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THE MONOMER–DIMER EQUILIBRIA OF LIQUID ALUMINUM ALKYLS
II. TRIISOBUTYLALUMINUM

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SUMMARY

The monomer–dimer equilibrium of liquid triisobutylaluminum (TiBA) has been studied by a thermochemical method applied earlier to triethylaluminum (TEA). The values obtained for the heat and entropy of dissociation of 1 mole of TiBA dimer are $8.1_6 \pm 0.1_2$ kcal and $30.4_9 \pm 0.3_4$ cal/deg. These values, compared with corresponding values for triethylaluminum (16.9 kcal and 32.2 cal/deg), indicate that a large steric effect is involved in the formation of the dimeric molecule. This suggests an appreciable increase in the (average) lengths of the Al–CH_2 and Al–Al bonds in the bridge accompanied by a significant increase in rotational restriction. Degrees of dissociation of TiBA in the pure liquid state and at various mole fractions in hydrocarbon solution are tabulated over a wide temperature range. The results, which are consistent with literature data, indicate that TiBA is 39.4% associated at 10° and 16.4% associated at 40°. This contradicts the widely held belief that (pure) TiBA is either "completely monomeric" or practically unassociated.

INTRODUCTION

Part I of this series[1] dealt with triethylaluminum (TEA) which is primarily dimeric both in the pure liquid state and in dilute hydrocarbon solution. The alkyl studied in the present investigation, triisobutylaluminum (TiBA) is, on the other hand, primarily monomeric in dilute solution as shown by molecular weight determinations[2]. The fact that TiBA is very largely monomeric in dilute solution does not eliminate the possibility of its being appreciably associated in the pure state. Nevertheless, it has often been stated that TiBA is completely (or virtually completely) monomeric[3-6].

Preliminary experiments in this laboratory had shown that the temperature drop obtained on mixing a small quantity of TiBA with a large quantity of a hydrocarbon is far too large to be accounted for by the heat of physical mixing alone. Since the existence of significant quantities of associated species in liquid TiBA (presumably dimers) was thereby demonstrated, the present investigation was undertaken to define the monomer–dimer equilibria of this alkyl.

EXPERIMENTAL SECTION

Materials

TiBA was prepared by purifying commercial TiBA supplied by Ethyl Corporation. The purification was effected by partial freezing, decantation, and re-melting, the cycle being repeated several times. Chemical analysis indicated that the product contained 98.75% TiBA and 1.25% (iso-$C_4H_9)_2AlH$. Thus it contained 2.98 isobutyl groups per aluminum atom. The TiBA was sealed in glass ampules which were stored under dry ice until just prior to use. (This was necessary since TiBA decomposes slowly at room temperature). Triisobutylboron (TiBB) supplied by the K&K Laboratories, Inc. was distilled. On the basis of NMR and chemical analysis, its purity was at least 99%. Normal tetradecane was ASTM grade (99% minimum) supplied by the Phillips Petroleum 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.

Heat-of-dilution experiments

The apparatus and procedure were as described in Part I[1] except for the following changes. Since TiBA is subject to thermal decomposition, experimental temperatures were kept below 45°. To permit determinations at 10°, n-tetradecane (m.p. 5.9°) was substituted for n-hexadecane (m.p. 18.2°). For experiments at 10° and 20°, the calorimeter was cooled by passing cold nitrogen through $\frac{1}{4}$ in. copper tubing into the glass well which normally housed the cartridge heater. The nitrogen was chilled by passing it through a coil of the copper tubing immersed in a trichloroethylene/solid CO_2 mixture. The nitrogen flow rate, and therefore the rate of cooling of the calorimeter, was adjusted by means of the cylinder regulator and a needle valve. The heating tape used for auxiliary heating in the earlier study was not required in the present experiments.

In the earlier study[1] with triethylaluminum, supplementary "B" experiments were performed in which the amount of aluminum alkyl preadded to the hydrocarbon was increased from 2 ml (used in the "A" experiments) to 10 ml. This increased preaddition served to suppress the dissociation of the TEA added later in the experiment. The heat absorbed due to dissociation was thus reduced far more than was the heat of physical mixing, and a basis for the evaluation of the latter was provided. This method of evaluating the heat of physical mixing was effective in the case of TEA because this compound is weakly dissociated, even in dilute solution (except at high temperatures where the heat of physical mixing is small). TiBA, however, is considerably (at least 50%) dissociated in the pure state and highly (at least 95%) dissociated in dilute solution. The reduction in the heat of dissociation that would be achieved here by the use of the increased preaddition is too small to be effective. Hence, instead of performing "B" experiments in the case of TiBA, a different approach was used to the evaluation of the heat of physical mixing.

Heat-of-mixing experiments

The changes accompanying dilution of TiBA with n-tetradecane may be regarded as occurring in the following order: (*1*) dissociation of dimer to produce the equilibrium mixture of monomer and dimer and (*2*) physical mixing of this mixture with n-tetradecane. Since the equilibrium mixture is primarily (at least 97%) monomeric, the heat of physical mixing should be very close to the heat of mixing of pure monomeric TiBA. The latter, in turn, because of structural similarity, should be close to the heat of mixing of TiBB since TiBB is known to be completely monomeric (see, for example, ref. 7). Measurements were therefore made of the heat of mixing of TiBB with n-tetradecane and assumed to represent the heat of physical mixing of TiBA with this solvent. The apparatus and procedure used in these experiments were essentially as described elsewhere[8]. Four ml of TiBB was added to 35 ml of n-tetradecane (premixed with 1 ml of TiBB) at 25.10° and the temperature drop measured. Similar measurements were made with successive additions of 6 ml, 7 ml and 9 ml of TiBB. The entire series was performed in duplicate.

The calorimetric data were smoothed and extended by means of the almost linear plot of $Z_i = q_{hi}/(X_{ai} - X_{a(i-1)})$ *vs.* $\bar{X}_{ai} = \frac{1}{2}(X_{ai} + X_{a(i-1)})$, where, for the i^{th} addition, q_{hi} is the observed heat absorbed in calories per mole of hydrocarbon and $X_{a(i-1)}$ and X_{ai} are the mole fractions of alkyl for the initial and final solutions. Molar heats of mixing, calculated from the smoothed and extended data, are plotted against composition in Fig. 1. The maximum occurs at $X_a = 0.473$, a composition close to the value (0.500) which would have been obtained if the simple relation $H_m = C \cdot X_a \cdot X_b$ held exactly. (If the simple relation held exactly, the Z_i values would have all been equal to each other and to the constant C. The actual Z_i's decreased from 282 for the first addition to 244 for the fourth addition.)

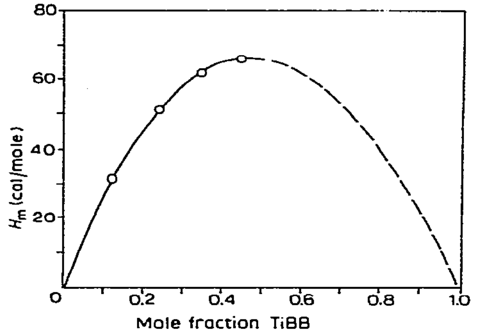

Fig. 1. Heat of mixing of TiBB with n-tetradecane at 25.10°.

Since $Z_i = (H_{mhi} - H_{mh(i-1)})/(X_{ai} - X_{a(i-1)}) = \Delta H_{mh}/\Delta X_a$, where H_{mh} is integral heat of mixing per mole of hydrocarbon, the Z_i *vs.* $\bar{X}_{ai}$ plot gives $Z = dH_{mh}/dX_a$ as a function of X_a. The value of Z at $X_a = 0.0224$ was read from the plot as 289 cal/mole. (This value of X_a is the midpoint of the interval 0.0221 to 0.0227 which is the range of the mean TiBA mole fractions for the heat of dilution experiments. The variation of Z over this narrow range is negligible).

Numerical constants

The energy measurements were expressed in terms of the thermochemical calorie (1 cal = 4.1840 absolute joules). Temperature conversions were based on the relation 0°C = 273.15°K. The 1961 International Atomic Weights were used. Gram formula weights of TiBA, TiBB, and n-tetradecane were 198.330, 182.160, and 198.395, respectively.

Heat capacity data

The specific heat of n-tetradecane was read from a plot of the measurements of Finke and others[9]. The specific heat of TiBA was determined over the temperature range 25–55° in this laboratory (data not published). The specific heat of monomeric TiBA was calculated from these data by correcting for heats due to the variation in dissociation with temperature. (These heats were obtained from a preliminary workup of the heat of dilution data.) The molar heat capacity of TiBB was calculated from that of monomeric TiBA by substituting B (atomic h.c. 4.7) for Al (atomic h.c. 8.0). For the heat of dilution experiments, the heat of "reaction" at the initial temperature was calculated using the heat capacity of the product, namely a solution of monomeric TiBA in n-tetradecane. An appropriate small (negative) correction was therefore made for the change in heat capacity accompanying the mixing of these liquids ($\Delta C_p = \partial \Delta H/\partial T$). A similar procedure was followed in the case of the heat of mixing experiments.

DERIVATION OF EQUATIONS

Heat due to dissociation

Consider the addition of f_0 gfw (gram formula weights) of TiBA to a solution of f_1 gfw of TiBA dissolved in n_h moles of n-tetradecane. Let f_2 = gfw of TiBA in final solution $:= f_0 + f_1$; $r_1 = n_h/f_1$; $r_2 = n_h/f_2$; 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; Q_T = total (experimental) heat absorbed on dilution, cal/gfw of alkyl added; 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[1] on the basis of appropriate assumptions, the following equations apply:

$$Q_T = Q_D + Q_P \tag{1}$$

$$K_D = \frac{X^2_{\text{monomer}}}{X_{\text{dimer}}} = \frac{4\beta_0^2}{1-\beta_0^2} \tag{2}$$

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

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

where

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

$$\ln K_D = (\Delta S_D^0/R) - [\Delta H_D^0/(R \cdot T)] \tag{5}$$

Heat of physical mixing

For the mixing of n_a moles of monomeric alkyl with n_h moles of hydrocarbon, let Q = heat absorbed in calories and $H_{mh} = Q/n_h$. For the addition of dn_a moles of alkyl to this mixture:

$$\frac{dQ}{dn_a} = n_h \cdot \frac{dH_{mh}}{dn_a} = n_h \cdot \frac{dH_{mh}}{dX_a} \cdot \frac{dX_a}{dn_a}$$

$$= n_h \cdot \frac{dH_{mh}}{dX_a} \cdot \frac{n_h}{(n_a+n_h)^2} = \frac{dH_{mh}}{dX_a} \cdot X_h^2$$

For a small addition of alkyl (Δn_a), the expression becomes, after substituting the value of dH_{mh}/dX_a derived from the heat of mixing experiments,

$$Q_P(25.10°) = \frac{\Delta Q}{\Delta n_a}(25.10°) = 289\ \bar{X}_h^2$$

where $\bar{X}_h$ is the average X_h in the solution before and after the addition. Since Q_P is assumed to vary linearly with temperature, the following equation is obtained:

$$Q_P = [289 + B\cdot(t - 25.10)]\cdot \bar{X}_h^2 \tag{6}$$

RESULTS AND DISCUSSION

The endothermic process accompanying each heat of dilution experiment was completed within 1 min (and probably much sooner), even at 10°. The experimental results are listed in the first seven columns of Table 1. The value of Q_T decreases rapidly with increasing temperature.

TABLE 1

HEATS OF DILUTION OF LIQUID TRIISOBUTYLALUMINUM WITH n-TETRADECANE

Expt. No.	Temp. (°C)	Initial solution		TiBA added (g)	$-\Delta t$ (°C)	Q_T (cal/gfw)		Q_P	Q_D
		Tetradecane (g)	TiBA (g)			Exptl.	Calcd.		
1	9.813	140.98	1.6095	3.3409	0.2868	1813	1816.0	351.4	1464.6
2	9.621	140.60	1.5955	3.3915	0.2936	1825	1822.3	352.3	1470.0
3	19.642	140.60	1.6437	3.2562	0.2224	1454	1451.7	303.1	1148.6
4	19.763	140.71	1.6129	3.3117	0.2246	1446	1447.6	302.5	1145.1
5	30.156	140.07	1.6352	3.1233	0.1602	1102	1104.2	251.6	852.6
6	29.994	140.48	1.5399	3.3098	0.1708	1111	1109.4	252.5	856.9
7	41.716	140.13	1.5927	3.2891	0.1188	789	790.1	194.7	595.4
8	41.730	140.00	1.6295	3.2208	0.1167	791	789.7	194.6	595.1

Values of the parameters ΔH_D^0, ΔS_D^0, and B were determined using a nonlinear least-squares computer program based on eqn. 1, 2, 4, 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. Since the greatest source of uncertainty in the results is the constant 289 representing the heat of physical mixing at 25.10°, the program was repeated using other values for this constant. It was found that ΔH_D^0 and ΔS_D^0 were not changed significantly even when large changes were made in the value of the constant. The accuracy limits applied in Table 2 correspond to an

TABLE 2

VALUES OF PARAMETERS DERIVED BY COMPUTER PROGRAM

ΔH_D^0, cal/mole of dimer	$81.{}_{60} \pm 1.{}_{20}$
ΔS_D^0, cal/mole of dimer-deg	$30.4_9 \pm 0.3_4$
B, cal/mole deg	$-5.1_5 \pm 0.5_3$

arbitrary change of ±40 in the constant's value. When the program was performed with no allowance for physical mixing, a much poorer fit of the experimental data was obtained, indicating that the inclusion of physical mixing is significant at a high level (again ΔH_D^0 and ΔS_D^0 were not changed significantly).

The $(-\Delta H)$ of association of TiBA (8.16 kcal/mole of dimer) is slightly less than half that of TEA (16.93). This would seem to indicate that because of the steric hindrance associated with β-branching in the alkyl groups, the (average) lengths of the Al–CH_2 and Al–Al bonds in the bridge of the dimeric molecule are appreciably greater in TiBA than in TEA. If this increased bond length represented the only significant difference between the TiBA and TEA dimeric molecules, it would be expected that the $(-\Delta S)$ of association of TiBA would be well below that of TEA. The fact that $(-\Delta S)$ for TiBA (30.5 cal/mole of dimer-deg) is only slightly below that of TEA (32.2) suggests that this increase in bridge bond lengths in TiBA is accompanied by a large increase in rotational restriction. It could also be postulated that since the $(-\Delta H)$ of association of TiBA is about half that of TEA, the dimeric molecule may be formed with a single isobutyl group in the bridge. This seems unlikely for various reasons but would appear to be ruled out entirely because the $(-\Delta S)$ accompanying such an association would surely be much less than the value actually found.

Calculated values of Q_T based on the numbers in Table 2 are given in column 8 of Table 1 where they are compared with experimental values (column 7). The rms difference between experimental and calculated values is 2.1 cal/gfw. Calculated values of the heat of physical mixing (Q_P) and the heat due to dissociation (Q_D) are given in the last two columns. As was the case with TEA, Q_P is positive in sign and decreases with increasing temperature. Whereas Q_D for TEA showed a rapid increase with rising temperature, Q_D for TiBA shows a rapid decrease. This result for TiBA would be

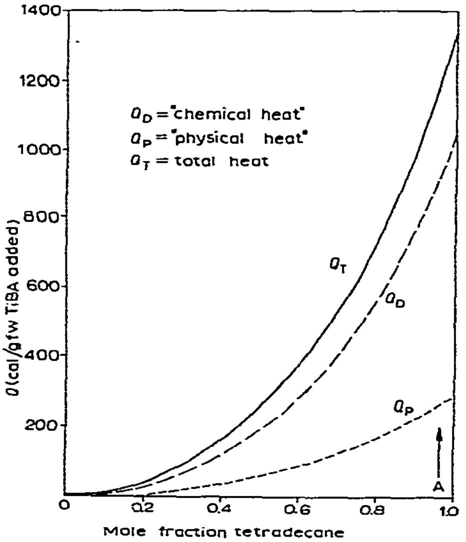

Fig. 2. Contributions of chemical and physical heat to total heat absorbed at 25° as functions of composition. These calculated values are for the addition of 4 ml of TiBA to various TiBA/tetradecane mixtures, each containing 184 ml of tetradecane. The composition designated as A is that used in the heat of dilution experiments. TiBA was taken as the monomer in computing mole fractions.

expected from the monomer–dimer equilibrium provided TiBA is already considerably dissociated in the pure state and therefore highly dissociated after dilution.

The contributions of "chemical heat" (Q_D) and "physical heat" (Q_P) to the total heat absorbed (Q_T) at 25° are shown graphically for the entire composition range in Fig. 2. In contrast to comparable results for TEA, the ratio of Q_D to Q_P is large at each composition in the range.

On substituting the values obtained for ΔH_D^0 and ΔS_D^0 in eqn. 5, the expression for the equilibrium constant becomes

$$\ln K_D = 15.34_{23} - (410_{5.5}/T) \tag{7}$$

Values of K_D calculated from this equation at 10° intervals are given in column 1 of Table 3. The degree of dissociation of pure TiBA at each of these temperatures was calculated from the equilibrium constant using the equation $\beta_0 = [K_D/(4+K_D)]^{\frac{1}{2}}$ which is derived from eqn. 2. These values, expressed as per cent of TiBA dissociated, are listed in column 3 of Table 3. Degrees of dissociation at various mole fractions in hydrocarbon solution, calculated from eqn. 3, are listed in the remaining columns of Table 3.

TABLE 3

EQUILIBRIUM CONSTANT AND DEGREE OF DISSOCIATION OF LIQUID TRIISOBUTYLALUMINUM[a]

Temp. (°C)	K_D	TiBA[b] dissociated (%) in hydrocarbon solution at TiBA mole fraction of:						
		1	0.5	0.2	0.1	0.01	0.001	0.0001
0	1.366	50.46	65.57	80.60	88.48	98.58	99.85	99.99
10	2.323	60.62	74.49	86.84	92.59	99.15	99.91	99.99
20	3.810	69.84	81.66	91.19	95.23	99.48	99.95	99.99
30	6.047	77.58	87.05	94.11	96.89	99.67	99.97	100.00
40	9.319	83.65	90.92	96.03	97.94	99.79	99.98	100.00
50	13.98	88.18	93.63	97.28	98.61	99.86	99.99	100.00
60	20.47	91.46	95.49	98.12	99.04	99.90	99.99	100.00
70	29.32	93.81	96.78	98.67	99.33	99.93	99.99	100.00
80	41.14	95.47	97.67	99.05	99.52	99.95	100.00	100.00
90	56.66	96.65	98.29	99.30	99.65	99.96	100.00	100.00
100	76.71	97.49	98.73	99.48	99.74	99.97	100.00	100.00
110	102.2	98.10	99.04	99.61	99.81	99.98	100.00	100.00
120	134.3	98.54	99.26	99.70	99.85	99.99	100.00	100.00
130	173.9	98.87	99.43	99.77	99.89	99.99	100.00	100.00
140	222.6	99.11	99.55	99.82	99.91	99.99	100.00	100.00
150	281.5	99.30	99.65	99.86	99.93	99.99	100.00	100.00
160	352.2	99.44	99.72	99.89	99.94	99.99	100.00	100.00

[a] Values at 0° and 50–160° are extrapolated. [b] TiBA was taken as the monomer in computing mole fractions.

Values of the ΔH of dissociation of TiBA (equilibrium mixture of monomer and dimer) into pure monomer were calculated from ΔH_D^0 and degrees of dissociation at several temperatures for the pure liquid and for two dilutions. These are listed in Table 4 where they are compared with corresponding values for TEA. The relative weakness of the TiBA association, particularly at elevated temperatures and/or upon dilution, is apparent. Where the heat of a reaction involving an alkyl is known, these heats of dissociation may be used to calculate the heat of the same reaction involving the monomeric form of the alkyl. For example, the heats of formation of the monomeric alkyls can be calculated from the heats of formation of the corresponding pure alkyls when reliable values for the latter become available.

The ΔH of reaction at 25° of pure TiBA with tetrahydrofuran (THF) to form the 1/1 complex was determined in this laboratory as -21.5 kcal/gfw. From Table 4, the ΔH of dissociation of TiBA into monomer is 1.06 kcal/gfw at 25°. The ΔH of reaction of monomeric TiBA with THF is then $-21.5-1.06=-22.6$ kcal/gfw. The ΔH of reaction at 25° of pure tri-n-butylaluminum (TnBA) with THF was determined as -14.6 kcal/gfw. Assuming that the ΔH of reaction with THF of monomeric TnBA is close to that of monomeric TiBA, it follows that the ΔH of dissociation of pure TnBA into monomer is close to $22.6-14.6=8.0$ kcal/gfw. This compares favorably with the corresponding value of 8.46 kcal/gfw for TEA (Table 4).

TABLE 4

HEATS OF DISSOCIATION OF ALKYLS[a] INTO MONOMERS

Temp. (°C)	ΔH of diss. (cal/gfw) at indicated alkyl mole fract.[b]					
	TiBA			TEA		
	1	0.1	0.01	1	0.1	0.01
10	1606	302	35	8461	8447	8408
25	1063	157	17	8456	8427	8343
40	667	84	9	8448	8390	8226
60	348	39	4	8426	8297	7933
80	185	20	2	8385	8122	7405
100	102	11	1	8312	7821	6560
120	60	6	0	8191	7348	5380
140	36	4	0	8003	6664	3980
160	23	2	0	7723	5762	2613

[a] By "alkyl" is meant here the equilibrium mixture of monomer and dimer. [b] TiBA and TEA were taken as the monomers in computing mole fractions.

Hoffmann and Tornau[10] measured the heats of complexation of several aluminum alkyls, pre-dissolved in cyclohexane (the alkyl mole fraction was about 0.05), with triethylamine. Their values of ΔH, in kcal/gfw, are -22.2 ± 0.2 for TiBA and -14.0 ± 0.2 for TnBA. From Table 4, the ΔH of dissociation of TiBA at this dilution and at 25° is about 0.1 kcal/gfw. The ΔH of reaction of monomeric TiBA with triethylamine is then $-22.2-0.1=-22.3$ kcal/gfw. Again assuming that the ΔH of reaction of monomeric TnBA is close to that of monomeric TiBA, it follows that the ΔH of dissociation of TnBA (diluted with cyclohexane) into monomer is close to $22.3-14.0=8.3$ kcal/gfw. This agrees very well with the value (8.0) derived in the preceding paragraph and indicates that, at room temperature, TnBA is primarily dimeric at this dilution as well as in the pure state.

From cryoscopic measurements in benzene at 5°, Hoffmann[2] determined the molecular weight of TiBA as 200 ± 2, corresponding to an *i*-factor range of 0.998 to 1.019 (i=molecular weight/formula weight). Values of the degree of association of TiBA in tetradecane at 5°, calculated from the present measurements, range from 0.12% to 1.05% as the TiBA mole fraction is increased from 0.001 to 0.01 (the concentration range of Hoffmann's data). The corresponding *i* factors range from 1.001 to 1.005. Although TiBA may not be equally associated in benzene and in tetradecane, it is concluded that the results of the present investigation agree well with the results of cryoscopic measurements.

As mentioned in the introduction, a number of statements have appeared in the literature[3-6] to the effect that TiBA is completely, or virtually completely, monomeric. These statements, now subject to correction, were apparently based on the fact that TiBA had been shown to be very largely monomeric *in dilute solution*. The results of the present investigation, while consistent with the results in dilute solution, indicate that pure TiBA is appreciably associated (39.4% at 10° and 16.4% at 40°, Table 3). It therefore has *some* association even at high dilution and is never completely monomeric.

When TiBA is mixed at 5° with $Al[CH_2CH(C_2H_5)C_4H_9]_3$, a molecule even more sterically hindered than TiBA, a rapid exchange of alkyl groups takes place between the two aluminum atoms[2]. This is readily explained in terms of the present investigation. TiBA is considerably associated and the other compound, because of its similarity in structure, may be presumed to be associated to an appreciable degree. The monomer–dimer equilibria are well-known to be extremely fast, with new dimers constantly being formed and then quickly re-dissociating. The rapid exchange observed can therefore occur via the formation of mixed dimers, some of which yield "mixed monomers" on re-dissociation.

Similar studies of the monomer–dimer equilibria of other aluminum alkyls are in progress.

REFERENCES

1 M. B. Smith, *J. Phys. Chem.*, 71 (1967) 364.
2 E. G. Hoffman, *Justus Liebigs Ann. Chem.*, 629 (1960) 104.
3 J. J. Eisch, *The Chemistry of Organometallic Compounds. The Main Group Elements*, Macmillan, New York, 1967, p. 38.
4 R. Köster and P. Binger in H. J. Emeleus and A. G. Sharpe (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 7 Academic Press, New York, 1965, p. 271.
5 O. Yamamoto and K. Hayamizu, *J. Phys. Chem.*, 72 (1968) 822.
6 J. N. Hay, P. G. Hooper and J. C. Robb, *Trans. Faraday Soc.*, 65 (1969) 1365.
7 K. Ziegler, in H. Zeiss (Ed.), *Organometallic Chemistry*, Reinhold, New York, 1960.
8 M. B. Smith and W. E. Becker, *Tetrahedron*, 22 (1966) 3027.
9 H. L. Finke, M. E. Gross, G. Waddington and H. M. Huffman, *J. Amer. Chem. Soc.*, 76 (1954) 333.
10 E. G. Hoffman and W. Tornau, *Z. Anal. Chem.*, 188 (1962) 321.