Journal of Organometallic Chemistry, 70 (1974) 13—33
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THE MONOMER—DIMER EQUILIBRIA OF LIQUID ALUMINUM ALKYLS

V. TRI-n-PROPYLALUMINUM, TRI-n-BUTYLALUMINUM AND TRI-n-OCTYLALUMINUM: THE EFFECT OF CHAIN LENGTH ON THE EQUILIBRIA

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(Received September 14th, 1973)

Summary

The monomer—dimer equilibria of three liquid aluminum n-alkyls have been studied in n-hexadecane solution by a thermochemical method applied earlier to triethylaluminum (TEA) and triisobutylaluminum (TiBA). The values obtained for the heat and entropy of dissociation of 1 mole of dimer are: for tri-n-propylaluminum (TnPA), $15.4_1 \pm 0.2_0$ kcal and $33.4_8 \pm 0.6_0$ cal · K^{-1}; for tri-n-butylaluminum (TnBA), $15.0_1 \pm 0.1_5$ kcal and $33.7_2 \pm 0.4_4$ cal · K^{-1}; for tri-n-octylaluminum (TnOA), $14.6_8 \pm 0.1_2$ kcal and $33.7_6 \pm 0.3_4$ cal · K^{-1}. Equilibrium constants and degrees of dissociation of the neat alkyls are tabulated over wide temperature ranges, as are degrees of dissociation at various mole fractions in hexadecane. The effects of chain length on the monomer—dimer equilibria are discussed. Plots of ΔH_d^0 and ΔS_d^0 vs. chain length are used to obtain estimated values for certain other alkyls. Heats of complexation of monomeric R_3Al with Et_3N are calculated from literature values for the heats of reaction of (primarily dimeric) R_3Al with Et_3N and plotted against chain length. The monomer—dimer equilibria of the aluminum n-alkyls in mesitylene and in benzene are estimated from experimental data for TEA in mesitylene. The effect of solvent type on the degree of dissociation of R_3Al in dilute solution is discussed. Heats of complexation of monomeric R_3Al with aromatic hydrocarbons are estimated and compared with corresponding values for stronger bases. The experimental and estimated K_d values are compared with values derived from cryoscopic molecular weight determinations. Applications of degrees and heats of dissociation of aluminum alkyls are discussed.

Introduction

Parts I, II and III of this series dealt with the monomer—dimer equilibria of triethylaluminum (TEA) [1], triisobutylaluminum (TiBA) [2] and trimethylaluminum (TMA) [3] in straight-chain saturated hydrocarbon solvents. Part IV

[4] was concerned with TEA in an aromatic solvent (mesitylene). In the present paper, the studies in aliphatic hydrocarbon solvents are extended to include tri-n-propylaluminum (TnPA), tri-n-butylaluminum (TnBA) and tri-n-octylaluminum (TnOA).

With the addition of the new data on the three longer-chain alkyls, it is now possible to study the effects of chain length on the monomer—dimer equilibria. ΔH_d^0, ΔS_d^0 and degree of dissociation will therefore be plotted against chain length. If appropriate, ΔH_d^0 and ΔS_d^0 values for other alkyls not studied experimentally will be read from the plots and used to estimate their monomer—dimer equilibria.

An illustration will be given of the utilization of heats of dissociation in the calculation of heats of complexation from heats of reaction of aluminum alkyls with bases. A plot will be made of the relative heat of complexation (referred to ΔH_c of TMA taken as unity) versus chain length. This plot will be used, in conjunction with experimental data for TEA in mesitylene, to estimate the monomer—dimer equilibria of the aluminum n-alkyls in mesitylene and also in benzene. The effect of solvent type on the degree of dissociation of R_3Al in dilute solution will be discussed. Estimated values for the heats of complexation of monomeric R_3Al with aromatic hydrocarbons will be compared with corresponding values for stronger bases.

The experimental and estimated K_d values will be compared with values derived from cryoscopic molecular weight measurements reported in the literature. Finally, applications of degrees and heats of dissociation of aluminum alkyls will be discussed.

Results

Equations

Consider the addition of f_0 gfw (gram formula weights) of aluminum alkyl (R_3Al) to a solution of f_1 gfw of R_3Al dissolved in n_h moles of (saturated) aliphatic hydrocarbon. Let $f_2 = f_0 + f_1$ = gfw of R_3Al in final solution; $r_1 = n_h/f_1$; $r_2 = n_h/f_2$; β = weight fraction of alkyl dissociated; $\beta_0 = \beta$ 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:

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

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

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

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

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

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

TABLE 1

HEATS OF DILUTION OF LIQUID TRI-n-PROPYLALUMINUM WITH n-HEXADECANE

Expt. No.	Temp. (°C)	Initial solution		TnPA added (g)	$-\Delta t$ (°C)	Q_T (cal·gfw^{-1})		Q_p	Q_d
		Hexadec. (g)	TnPA (g)			Found	Calcd.		
40 A1	40.342	141.84	1.8846	3.3319	0.0594	310	305.9	87.8	218.1
40 A2	40.172	142.28	1.7723	3.4093	0.0602	307	308.9	88.1	220.8
40 B1	40.541	140.32	8.6686	3.3850	0.0338	178	182.5	81.9	100.6
40 B2	40.219	142.09	8.7144	3.4911	0.0360	185	181.8	82.2	99.6
60 A1	59.749	140.96	1.7302	3.3874	0.1007	528	526.4	68.6	457.8
60 A2	59.943	141.84	1.7418	3.5437	0.1033	521	524.4	68.3	456.1
60 B1	59.790	141.66	8.3981	3.4274	0.0522	280	274.8	64.1	210.7
60 B2	60.137	142.17	8.2947	3.5123	0.0525	276	278.7	63.9	214.8
80 A1	79.572	142.30	1.7131	3.5252	0.1748	914	918.3	48.8	869.6
80 A2	79.908	141.16	1.8145	3.4818	0.1735	914	907.3	48.4	858.9
80 B1	79.125	141.18	8.4148	3.5058	0.0801	432	440.9	46.1	394.8
80 B2	79.684	141.83	8.6091	3.5341	0.0828	445	442.4	45.5	396.9
100 A1	100.754	140.87	1.7506	3.5370	0.2920	1558	1565.0	27.6	1537.3
100 A2	100.439	142.13	1.7190	3.5119	0.2922	1579	1573.6	28.0	1545.7
100 B1	100.773	141.55	8.1449	3.4329	0.1359	773	778.5	25.9	752.6
100 B2	100.518	140.68	8.4304	3.4395	0.1350	764	754.5	26.1	728.4

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

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.

Tri-n-propylaluminum

The experimental results for TnPA are listed in the first seven columns of Table 1. At each temperature the total heat absorbed (Q_T) is approximately half as great for a "B" experiment (in which the initial solution contained about 10 ml of TnPA) as it is for an "A" experiment (in which the initial solution contained about 2 ml of TnPA). This reflects the inhibiting effect of monomeric molecules present in the initial solution on the dissociation of added TnPA. Within either the "A" series or the "B" series, the value of Q_T 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 equations (1—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 accuracy limits. Calculated values of Q_T based on these

TABLE 2

VALUES OF PARAMETERS FOR TnPA DERIVED BY COMPUTER PROGRAM

ΔH_d^0, cal · (mole of dimer)$^{-1}$	154_{08}	± 2_{00}
ΔS_d^0, cal · K^{-1} · (mole of dimer)$^{-1}$	33.4_8	± 0.6_0
A, cal · (mole of dimer)$^{-1}$	26_5	± 2_0
B, cal · K^{-1} · (mole of dimer)$^{-1}$	-2.0_7	± 0.2_7

TABLE 3

EQUILIBRIUM CONSTANT[a] AND PERCENT DISSOCIATION OF LIQUID TnPA

Temp. (°C)	K_d	TnPA dissociated (%) in aliphatic hydrocarbon solution at TnPA mole fraction[b] of:						
		1	0.5	0.2	0.1	0.01	0.001	0.0001
0	9.729×10^{-6}	0.1560	0.2699	0.4669	0.6776	2.176	6.734	19.76
10	2.651×10^{-5}	0.2574	0.4453	0.7697	1.116	3.567	10.87	30.38
20	6.747×10^{-5}	0.4107	0.7097	1.225	1.775	5.629	16.75	43.61
30	1.615×10^{-4}	0.6353	1.096	1.890	2.733	8.571	24.66	58.13
40	3.654×10^{-4}	0.9557	1.646	2.831	4.084	12.61	34.57	71.79
50	7.862×10^{-4}	1.402	2.408	4.128	5.936	17.92	46.05	82.63
60	1.616×10^{-3}	2.009	3.440	5.869	8.403	24.63	58.14	89.98
70	3.183×10^{-3}	2.820	4.805	8.148	11.60	32.68	69.58	94.40
80	6.036×10^{-3}	3.882	6.574	11.06	15.62	41.84	79.21	96.89
90	1.105×10^{-2}	5.248	8.819	14.68	20.53	51.63	86.47	98.25
100	1.958×10^{-2}	6.979	11.61	19.08	26.35	61.41	91.46	99.00
110	3.368×10^{-2}	9.137	15.01	24.27	33.02	70.47	94.68	99.41
120	0.05635	11.79	19.07	30.24	40.37	78.25	96.68	99.65
130	0.09190	14.99	23.81	36.87	48.17	84.46	97.91	99.78
140	0.1464	18.79	29.21	43.99	56.08	89.14	98.67	99.86
150	0.2281	23.23	35.20	51.37	63.73	92.50	99.14	99.91
160	0.3482	28.30	41.66	58.71	70.79	94.83	99.43	99.94
170	0.5215	33.96	48.41	65.71	77.00	96.43	99.62	99.96
180	0.7673	40.12	55.23	72.11	82.22	97.52	99.74	99.97
190	1.110	46.61	61.88	77.73	86.45	98.26	99.82	99.98
200	1.581	53.23	68.12	82.48	89.76	98.77	99.87	99.99

[a] $\ln K_d = 16.84571 - 7753.67/T$. [b] TnPA was taken as the monomer in computing mole fractions.

values are given in column 8 of Table 1 where they are compared with experimental values (column 7). The rms difference between calculated and experimental values is 5.3 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. Within either the "A" series or the "B" series, Q_d increases exponentially with increasing temperature while Q_p decreases linearly.

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

$$\ln K_d = 16.8457 - 7753.7/T \tag{7}$$

Values of K_d calculated from this equation at 10° intervals are listed in column 2 of Table 3. The degree of dissociation of pure TnPA at each of these temperatures was calculated from the equilibrium constant using the equation $\beta_0 = \sqrt{K_d/(4 + K_d)}$ which is derived from eqn. (2). These values, expressed as percent of TnPA dissociated, are given in column 3 of Table 3. Degrees of dissociation at various mole fractions in aliphatic hydrocarbon solution, calculated from eqn. (3), are listed in the remaining columns of the table.

Tri-n-butylaluminum

The experimental results for TnBA are given in the first seven columns of Table 4. The values of ΔH_d^0, ΔS_d^0, A and B determined with the aid of the

TABLE 4

HEATS OF DILUTION OF LIQUID TRI-n-BUTYLALUMINUM WITH n-HEXADECANE

Expt. No.	Temp. (°C)	Initial solution		TnBA added (g)	$-\Delta t$ (°C)	Q_T (cal·gfw^{-1})		Q_p	Q_d
		Hexadec. (g)	TnBA (g)			Found	Calcd.		
40 A1	40.055	141.60	1.6803	3.3885	0.0716	463	468.5	99.2	369.3
40 A2	40.146	141.22	1.7254	3.4804	0.0740	465	463.0	99.0	364.0
40 B1	40.103	142.32	8.8663	3.4501	0.0405	267	260.4	93.7	166.7
40 B2	40.217	141.87	8.6124	3.4918	0.0401	260	263.5	93.7	169.8
60 A1	59.871	141.90	1.7505	3.3567	0.1212	815	815.6	73.2	742.4
60 A2	59.852	140.75	1.7308	3.3695	0.1230	820	813.7	73.2	740.5
60 B1	59.982	141.61	8.6734	3.4204	0.0607	413	414.1	69.2	344.9
60 B2	59.783	142.04	8.5243	3.4026	0.0601	412	416.7	69.5	347.2
80 A1	79.917	140.70	1.8006	3.4084	0.2043	1386	1395.9	46.9	1349.0
80 A2	78.256	142.95	1.6591	3.4896	0.2068	1382	1377.0	49.1	1327.9
80 B1	80.047	142.43	8.6525	3.4576	0.0995	693	696.7	44.3	652.4
80 B2	79.929	141.85	8.6149	3.4743	0.1018	704	694.0	44.4	649.6
100 A1	99.600	141.65	1.7936	3.5045	0.3246	2215	2221.7	21.1	2200.6
100 A2	99.467	142.87	1.9130	3.4846	0.3177	2194	2184.8	21.2	2163.6
100 B1	100.623	141.14	8.3279	3.4050	0.1631	1181	1174.8	18.7	1156.0
100 B2	100.389	142.06	8.5287	3.5266	0.1628	1144	1153.5	19.0	1134.5

computer program are listed in Table 5 along with their estimated accuracy limits. Calculated values of Q_T based on these values are given in column 8 of Table 4 where they are compared with experimental values (column 7). The rms difference between calculated and experimental values is 6.4 cal · gfw^{-1}.

The expression for the equilibrium constant, derived from eqn. (5), is:

$$\ln K_d = 16.9704 - 7555.2/T \qquad (8)$$

Values of K_d calculated from this equation at 10° intervals are listed in column 2 of Table 6. Degrees of dissociation of pure TnBA are given in column 3. Degrees of dissociation at various mole fractions in aliphatic hydrocarbon solution are listed in the remaining columns of the table.

Tri-n-octylaluminum

The experimental results for TnOA are given in the first seven columns of Table 7. The values of ΔH_d^0, ΔS_d^0, A and B determined with the aid of the computer program are listed in Table 8 along with their estimated accuracy limits. Calculated values of Q_T based on these values are given in column 8 of Table 7 where they are compared with experimental values (column 7). The rms difference between calculated and experimental values is 10.8 cal · gfw^{-1}.

TABLE 5

VALUES OF PARAMETERS DERIVED FOR TnBA

ΔH_d^0, cal · (mole of dimer)$^{-1}$	150_{14}	$\pm 1_{50}$
ΔS_d^0, cal · K^{-1} · (mole of dimer)$^{-1}$	33.7_2	$\pm 0.4_4$
A, cal · (mole of dimer)$^{-1}$	31_2	$\pm 2_4$
B, cal · K^{-1} · (mole of dimer)$^{-1}$	-2.6_9	$\pm 0.3_2$

TABLE 6

EQUILIBRIUM CONSTANT[a] AND PERCENT DISSOCIATION OF LIQUID TnBA

Temp. (°C)	K_d	TnBA dissociated (%) in aliphatic hydrocarbon solution at TnBA mole fraction[b] of:						
		1	0.5	0.2	0.1	0.01	0.001	0.0001
0	2.279×10^{-5}	0.2387	0.4128	0.7137	1.035	3.311	10.12	28.53
10	6.052×10^{-5}	0.3890	0.6722	1.161	1.682	5.340	15.95	41.92
20	1.504×10^{-4}	0.6132	1.058	1.824	2.639	8.285	23.91	56.92
30	3.519×10^{-4}	0.9379	1.616	2.779	4.010	12.39	34.06	71.19
40	7.800×10^{-4}	1.396	2.399	4.112	5.913	17.86	45.92	82.53
50	1.646×10^{-3}	2.028	3.472	5.921	8.477	24.82	58.46	90.13
60	3.320×10^{-3}	2.880	4.906	8.314	11.83	33.23	70.26	94.61
70	6.429×10^{-3}	4.006	6.780	11.39	16.08	42.81	80.06	97.07
80	0.01199	5.467	9.175	15.25	21.29	53.01	87.29	98.39
90	0.02161	7.331	12.17	19.95	27.48	63.10	92.14	99.09
100	0.03775	9.669	15.84	25.51	34.56	72.28	95.20	99.48
110	0.06403	12.55	20.22	31.88	42.34	79.99	97.06	99.69
120	0.1057	16.05	25.34	38.93	50.51	86.00	98.18	99.81
130	0.1703	20.21	31.16	46.45	58.69	90.40	98.85	99.88
140	0.2680	25.06	37.58	54.15	66.47	93.48	99.26	99.93
150	0.4130	30.59	44.45	61.68	73.49	95.58	99.52	99.95
160	0.6236	36.73	51.54	68.73	79.51	96.98	99.68	99.97
170	0.9244	43.33	58.58	75.02	84.45	97.93	99.78	99.98
180	1.347	50.19	65.31	80.41	88.34	98.56	99.85	99.98
190	1.930	57.05	71.49	84.85	91.32	98.98	99.90	99.99
200	2.725	63.65	76.94	88.39	93.55	99.28	99.93	99.99

[a] $\ln K_d = 16.97036 - 7555.25/T$. [b] TnBA was taken as the monomer in computing mole fractions.

TABLE 7

HEATS OF DILUTION OF LIQUID TRI-n-OCTYLALUMINUM WITH n-HEXADECANE

Expt. No.	Temp. (°C)	Initial solution		TnOA added (g)	$-\Delta t$ (°C)	Q_T (cal. gfw^{-1})		Q_p	Q_d
		Hexadec. (g)	TnOA (g)			Found	Calcd.		
40 A1	40.165	141.75	1.7706	3.6065	0.0664	748	739.1	73.5	665.6
40 A2	40.716	142.08	1.9218	3.6562	0.0652	726	732.3	72.8	659.5
40 B1	40.106	140.42	8.5710	3.4416	0.0337	407	402.3	71.4	330.9
40 B2	40.324	141.23	8.4716	3.5212	0.0338	401	407.4	71.2	336.2
60 A1	59.896	142.14	1.7194	3.4258	0.1133	1383	1391.1	52.1	1338.9
60 A2	60.064	141.86	1.7740	3.4914	0.1153	1379	1377.0	51.9	1325.1
60 B1	60.267	141.26	8.6818	3.4828	0.0591	730	716.4	50.2	666.2
60 B2	60.015	142.17	8.4907	3.5279	0.0583	714	721.3	50.5	670.8
80 A1	80.081	141.48	1.7685	3.3395	0.1850	2377	2363.1	30.3	2332.8
80 A2	80.086	141.70	1.8978	3.4679	0.1846	2289	2299.1	30.3	2268.8
80 B1	80.070	141.78	8.6683	3.6207	0.0996	1223	1234.6	29.4	1205.2
80 B2	80.008	141.71	8.2829	3.4020	0.0978	1274	1269.2	29.5	1239.7
100 A1	99.965	143.12	1.8187	3.1583	0.2452	3452	3470.4	8.8	3461.7
100 A2	100.001	139.89	1.8627	3.4834	0.2685	3381	3365.3	8.7	3356.6
100 B1	99.505	140.60	8.3239	3.3932	0.1476	1973	1983.9	9.0	1974.9
100 B2	99.856	141.73	8.2838	3.3832	0.1504	2028	2012.4	8.6	2003.8

TABLE 8

VALUES OF PARAMETERS DERIVED FOR TnOA

ΔH_d^0, cal · (mole of dimer)$^{-1}$	1468$_2$ ± 12$_0$
ΔS_d^0, cal · K^{-1} · (mole of dimer)$^{-1}$	33.7$_6$ ± 0.3$_4$
A, cal · (mole of dimer)$^{-1}$	23$_7$ ± 4$_2$
B, cal · K^{-1} · (mole of dimer)$^{-1}$	—2.2$_0$ ± 0.5$_4$

The expression derived from eqn. (5) for the equilibrium constant is:

$$\ln K_d = 16.9890 - 7388.4/T \tag{9}$$

Values of K_d calculated from this equation at 10° intervals are listed in column 2 of Table 9. Corresponding values of the degree of dissociation of pure TnOA are given in column 3. Degrees of dissociation at various mole fractions in aliphatic hydrocarbon solution are listed in the remaining columns of the table.

Discussion

Effect of chain length on the monomer—dimer equilibria

Experimental values of ΔH_d^0 and ΔS_d^0 for R_3Al in the pure liquid state and in aliphatic hydrocarbon solution are plotted against chain length in Figs. 1 and

TABLE 9

EQUILIBRIUM CONSTANT[a] AND PERCENT DISSOCIATION OF LIQUID TnOA

Temp. (°C)	K_d	TnOA dissociated (%) in aliphatic hydrocarbon solution at TnOA mole fraction[b] of:						
		1	0.5	0.2	0.1	0.01	0.001	0.0001
0	4.276 × 10^{-5}	0.3270	0.5653	0.9766	1.416	4.508	13.59	36.77
10	1.112 × 10^{-4}	0.5272	0.9103	1.570	2.273	7.167	20.96	51.77
20	2.707 × 10^{-4}	0.8227	1.418	2.441	3.526	10.95	30.64	66.92
30	6.217 × 10^{-4}	1.247	2.144	3.678	5.296	16.11	42.33	79.61
40	1.354 × 10^{-3}	1.840	3.152	5.385	7.719	22.81	55.12	88.44
50	2.810 × 10^{-3}	2.650	4.519	7.673	10.93	31.07	67.53	93.74
60	5.581 × 10^{-3}	3.733	6.328	10.65	15.07	40.64	78.13	96.65
70	1.065 × 10^{-2}	5.154	8.664	14.43	20.20	51.01	86.08	98.19
80	0.01960	6.982	11.62	19.09	26.36	61.42	91.46	99.00
90	0.03487	9.296	15.26	24.64	33.48	71.02	94.84	99.43
100	0.06014	12.17	19.65	31.07	41.37	79.15	96.88	99.67
110	0.1008	15.68	24.81	38.22	49.71	85.49	98.09	99.80
120	0.1647	19.89	30.71	45.90	58.11	90.13	98.81	99.88
130	0.2625	24.81	37.26	53.78	66.12	93.36	99.25	99.92
140	0.4090	30.46	44.29	61.51	73.34	95.54	99.52	99.95
150	0.6241	36.74	51.55	68.74	79.52	96.99	99.68	99.97
160	0.9340	43.51	58.77	75.18	84.57	97.95	99.79	99.98
170	1.372	50.54	65.65	80.66	88.52	98.58	99.85	99.99
180	1.983	57.57	71.93	85.15	91.52	99.01	99.90	99.99
190	2.819	64.30	77.45	88.71	93.75	99.30	99.93	99.99
200	3.950	70.49	82.13	91.46	95.38	99.50	99.95	99.99

[a] $\ln K_d = 16.98903 - 7388.39/T$. [b] TnOA was taken as the monomer in computing mole fractions.

TABLE 10

SUMMARY OF MONOMER—DIMER EQUILIBRIA OF ALUMINUM n-ALKYLS IN THE PURE LIQUID STATE AND IN ALIPHATIC HYDROCARBON SOLUTION

Quantity	Aluminum n-alkyl, $(C_NH_{2N+1})_3Al$							
	TMA (ref. 3)	TEA (ref. 1)	TnPA[a]	TnBA[a]	TnHA	TnOA[a]	TnDA	TnDDA
N	1	2	3	4	6	8	10	12
ΔH_d^0, cal·(mole of dimer)$^{-1}$	19400	16930	15408	15014	14780[b]	14682	14610[b]	14560[b]
ΔS_d^0, cal · K^{-1} · (mole of dimer)$^{-1}$	29.30	32.19	33.48	33.72	33.74[c]	33.76	33.77[c]	33.78[c]
A (in $\ln K_d = A - B/T$)	14.7444	16.1987	16.8457	16.9704	16.979	16.9890	16.994	16.999
B	9762.5	8519.5	7753.7	7555.2	7438	7388.4	7352	7327
K_d at: 0°	7.61×10^{-10}	3.07×10^{-7}	9.73×10^{-6}	2.28×10^{-5}	3.53×10^{-5}	4.28×10^{-5}	4.91×10^{-5}	5.41×10^{-5}
25°	1.52×10^{-8}	4.20×10^{-6}	1.05×10^{-4}	2.32×10^{-4}	3.47×10^{-4}	4.13×10^{-4}	4.69×10^{-4}	5.13×10^{-4}
50°	1.92×10^{-7}	3.83×10^{-5}	7.86×10^{-4}	1.65×10^{-3}	2.39×10^{-3}	2.81×10^{-3}	3.16×10^{-3}	3.43×10^{-3}
100°	1.10×10^{-5}	1.31×10^{-3}	1.96×10^{-2}	3.78×10^{-2}	5.22×10^{-2}	6.01×10^{-2}	6.66×10^{-2}	7.16×10^{-2}
150°	2.42×10^{-4}	1.95×10^{-2}	2.28×10^{-1}	4.13×10^{-1}	5.50×10^{-1}	6.24×10^{-1}	6.83×10^{-1}	7.29×10^{-1}
% dissoc., pure, at:								
0°		0.0277	0.156	0.239	0.297	0.327	0.350	0.368
25°	0.00616	0.102	0.513	0.761	0.931	1.02	1.08	1.13
50°	0.0219	0.310	1.40	2.03	2.44	2.65	2.81	2.93
100°	0.166	1.81	6.98	9.67	11.3	12.2	12.8	13.3
150°	0.778	6.96	23.2	30.6	34.8	36.7	38.2	39.3
% dissoc. at R_3Al mole fract.[d] of 0.01 at:								
0°	0.0195	0.390	2.18	3.31	4.11	4.51	4.82	5.06
25°	0.0869	1.44	6.98	10.2	12.3	13.4	14.2	14.8
50°	0.309	4.27	17.9	24.8	29.1	31.1	32.6	33.7
100°	2.31	22.5	61.4	72.3	77.2	79.2	80.5	81.5
150°	10.4	61.3	92.5	95.6	96.6	97.0	97.2	97.4

[a] Experimental (this paper). [b] Read from Fig. 1; estimated uncertainties: ±150 (TnHA), ±150 (TnDA), ±200 (TnDDA). [c] Read from Fig. 2; estimated uncertainties: ±0.44 (TnHA), ±0.44(TnDA), ±0.54 (TnDDA). [d] Aluminum alkyls were taken as monomers in computing mole fractions.

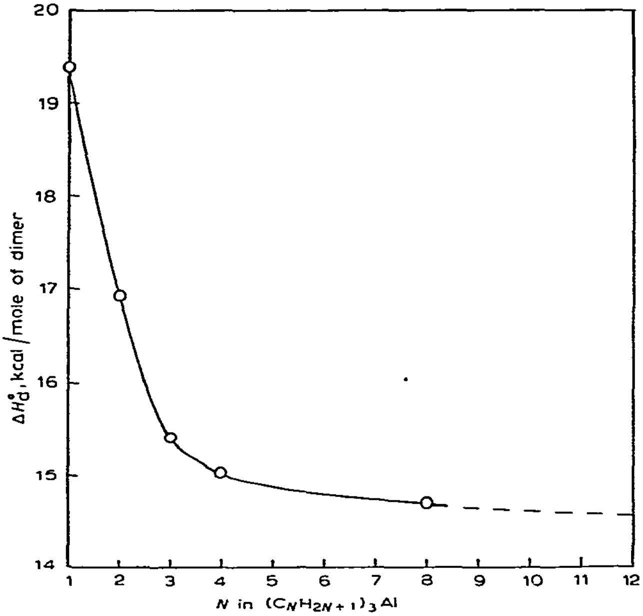

Fig. 1. Variation of ΔH^0_d of liquid (n-R)$_3$Al with chain length.

2. Interpolated values for TnHA ($N = 6$) and extrapolated values for TnDA ($N = 10$) and TnDDA ($N = 12$) were read from these plots and used to derive the monomer—dimer equilibria for these alkyls. The monomer—dimer equilibria for all eight aluminum n-alkyls in the pure liquid state and in aliphatic hydrocarbon solution are summarized in Table 10. Degree (%) of dissociation is plotted against chain length in Fig. 3 at four different temperatures.

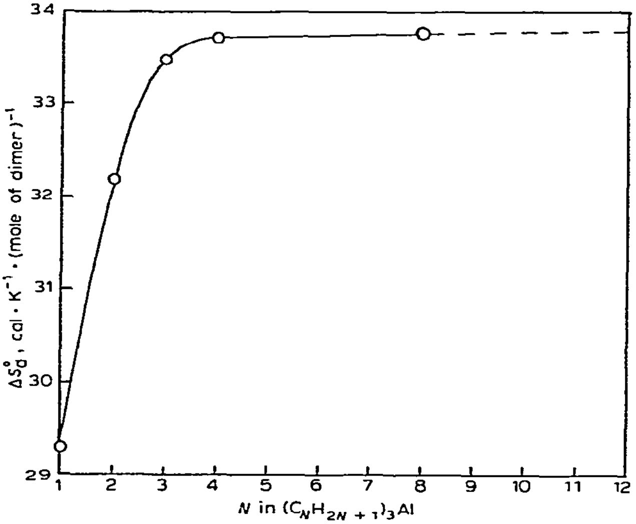

Fig. 2. Variation of ΔS^0_d of liquid (n-R)$_3$Al with chain length.

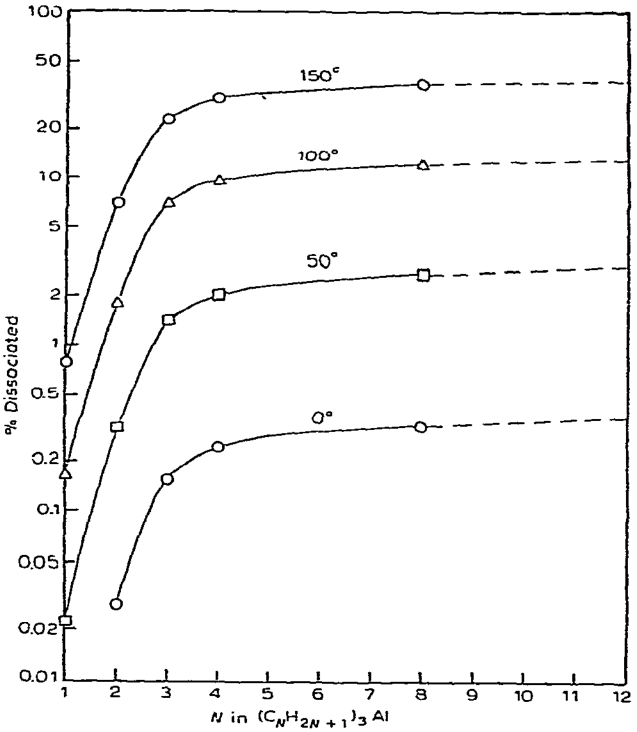

Fig. 3. Variation of degree (%) of dissociation of pure liquid (n-R)$_3$Al with chain length.

The rapid decrease in ΔH_d^0 from TMA to TnPA (Fig. 1) reflects a significant increase in the steric hindrance to dimerization, presumably leading to appreciable increases in the lengths of the Al—CH$_2$ and Al—Al bridge bonds. The accompanying rapid increase in ΔS_d^0 (Fig. 2) also suggests a significant increase in the amount of rotational restriction (or "strain") present in the dimeric molecule. The changes in ΔH_d^0 and ΔS_d^0 are still appreciable from TnPA to TnBA but are minimal thereafter. Degree of dissociation varies similarly with chain length (Fig. 3), increasing rapidly from TMA to TnPA and slowly after TnBA.

Calculation of heats of complexation from heats of reaction of R_3Al with bases

When an aluminum alkyl is reacted with a base such as Et$_3$N, the product is generally the 1/1 complex between the alkyl monomer and the base. The measured heat of reaction (ΔH_r) is the sum of the heat of dissociation (ΔH_d) and the heat of complexation (ΔH_c):

$$R_3Al(l) \rightarrow R_3Al(M,l) \qquad \Delta H = \Delta H_d{}^*$$

$$\underline{R_3Al(M,l) + Et_3N(l) \rightarrow R_3Al \cdot Et_3N(l) \qquad \Delta H = \Delta H_c}$$

$$R_3Al(l) + Et_3N(l) \rightarrow R_3Al \cdot Et_3N(l)$$

$$\Delta H = \Delta H_r = \Delta H_d + \Delta H_c$$

$$\Delta H_c = \Delta H_r - \Delta H_d$$

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* Heat of dissociation of the dimeric portion of the R$_3$Al, (kcal·gfw^{-1})

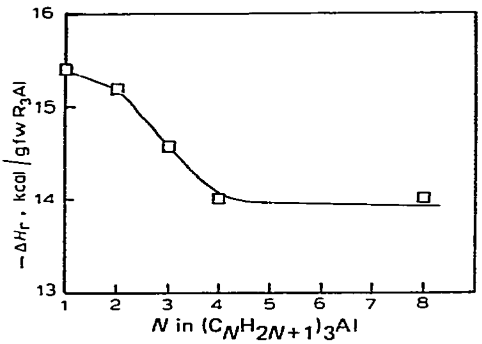

Fig. 4. Heat of reaction of liquid $(n\text{-}R)_3Al$ with Et_3N [5] as a function of chain length.

In order to evaluate ΔH_c (normally of more theoretical interest than ΔH_r), ΔH_d must be subtracted from the measured value, ΔH_r. This procedure may be illustrated using the data of Hoffmann and Tornau [5]. In these experiments, R_3Al (in cyclohexane, mole fraction $R_3Al \approx 0.05$) was titrated with pure $Et_3N(l)$. The measured $-\Delta H_r$ values are listed in column 2 of Table 11 and plotted against N in Fig. 4. Degrees of dissociation (β) of R_3Al, calculated* from the K_d equations (Table 10), are given in column 3 of Table 11. The ΔH_d "corrections" (column 5) were calculated using the equation

$$\Delta H_d = (1-\beta)\cdot(\tfrac{1}{2}\,\Delta H_d^0)$$

The derived values of $-\Delta H_c$ are listed in column 6 of Table 11. It is interesting to compare the plots of $-\Delta H_r$ vs. N before and after "correcting" for heat of dissociation. The "before correction" plot (Fig. 4) is flat (1.4 kcal range in $-\Delta H$ values), with an apparent inflexion point. The "after correction" plot (Fig. 5), on the other hand, is steep rather than flat (4.1 kcal range in $-\Delta H$ values) and has no inflexion point. Its shape is similar, in fact, to the plot of ΔH_d^0 vs. N (Fig. 1).

TABLE 11

CALCULATION OF HEATS[a] OF COMPLEXATION OF R_3Al WITH Et_3N FROM EXPERIMENTAL DATA

R_3Al	$-\Delta H_r$ (ref. 5)	β[b]	$\frac{1}{2}\Delta H_d^0$[c]	ΔH_d[d]	$-\Delta H_c$[e]	$-\Delta H_c(R_3Al)$/ $-\Delta H_c$(TMA)
TMA	15.4	0.00029	9.70	9.70	25.10	1.000
TEA	15.2	0.00501	8.47	8.43	23.63	0.941
TnPA	14.6	0.0253	7.70	7.50	22.10	0.880
TnBA	14.0	0.0376	7.51	7.23	21.23	0.846
TnOA	14.0	0.0501	7.34	6.97	20.97	0.835

[a] Values of $-\Delta H_r$, $\frac{1}{2}\Delta H_d^0$, ΔH_d and $-\Delta H_c$ are in kcal·gfw^{-1} of R_3Al. [b] Fraction dissociated at 20° and at 0.05 mole fraction in cyclohexane (calculated assuming β to be the same in this solvent as it is in aliphatic hydrocarbons). [c] From Table 10. [d] $\Delta H_d = (1-\beta)\cdot(\frac{1}{2}\Delta H_d^0)$. [e] $-\Delta H_c = -\Delta H_r + \Delta H_d$.

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* It was assumed that β is the same in cyclohexane as in aliphatic hydrocarbons. R_3Al mole fraction was taken as 0.05 and reaction temperature as 20°.

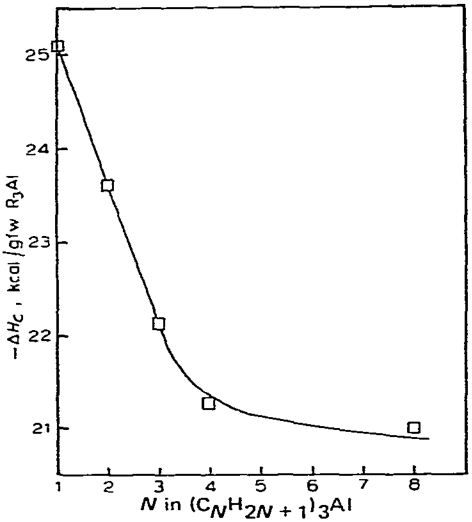

Fig. 5. Heat of complexation of monomeric $(n\text{-}R)_3Al$ with Et_3N as a function of chain length (heat of reaction of liquid R_3Al with base after "correcting" for heat of dissociation of dimeric portion of the R_3Al).

Relative heats of complexation of R_3Al with bases

Values of the relative heat of complexation of R_3Al monomer with Et_3N (referred to ΔH_c of TMA taken as unity) are listed in the last column of Table 11 and plotted against N in Fig. 6 (upper curve). Also plotted are points representing the results of similar experiments [6] in which the base reacted with R_3Al was isoquinoline. The results for the two bases agree within experimental error and are all represented by the upper curve. The lower curve, corresponding to self-complexation, is steeper since, in this case, the "base" complexed increases in molecular size as N increases.

Estimation of monomer—dimer equilibria in aromatic solvents

In Part IV [4] of this series, ΔH_d^0 for TEA in mesitylene was determined experimentally as 13307 ± 180 cal · (mole of dimer)$^{-1}$. The difference between this value and the value (16930 ± 230) of ΔH_d^0 for TEA in hexadecane, —3623 ± 292* cal·(mole of dimer)$^{-1}$, was termed the "gross heat of complexation" of TEA monomer with mesitylene. In the present study, estimated values for the gross heats of complexation of other R_3Al monomers with mesitylene were calculated from that of TEA monomer using ratios read from the upper curve in Fig. 6 (for the purpose of making these estimates, it was assumed that the curve, derived from data on strong bases, also applies approximately to the weak base mesitylene). Estimated values of ΔH_d^0 in mesitylene for the other alkyls were obtained by adding the gross heats of complexation to the respective values of ΔH_d^0 in hexadecane. From Fig. 6, for example, the relative heat of complexation with base is 1.000 for TMA and 0.945 for TEA. The estimated gross heat of complexation of TMA monomer with mesitylene is (1.000) · (—3623)/(0.945)

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* Uncertainties were combined by summing their squares and extracting the square root.

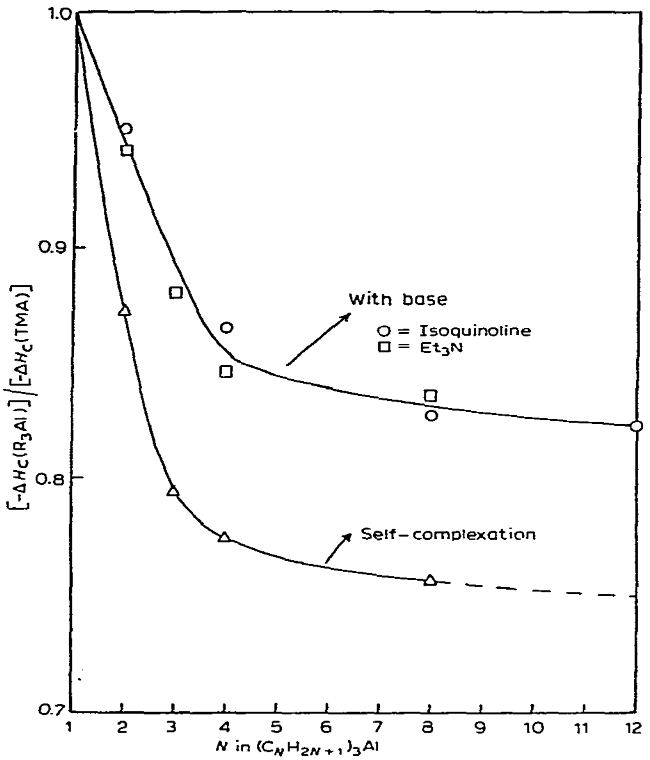

Fig. 6. Relative heat of complexation of monomeric (n-R)$_3$Al (referred to TMA as unity).

= —3834* ± 317 cal · (mole of dimer)$^{-1}$. The estimated ΔH_d^0 for TMA in mesitylene is then —3834 + 19400 (from Table 10) = 15566 ± 437 cal·(mole of dimer)$^{-1}$. The estimated values of ΔH_d^0 in mesitylene for all the alkyls are included in Table 12, as well as the gross heats of complexation.

Gross heats of complexation of R_3Al monomers with benzene were calculated from the corresponding values for mesitylene by multiplying by the factor 0.860**, the basis for which was discussed in Part IV [4]. The estimated gross heat of complexation of TMA monomer with benzene, for example, is (0.860) · (—3834) = —3297 ± 296 cal · (mole of dimer)$^{-1}$. The estimated ΔH_d^0 for TMA in benzene is then —3297 + 19400 = 16103 ± 421 cal · (mole of dimer)$^{-1}$. The estimated values of ΔH_d^0 in benzene for all the alkyls are included in Table 13 along with the gross heats of complexation.

The experimental value for the "gross entropy of complexation" of TEA monomer with mesitylene was evaluated as —8.20 ± 0.77 cal · K^{-1} · (mole of dimer)$^{-1}$ by subtracting ΔS_d^0 for TEA in hexadecane (32.19 ± 0.63, Table 10) from ΔS_d^0 for TEA in mesitylene (23.99 ± 0.45). Since the "gross free energy of complexation" is given by the equation $\Delta F_c(\text{gr.}) = \Delta H_c(\text{gr.}) - T\Delta S_c(\text{gr.})$, the

(continued on p. 28)

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* This differs from the value —4150 ± 700 estimated earlier [4] by a less accurate method.

** The corresponding factor for toluene is 0.907; for *m*-xylene, 0.953.

TABLE 12

ESTIMATED[a] MONOMER—DIMER EQUILIBRIA OF ALUMINUM n-ALKYLS IN MESITYLENE SOLUTION

Quantity	Aluminum n-alkyl, $(C_NH_{2N+1})_3Al$							
	TMA	TEA[a]	TnPA	TnBA	TnHA	TnOA	TnDA	TnDDA
N	1	2	3	4	6	8	10	12
$\Delta H_c(R_3Al)/\Delta H_c(TMA)$[b]	1.000	0.945	0.894	0.855	0.839	0.832	0.827	0.824
$-\Delta H_c$ (mesitylene, gross)[c]	3834	3623	3427	3278	3218	3190	3172	3159
$-\Delta S_c$ (mesitylene, gross)[d]	8.63	8.20	7.80	7.49	7.36	7.30	7.27	7.24
ΔH_d^0[c]	15566	13307	11981	11735	11562	11490	11438	11401
ΔS_d^0[d]	20.67	23.99	25.68	26.23	26.38	26.46	26.50	26.54
A (in $\ln K_d = A - B/T$)	10.402	12.0723	12.921	13.201	13.275	13.315	13.335	13.355
B	7833	6696.4	6029	5906	5818	5783	5756	5737
K_d at: 0°	1.15×10^{-8}	3.95×10^{-6}	1.06×10^{-4}	2.21×10^{-4}	3.27×10^{-4}	3.87×10^{-4}	4.37×10^{-4}	4.77×10^{-4}
25°	1.28×10^{-7}	3.08×10^{-5}	6.75×10^{-4}	1.35×10^{-3}	1.95×10^{-3}	2.29×10^{-3}	2.55×10^{-3}	2.77×10^{-3}
50°	9.78×10^{-7}	1.75×10^{-4}	3.23×10^{-3}	6.26×10^{-3}	8.83×10^{-3}	1.02×10^{-2}	1.14×10^{-2}	1.23×10^{-2}
100°	2.52×10^{-5}	2.81×10^{-3}	3.93×10^{-2}	7.24×10^{-2}	9.86×10^{-2}	1.13×10^{-1}	1.24×10^{-1}	1.33×10^{-1}
% dissoc. at R_3Al mole fract.[e] of 0.01 at:								
0°	0.0759	1.39	7.00	9.94	12.0	13.0	13.7	14.3
25°	0.252	3.84	16.7	22.8	26.7	28.5	29.9	30.9
50°	0.695	8.91	32.9	42.4	47.9	50.4	52.1	53.4
100°	3.48	31.1	72.9	81.6	85.2	86.7	87.6	88.3

[a] Values for TEA were determined experimentally [4]. [b] From Fig. 6. [c] Cal·(mole of dimer)$^{-1}$; estimated uncertainties in ΔH_d^0: ± 180 (TEA); others range from ± 293 (TnOA) to ± 437 (TMA). [d] Cal·K^{-1}·(mole of dimer)$^{-1}$; estimated uncertainties in ΔS_d^0: ±0.45 (TEA); others range from ±0.70 (TnOA) to ±0.89 (TnPA). [e] Aluminum alkyls were taken as monomers in computing mole fractions.

TABLE 13

ESTIMATED MONOMER—DIMER EQUILIBRIA OF ALUMINUM *n*-ALKYLS IN BENZENE SOLUTION

Quantity	Aluminum n-alkyl, $(C_NH_{2N+1})_3Al$							
	TMA	TEA	TnPA	TnBA	TnHA	TnOA	TnDA	TnDDA
N	1	2	3	4	6	8	10	12
$-\Delta H_c$ (benzene, gross)[a]	3297	3116	2948	2819	2768	2743	2728	2717
$-\Delta S_c$ (benzene, gross)[b]	7.53	7.15	6.79	6.52	6.41	6.36	6.33	6.30
ΔH_d^0[a]	16103	13814	12460	12195	12012	11939	11882	11843
ΔS_d^0[b]	21.77	26.04	26.69	27.20	27.33	27.40	27.44	27.48
A (in $\ln K_d = A - B/T$)	10.955	12.601	13.429	13.689	13.753	13.788	13.808	13.828
B	8103	6951	6270	6137	6045	6008	5979	5960
K_d at: 5.5°[c]	1.34×10^{-8}	4.35×10^{-6}	1.15×10^{-4}	2.40×10^{-4}	3.56×10^{-4}	4.21×10^{-4}	4.76×10^{-4}	5.22×10^{-4}
25°	8.99×10^{-8}	2.22×10^{-5}	5.00×10^{-4}	1.01×10^{-3}	1.47×10^{-3}	1.72×10^{-3}	1.94×10^{-3}	2.11×10^{-3}
50°	7.37×10^{-7}	1.35×10^{-4}	2.54×10^{-3}	4.99×10^{-3}	7.07×10^{-3}	8.20×10^{-3}	9.14×10^{-3}	9.91×10^{-3}
100°	2.12×10^{-5}	2.41×10^{-3}	3.42×10^{-2}	6.35×10^{-2}	8.66×10^{-2}	9.90×10^{-2}	1.09×10^{-1}	1.17×10^{-1}
% dissoc. at R_3Al mole fract.[d] of 0.01 at:								
5.5°	0.0822	1.46	7.28	10.4	12.5	13.5	14.3	14.9
25°	0.211	3.27	14.6	20.1	23.7	25.3	26.6	27.6
50°	0.604	7.86	29.8	39.0	44.3	46.7	48.5	49.8
100°	3.20	29.2	70.7	79.9	83.8	85.3	86.3	87.1

[a] Cal·(mole of dimer)$^{-1}$; estimated uncertainties in ΔH_d^0 range from ±276 (TnOA) to ±421 (TMA). [b] Cal·K^{-1}·(mole of dimer)$^{-1}$; estimated uncertainties in ΔS_d^0 range from ± 0.69 (TnOA) to ± 0.87 (TnPA). [c] Approximate freezing point of pure benzene. [d] Aluminum alkyls were taken as monomers in computing mole fractions.

temperature at which ΔF_c(gr.) becomes zero is $T_0 = \Delta H_c$(gr.)/ΔS_c(gr.). For TEA in mesitylene, $T_0 = (-3623)/(-8.20) = 441.8$ K (168.7°C). For values of $-\Delta H_c$(gr.) less than 3623, corresponding to weaker complexes, T_0 would be expected to be lower than 441.8 K, and vice versa. The following equation, based on the TEA—mesitylene values, but assumed to apply to other alkyls and other aromatic solvents, takes this into account:

$$-\Delta S_c(\text{gr.}) = \frac{-\Delta H_c(\text{gr.})}{399.0 + 0.0118[-\Delta H_c(\text{gr.})]} \tag{10}$$

For TnOA—benzene, for example, $-\Delta H_c$ (gr.) = 2743 ± 249 cal·(mole of dimer)$^{-1}$ (Table 13). Using eqn. (10), $-\Delta S_c$(gr.) is calculated as 6.36 ± 0.60 cal · K^{-1} · (mole of dimer)$^{-1}$. This corresponds to $T_0 = 2743/6.36 = 431.3$ K (158.1°C), which is ≈ 11° lower than T_0 for TEA—mesitylene. The estimated value of ΔS_d^0 for TnOA in benzene is then $-6.36 + 33.76$ (Table 10) = 27.40 ± 0.69 cal · K^{-1} · (mole of dimer)$^{-1}$. For TMA—mesitylene, on the other hand, $-\Delta H_c$(gr.) = 3834 ± 317; $-\Delta S_c$(gr.) is calculated as 8.63 ± 0.71 and T_0 as 444.3 K (171.1°C), which is 2.4° higher than T_0 for TEA—mesitylene. The estimated value of ΔS_d^0 for TMA in mesitylene is $-8.63 + 29.30$ (Table 10) = 20.67 ± 0.77 cal · K^{-1} · (mole of dimer)$^{-1}$. The estimated $-\Delta S_c$(gr.) and ΔS_d^0 values for the various alkyls are included in Table 12 (mesitylene) and in Table 13 (benzene).

The estimated monomer—dimer equilibria of the aluminum n-alkyls in aromatic solvents, derived from the ΔH_d^0 and ΔS_d^0 values, are summarized in Table 12 (mesitylene) and in Table 13 (benzene). Degree (%) of dissociation at 25° and at R_3Al mole fraction 0.01 is plotted against chain length in Fig. 7. Curves for mesitylene and benzene are compared in the figure with corresponding curves for aliphatic hydrocarbons and for pure alkyls.

As was the case for the pure liquid alkyls and in aliphatic hydrocarbon solution, ΔH_d^0, ΔS_d^0 and degree of dissociation in aromatic hydrocarbon solution change rapidly from TMA to TnPA, appreciably from TnPA to TnBA, and slowly thereafter (Tables 12 and 13, Fig. 7). The degree of dissociation of any given alkyl at 25° is increased considerably (about 13.5 times) by dilution to R_3Al mole fraction 0.01 with an aliphatic hydrocarbon (Fig. 7). When the solvent is changed from aliphatic hydrocarbon to benzene, the degree of dissociation is approximately doubled. The additional increase in degree of dissociation on substituting mesitylene for benzene is relatively slight (by a factor of only about 1.15).

(Actual) heats of complexation of R_3Al with aromatic hydrocarbons

As shown in Part IV [4], the "gross" heat of complexation of TEA monomer with mesitylene [$-\Delta H_c$(gr.) = 3623 ± 292 cal · (mole of dimer)$^{-1}$] is equal to the (actual) heat of complexation of the monomer ($-\Delta H_{cM}$) less that of the dimer ($-\Delta H_{cD}$ = 370 ± 130). The (actual) heat of complexation of TEA monomer with mesitylene is then $-\Delta H_{cM}$ = 3623 + 370 = 3993 ± 320 cal · (mole of dimer)$^{-1}$ or 2000 ± 160 cal · (mole of monomer)$^{-1}$. This value was used to obtain estimated values of $-\Delta H_{cM}$ for the other alkyls in mesitylene, and for all the alkyls in benzene, by the same methods employed in the previous section. The results, summarized in Table 14, show that the aromatic hydrocarbons are

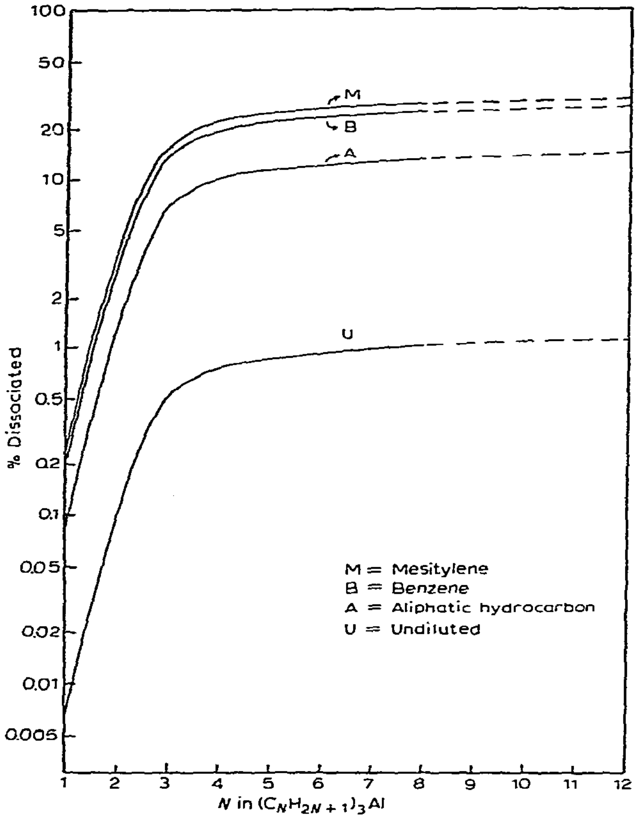

Fig. 7. Effect of dilution (to R_3Al mole fraction 0.01) and solvent type on degree (%) of dissociation of R_3Al at 25°.

TABLE 14

ESTIMATED (ACTUAL) HEATS OF COMPLEXATION[a] OF R_3Al WITH AROMATIC SOLVENTS

R_3Al	$-\Delta H_{cM}$ [cal · (mole of monomer)$^{-1}$]	
	Mesitylene[b]	Benzene[c]
TMA	2110	1820
TEA	2000	1720
TnPA	1890	1620
TnBA	1810	1550
TnHA	1770	1530
TnOA	1760	1510
TnDA	1750	1500
TnDDA	1740	1500

[a] The "actual" heat of complexation is the "gross" $-\Delta H_c$ of R_3Al monomer plus the $-\Delta H_c$ of R_3Al dimer [4]. [b] Estimated uncertainties range from ± 180 for TMA to ± 150 for TnDDA. [c] Estimated uncertainties range from ± 160 for TMA to ± 140 for TnDDA.

relatively weak in basic strength. Based on comparative $-\Delta H_{cM}$ values for the same alkyl, mesitylene is about 1/6 as strong a base as anisole [6,7] and about 1/12 as strong as Et_3N [5]. Benzene is about 1/7 as strong as anisole and about 1/14 as strong as Et_3N.

Comparison of experimental K_d values with values derived from cryoscopic molecular weight measurements

Smith and Hamilton [8] performed cryoscopic molecular weight measurements on solutions of TnPA in benzene over the TnPA mole fraction range 0.0013—0.0142. Apparent K_d values calculated from their data are plotted against mole fraction in Fig. 8. As shown in the figure, the apparent K_d is very high at the lowest concentration, drops sharply with increasing concentration, and nearly levels out at the higher concentrations. This suggests a fairly constant systematic error in the measured ΔT whose effect on the calculated K_d is much greater at low concentrations, where ΔT is small, than at high concentrations where ΔT is large. Such error could be due, for example, to a recurring reaction between alkyl and traces of moisture. The number of solute particles would thereby be increased, leading to somewhat higher ΔT values. Line A in the figure represents the K_d value (1.15×10^{-4}, Table 13) derived in this paper. Theoretical ΔT values were calculated from this K_d value at several concentrations. "Modified" ΔT values were obtained by adding 0.012° to each theoretical ΔT value. "Modified" K_d values were then calculated from the modified ΔT values. Dashed line B in Fig. 8 is drawn through these modified K_d values. The goodness of fit of line B to Smith and Hamilton's apparent K_d values lends strong support to this explanation. If one accepts this explanation, the (corrected) measurements of Smith and Hamilton show excellent agreement with the K_d value for TnPA derived in this paper. Even if one does not accept this explanation, it is clear that (1) "perfect experiments" should all give the same apparent

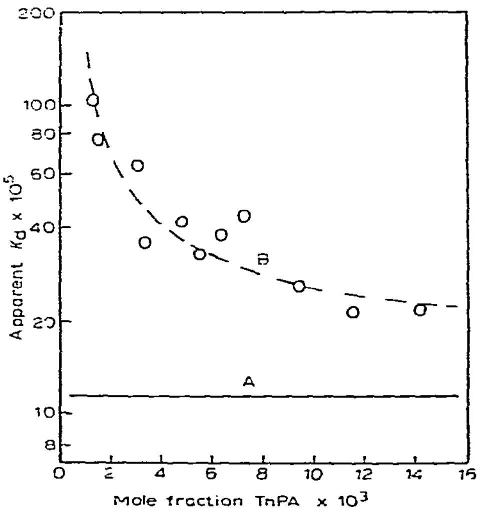

Fig. 8. Apparent K_d for TnPA from measurements of Smith and Hamilton [8].

K_d value* and (2) the apparent K_d values obtained at the highest TnPA concentrations are more nearly correct. The latter K_d values ($\approx 2.2 \times 10^{-4}$) agree fairly well with the K_d value (1.15×10^{-4}) derived in this paper.

Pitzer and Gutowsky [10] also performed cryoscopic molecular weight measurements on solutions of TnPA in benzene. Apparent K_d** values calculated from their results decrease from 6.4×10^{-4} to 1.2×10^{-4} as TnPA mole fraction (X_2) increases from 0.0033 to 0.024. Most of this decrease in apparent K_d occurs at the lower concentrations with a near leveling out at the higher concentrations. From $X_2 = 0.013$ to $X_2 = 0.024$, the apparent K_d decreases only from 1.7×10^{-4} to 1.2×10^{-4}. As discussed in the previous paragraph, the most nearly correct apparent K_d value is 1.2×10^{-4} which shows excellent agreement with the K_d value (1.15×10^{-4}) derived herein.

Hoffmann [9] measured the molecular weight of TnBA in benzene at 12 concentrations ranging from $X_2 = 0.0009$ to $X_2 = 0.011$. Apparent K_d values calculated for the six lowest concentrations ($X_2 = 0.0009$ to 0.005) fall within the narrow range 0.00014—0.00019. The mean value for these concentrations (0.00016) shows satisfactory agreement with the corresponding value from Table 13 (0.00024). For the six highest concentrations ($X_2 = 0.006$ to 0.011), the apparent K_d decreases uniformly with increasing concentration, from 0.00011 to 0.000027. This is presumably indicative of experimental error, hence this portion of the results was disregarded.

From molecular weight measurements [6] in this laboratory, the apparent K_d for TnOA in benzene was calculated as 0.00032 at $X_2 = 0.0049$, 0.00029 at $X_2 = 0.0092$ and 0.00029 at $X_2 = 0.016$. These K_d values agree reasonably well with the corresponding value from Table 12 (0.00042).

A few molecular weight measurements have been reported [11] for 0.05 molar solutions in cyclohexane at 6°. The degree of dissociation was reported as 7% for TnBA and 10% for TnHA. For TnBA the apparent K_d was calculated as 5.6×10^{-5} which compares favorably with the corresponding value (4.1×10^{-5}) derived from Table 10. For TnHA the apparent K_d was calculated as 11.2×10^{-5} which agrees fairly well with the value (6.3×10^{-5}) derived from Table 10.

Some applications of degrees and heats of dissociation of aluminum alkyls

The monomeric form of any given aluminum alkyl is far more reactive than its dimeric counterpart. In many reactions involving aluminum alkyls, such as the commercially important "growth reaction", it is only the monomer which reacts, hence monomer concentration has an important effect on the reaction rates. The degrees of dissociation presented in this paper are useful in the calculation of monomer concentrations at different conditions of temperature, dilution and solvent type in connection with obtaining the desired reaction kinetics.

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* Even considering the tendency of benzene to complex with TnPA, K_d would not be expected to vary appreciably over this concentration range. For example, Hoffmann [9] has shown from cryoscopic molecular weight measurements that the apparent K_d for benzoic acid in *p*-xylene is practically constant at 1.54×10^{-4} for the entire concentration range studied (benzoic acid mole fraction range 0.0003 to 0.016; see Fig. 5 in Hoffmann's paper).

** Not to be confused with the K_a values given by Pitzer and Gutowsky [10]. The latter are molality association constants, rather than mole fraction dissociation constants as in the present study.

For a reaction involving a primarily dimeric aluminum alkyl, the measured heat of reaction is the sum of the (endothermic) heat of dissociation to monomer and the (exothermic) heat of reaction of the monomer with the other component. The latter quantity is often of theoretical interest. For example, one may wish to compare the heats of reaction of R_3X for the series X = B, Al, Ga, In, Tl. Except for R_3Al, each of these alkyls is monomeric, hence the heat of reaction of R_3Al needs to be converted to that of the monomer. The heats of dissociation derived herein, used in conjunction with degrees of dissociation, are useful for this purpose. An example of this application (calculation of heats of complexation with bases) was given earlier in the paper. Conversely, if an estimate is available for the heat of a reaction involving R_3Al monomer, the heat of the same reaction involving liquid R_3Al (assumed not to be known) can be calculated by adding the heat of dissociation.

Standard heats of formation of monomeric aluminum alkyls can be calculated from the corresponding experimental ΔH_f^0(l) values by the addition of heats of dissociation. ΔH_f^0 values for the monomers are needed, for example, in the systematic treatment of heats of formation for the series of aluminum n-alkyls, as detailed in a forthcoming paper [12] entitled "The Heats of Formation of Aluminum Alkyls and Related Compounds".

Experimental

The aluminum alkyls were supplied by Ethyl Corporation. As shown by chemical analysis, the TnPA contained 98.4% $(n\text{-}C_3H_7)_3Al$ and 1.6% $(n\text{-}C_4H_9)_3Al$ (2.96 propyl groups per Al atom). The TnBA contained 96.5% $(n\text{-}C_4H_9)_3Al$ and 3.5% $(n\text{-}C_4H_9)_2AlO\text{-}n\text{-}C_4H_9$ (2.97 butyl groups per Al atom). The TnOA consisted of 97.9% $(n\text{-}C_8H_{17})_3Al$ and 2.1% $(n\text{-}C_8H_{17})_2AlH$ (2.97 octyl groups per Al atom). The compositions of the alkyls were used to calculate adjusted gram formula weights: 156.78 g per mole of Al for TnPA (adjusted from 156.25), 198.85 for TnBA (adjusted from 198.33), and 363.30 g per mole of Al for TnOA (adjusted from 366.66). The adjusted gram formula weights were used to convert grams of alkyl added in the dilution experiments to gfw (that is, moles of Al added). As in the preceding papers of this series, no further corrections were applied for impurities. (As discussed in Part I [1], the heat of dilution of TEA in cal per mole of Al added is not changed appreciably by the presence of small quantities of impurities such as alkoxide groups.) Hexadecane (Humphrey Chemical Co.) of 99+% purity was deoxygenated by bubbling dry nitrogen through it for several hours 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].

Acknowledgement

The author wishes to thank Dr. G. Bruno and Mr. H.J. Cragg for preparation of the aluminum alkyl samples.

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