΔH_d^0, cal·(mole of dimer)$^{-1}$	133_{07}	$\pm 1_{80}$
ΔS_d^0, cal·K^{-1}·(mole of dimer)$^{-1}$	23.9_9	$\pm 0.4_5$
A, cal·mole^{-1}	$55._8$	$\pm 3._8$
B, cal·K^{-1}·mole^{-1}	-0.50_2	$\pm 0.04_5$

accuracy limits. Calculated values of Q_T based on these values are given in column 8 of Table 1 where they are compared with experimental values (column 7). The r.m.s. difference between calculated and experimental values is 3.5 cal·gfw^{-1}.

Calculated values of the heat of physical mixing (Q_p) and the heat due to dissociation (Q_d) given in the last two columns of Table 1 are all positive in sign. With increasing temperature, Q_d increases exponentially while Q_p decreases. For each experiment, Q_p is much smaller than Q_d. At each temperature, however, Q_p is larger relative to Q_d for a "B" experiment than for an "A" experiment. The Q_p values are smaller than corresponding values for TEA in n-hexadecane[1]. This is ascribed to (exothermic) heat of solvation of TEA dimer with mesitylene since, if there were no solvation, the (endothermic) heat of physical mixing would be expected to be greater in mesitylene than in hexadecane. After consideration of this and related heat of mixing data, the heat of solvation of TEA dimer with mesitylene was estimated as $\Delta H = -370 \pm 130$ cal·(mole of dimer)$^{-1}$.

On substituting the values obtained for ΔH_d^0 and ΔS_d^0 in eqn. (5), the expression for the equilibrium constant becomes:

TABLE 3

EQUILIBRIUM CONSTANT AND DEGREE OF DISSOCIATION OF LIQUID TRIETHYLALUMINUM IN MESITYLENE AND IN HEXADECANE[a]

Temp. (°C)	K_d		*% of TEA dissociated at TEA mole fraction[b] of*					
			0.1		0.01		0.001	
	Mesitylene	*Hexadecane*	*Mesitylene*	*Hexadecane*	*Mesitylene*	*Hexadecane*	*Mesitylene*	*Hexadecane*
0	3.941×10^{-6}	3.072×10^{-7}	0.4318	0.1207	1.390	0.3901	4.341	1.231
10	9.367×10^{-6}	9.243×10^{-7}	0.6649	0.2093	2.136	0.6758	6.612	2.126
20	2.099×10^{-5}	2.580×10^{-6}	0.9938	0.3495	3.180	1.127	9.731	3.527
30	4.459×10^{-5}	6.729×10^{-6}	1.445	0.5639	4.601	1.813	13.86	5.634
40	9.028×10^{-5}	1.651×10^{-5}	2.051	0.8819	6.482	2.825	19.11	8.681
50	1.750×10^{-4}	3.832×10^{-5}	2.844	1.341	8.907	4.272	25.52	12.91
60	3.259×10^{-4}	8.456×10^{-5}	3.862	1.985	11.95	6.280	33.03	18.55
70	5.855×10^{-4}	1.782×10^{-4}	5.143	2.869	15.68	8.984	41.41	25.72
80	0.001017	3.599×10^{-4}	6.726	4.054	20.12	12.52	50.28	34.36
90	0.001715	6.994×10^{-4}	8.646	5.608	25.27	17.00	59.17	44.18
100	0.002811	0.001312	10.94	7.602	31.07	22.50	67.54	54.57
110	0.004491	0.002380	13.62	10.11	37.43	29.01	74.97	64.76
120	0.007005	0.004190	16.72	13.19	44.16	36.44	81.18	73.92
130	0.01069	0.007173	20.23	16.90	51.07	44.54	86.12	81.49
140	0.01598	0.01196	24.14	21.27	57.92	52.98	89.89	87.27
150	0.02343	0.01948	28.43	26.29	64.47	61.32	92.67	91.42
160	0.03377	0.03101	33.05	31.93	70.51	69.13	94.69	94.27

[a] Values for mesitylene at 0–30 and 110–160 were extrapolated, as were values for hexadecane at 0–50 and at 160° C.

[b] TEA was taken as the monomer in computing mole fractions.

$$\ln K_d = 12.0715 - 6696.4/T \tag{7}$$

Values of K_d calculated from this equation at 10° intervals are given in column 2 of Table 3 where they are compared with corresponding values for hexadecane (column 3). The ratio K_d(mesitylene)/K_d (hexadecane) decreases from ~13 at 0° C to ~1.1 at 160° C. This indicates that the degree of complexation of TEA monomer with mesitylene decreases with increasing temperature and becomes negligible in the vicinity of 170° C. Degrees of dissociation of TEA in mesitylene at various mole fractions were calculated from eqns. (2) and (3). These values, expressed as per cent of TEA dissociated, are listed in columns 4, 6 and 8 where they are compared with corresponding values in hexadecane (columns 5, 7 and 9). The figures indicate that TEA is about 3.6 times as dissociated in mesitylene as in a saturated hydrocarbon at 0° C. The ratio decreases with increasing temperature and becomes unity in the neighborhood of 170° C.

The derivation[1] of eqns. (3) and (4) is based on the assumption that K_d does not vary with the concentration of the alkyl in the solvent (for the concentration range studied). There is naturally more concern about the validity of this assumption in the case of a complexing solvent such as mesitylene than in the case of a non-complexing solvent such as hexadecane. Although K_d might vary considerably over the entire concentration range in the case of mesitylene, it would not be expected to vary significantly over the narrow experimental range (mole fraction of TEA dimer $=0.006$–0.04). The close agreement between experimental and calculated values of Q_T (Table 1) tends to confirm this. In addition, values of K_d derived from the "A" data alone (mean mole fraction of TEA dimer ≈ 0.012) agree within experimental error with corresponding values derived from the "B" data alone (mean mole fraction of TEA dimer ≈ 0.035). It is concluded that K_d did not vary appreciably over the narrow concentration range studied. At the same time, it is emphasized that the derived K_d values are strictly applicable only for the dilute range and should not be expected to apply to concentrated solutions or to the pure alkyl.

The heat of dissociation of TEA in mesitylene ($\Delta H_d^0 = 13307$ cal·(mole of dimer)$^{-1}$) is considerably smaller than the value in hexadecane ($\Delta H_d^0 = 16930$ cal·(mole of dimer)$^{-1}$, ref. 1). The difference is ascribed primarily to the (exothermic) complexation of TEA monomer in the case of mesitylene (solvation effects are assumed to be negligible in the case of hexadecane). TEA dimer is also presumed to be solvated to some degree in mesitylene ($\Delta H_c = -370 \pm 130$ cal·(mole of dimer)$^{-1}$ as per the previous estimate). The difference in the two values of ΔH_d^0 (-3623 cal·(mole of dimer)$^{-1}$), which we will call the "gross heat of complexation" of TEA monomer, is equal to the (actual) heat of complexation of the monomer less that of the dimer. As shown by summing the following equations, the (actual) heat of complexation of TEA monomer with mesitylene is $\Delta H_c = -3623 - 370 \approx -4000$ cal·(mole of dimer)$^{-1}$ or ~ -2000 cal·(mole of monomer)$^{-1}$.

$$\begin{array}{ll}
2\,\mathrm{M} \longrightarrow \mathrm{D} & \Delta H = -16930\ \mathrm{cal \cdot mole^{-1}} \\
\mathrm{D} + y\ \text{mesitylene} \longrightarrow \mathrm{D} \cdot y\ \text{mesitylene} & \Delta H = -370\ \mathrm{cal \cdot mole^{-1}} \\
\mathrm{D} \cdot y\ \text{mesitylene} + (2x - y)\ \text{mesitylene} \longrightarrow 2\,\mathrm{M} \cdot x\ \text{mesitylene} & \Delta H = 13307\ \mathrm{cal \cdot mole^{-1}} \\
\hline
2\,\mathrm{M} + 2x\ \text{mesitylene} \longrightarrow 2\,\mathrm{M} \cdot x\ \text{mesitylene} & \Delta H = -3993\ \mathrm{cal \cdot mole^{-1}}
\end{array}$$

It would be of considerable interest to know the heat of dissociation of TMA in mesitylene and also in other aromatic solvents, particularly toluene. As pointed out elsewhere[3], TMA is not well adapted to the present experimental techniques. We will therefore extend the results for TEA in mesitylene to TMA and to other aromatic solvents. The heat of dimerization of TMA monomer ($\Delta H = -19400$ cal·(mole of dimer)$^{-1}$, ref. 3) exceeds that of TEA monomer ($\Delta H = -16930$ cal·(mole of dimer)$^{-1}$, ref. 1) because the steric effect accompanying bridge formation is less with methyl groups than with ethyl groups. Assuming that the gross heat of complexation of TMA monomer with mesitylene exceeds that of TEA monomer in the same proportion (the steric effect should again be less with methyl groups), the gross heat of complexation of TMA monomer with mesitylene is estimated as $\Delta H = -4150 \pm 700$ cal·(mole of dimer)$^{-1}$. The corresponding value for the heat of dissociation of TMA in mesitylene is $\Delta H_d^0 = 19400 - 4150 = 15250 \pm 1000$ cal·(mole of dimer)$^{-1}$.

H. C. Brown and co-workers[4] determined the heats of complexation of various aromatic solvents with three different Lewis acids. Their data show that for each Lewis acid studied, the magnitude of the heat of complexation increases moderately in the order benzene < toluene < *m*-xylene < mesitylene. For a given aromatic, the ratio of its heat of complexation to that of mesitylene has about the same value for each of the Lewis acids. For toluene, for example the values of the ratio are 0.91 (HCl in n-heptane solution), 0.90 (HBr in n-heptane solution), and 0.94 (solid Al_2Br_6). The following values for the ratios were selected as best representing all the data: 0.86 for benzene, 0.91 for toluene, 0.95 for *m*-xylene and, by definition, 1.00 for mesitylene. These ratios were applied to the gross heat of complexation of mesitylene with TMA monomer to obtain the following estimated values for the other solvents: -3570 ± 500 for benzene, -3780 ± 400 for toluene, and -3940 ± 300 cal·(mole of dimer)$^{-1}$ for *m*-xylene (the indicated uncertainties are in addition to the uncertainty in the gross heat of complexation of mesitylene with TMA monomer). The corresponding estimated values for the heats of dissociation of TMA in these solvents are $\Delta H_d^0 = 15830 \pm 1500$ in benzene, 15620 ± 1400 in toluene, and 15460 ± 1300 cal·(mole of dimer)$^{-1}$ in *m*-xylene.

Williams and Brown[5] studied the exchange of methyl groups between bridge and terminal positions in TMA in toluene solution using PMR spectroscopy. Their results strongly indicate that the exchange must occur via the dissociation of dimeric TMA molecules to monomers as the rate-determining step. In order for this mechanism to be valid, the Arrhenius activation energy for the exchange, which they determined as 15.4 ± 2.0 kcal·mole^{-1}, should equal or exceed the heat of dissociation of TMA in toluene. The value derived herein for the latter quantity is 15.6 ± 1.4 kcal·(mole of dimer)$^{-1}$ which falls well below the upper limit for the activation energy. It is therefore concluded that the results of the present investigation are consistent with the dissociative mechanism for bridge–terminal exchange in toluene solution as proposed by Williams and Brown.

Ramey *et al.*[6] determined the enthalpy of activation for bridge-terminal exchange in TMA in cyclopentane solution as 15.6 ± 0.2 kcal·mole^{-1}. This is well below the heat of dissociation of TMA in aliphatic hydrocarbon solution* (19.4 kcal·(mole

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* The heat of dissociation is assumed to be the same in cyclopentane as it is in n-hexadecane and other (saturated) aliphatic hydrocarbons.

of dimer)$^{-1}$). As already pointed out by Ramey, therefore, it appears unlikely that bridge–terminal exchange in cyclopentane solution occurs with simple dissociation as the rate determining step. Jeffery and Mole[7] reported that the rate of exchange at −49° C is about 20 times faster in toluene than in cyclopentane. This also suggests that the mechanism for exchange may be different in the two solvents. Calculations based on the present results indicate that the equilibrium concentration of TMA monomer at −50° (roughly the mean temperature of the exchange experiments) is approximately eight times as great in toluene solution as it is in a cyclopentane solution of the same molarity. It is not known what bearing this might have, if any, on a difference in exchange mechanisms in the two solvents.

EXPERIMENTAL

The TEA was supplied by Ethyl Corporation. Chemical analysis showed it to contain 95.1 % $(C_2H_5)_3Al$, 1.4 % $(C_2H_5)_2AlH$, and 3.5 % $(C_4H_9)_3Al$. Mesitylene of 99+ % purity was supplied by the Aldrich Chemical Co. It was deoxygenated by bubbling dry nitrogen through it for 2 h and was stored over molecular sieves. Triply distilled mercury was deoxygenated similarly.

The apparatus and procedure were the same as described in part I[1] except that mesitylene was used instead of n-hexadecane. The specific heat of mesitylene was read from a plot obtained by extrapolating the measurements of Taylor, Johnson and Kilpatrick[8].

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