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THE MONOMER–DIMER EQUILIBRIA OF LIQUID ALUMINUM ALKYLS

III. TRIMETHYLALUMINUM: THE MONOMER–DIMER EQUILIBRIA OF LIQUID AND GASEOUS TRIMETHYLALUMINUM AND TRIETHYLALUMINUM

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SUMMARY

There has been a dichotomy of opinion concerning the values for the heats of dissociation of trimethylaluminum (TMA) and triethylaluminum (TEA) in the liquid phase. It is believed that the results reported herein will enable these differences to be resolved. In the present study, the heat of dissociation (ΔH_d^0) of liquid TMA is evaluated as $19.4_0 \pm 0.3_0$ kcal·(mole of dimer)$^{-1}$ from the previously determined ΔH_d^0 of liquid TEA and new heat of mixing data for TMA–TEA. Essentially the same result is derived from the established ΔH_d^0 of gaseous TMA by application of a thermodynamic relationship between heats of dissociation and heats of vaporization (the "Dissociation–Vaporization Rule"). It is concluded that the experimental ΔH_d^0 values for liquid TEA (16.9_3 kcal·(mole of dimer)$^{-1}$) and gaseous TMA (20.4_0) are thermodynamically consistent. The ΔS_d^0 of liquid TMA is evaluated as 29.3 ± 0.3 cal·K^{-1}·(mole of dimer)$^{-1}$. The ΔH_d^0 and ΔS_d^0 values for liquid and gaseous TMA are shown to be thermodynamically consistent with vapor pressure data. Boiling points derived for pure TMA monomer and pure dimer are 8.1 ± 2.1 and 131.95 ± 0.02°C, respectively. Degrees of dissociation of TMA in the pure liquid state and at various mole fractions in aliphatic hydrocarbon solution are tabulated over a wide temperature range. The results indicate that the extent of dissociation of liquid TMA is 0.0047% at 20, 0.053% at 70, and 0.32% at 120°C.

The ΔH_d^0 and ΔS_d^0 of gaseous TEA are derived as $18.17 \pm 0.3_0$ kcal·(mole of dimer)$^{-1}$ and $45.5_1 \pm 0.7_0$ cal·K^{-1}·(mole of dimer)$^{-1}$ from the experimental values for liquid TEA. The ΔH_d^0 and ΔS_d^0 values for liquid and gaseous TEA are shown to be thermodynamically consistent with vapor pressure data. It is also shown that the values $\Delta H_{d(l)}^0 = 11 \pm 3$ kcal·(mole of dimer)$^{-1}$ and $\Delta H_{d(g)}^0 = 10.2 \pm 1.0$ kcal·(mole of dimer)$^{-1}$ proposed in the literature are far too low. They are thermodynamically inconsistent with the established $\Delta H_{d(g)}^0$ for TMA and also with TEA vapor pressure data.

INTRODUCTION

A serious dichotomy of opinion exists as to the correct value for the liquid phase heat of dissociation of triethylaluminum (TEA). In 1967 this writer reported $\Delta H^0_{d\,(l)}$ for TEA as $16.9_3 \pm 0.2_3$ kcal·(mole of dimer)$^{-1}$, based on thermochemical measurements. In 1969, Hay, Hooper and Robb[2] reported the gas phase heat of dissociation of TEA, $\Delta H^0_{d\,(g)}$, as 10.2 ± 1.0 kcal·(mole of dimer)$^{-1}$, based on vapor density measurements. In 1971, these authors[3] calculated $\Delta H^0_{d(l)}$ from $\Delta H^0_{d(g)}$ as 12.5 ± 2.0 kcal·(mole of dimer)$^{-1}$. After a lengthy discussion, they gave the value $\Delta H^0_{d(l)} = 11 \pm 3$ kcal·mole^{-1} as the "best estimate available." The $\Delta H^0_{d(l)}$ for TEA is frequently required for the interpretation of kinetic data*; in order for a reaction involving TEA to proceed by a dissociative mechanism, the energy of activation must be equal to or exceed $\Delta H^0_{d(l)}$. It is therefore important that this dichotomy be resolved and that the correct value for $\Delta H^0_{d(l)}$ of TEA be established. To accomplish the latter is one objective of the present investigation.

A similar dichotomy of opinion exists as to the correct value of ΔH^0_d for liquid trimethylaluminum (TMA). The value proposed by Hay, Hooper and Robb[3] (16.3 kcal·(mole of dimer)$^{-1}$) appears to the writer to be about 3 kcal·(mole of dimer)$^{-1}$ too low when compared with the established value (20.4_0 kcal·(mole of dimer)$^{-1}$) for gaseous TMA. Since the ΔH^0_d of liquid TMA is also often needed for the interpretation of kinetic data, it is important that the correct value be established. To accomplish this is a second objective of this paper.

The broad objective of the present investigation is to determine the monomer–dimer equilibria of both TMA and TEA in both the liquid and gaseous states. In the case of gaseous TMA, the monomer–dimer equilibria are already well-defined[5] and the values derived for $\Delta H^0_{d(g)}$ (20.4_0 kcal·(mole of dimer)$^{-1}$) and for $\Delta S^0_{d(g)}$ (43.1_9 cal·K^{-1}·mole^{-1}) have received general acceptance. For liquid TEA, the monomer–dimer equilibria were reported earlier[1]. The values derived for $\Delta H^0_{d(l)}$ (16.9_3 kcal·(mole of dimer)$^{-1}$) and $\Delta S^0_{d(l)}$ (32.1_9 cal·K^{-1}·mole^{-1}) will be subjected to further testing. For liquid TMA and gaseous TEA, achievement of the broad objective requires the evaluation of ΔH^0_d and ΔS^0_d for each.

OUTLINE OF METHOD

In parts I and II of this series[1,6], the monomer–dimer equilibria of liquid TEA and liquid triisobutylaluminum (TiBA) were derived directly from heat of dilution measurements. This method was effective in the case of TEA, which is primarily dimeric, because the temperature drop accompanying dilution was appreciable at 60°C and *increased* rapidly as the experimental temperature was increased. The high boiling point of TEA (~186.6°C) permitted the use of experimental temperatures as high as 150°C. In the case of TiBA, which is primarily monomeric in the liquid state, the temperature drop accompanying dilution was relatively large at 10°C (corresponding to dissociation of practically all the dimeric molecules) and *decreased* rapidly as the experimental temperature was increased (since there were fewer dimeric molecules to dissociate).

TMA, however, is not well adapted to heat of dilution measurements. Because it is much less dissociated than TEA (about 14 times less at 60°C), the temperature drop accompanying dilution of TMA is much less and is difficult to measure with suf-

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* For a recent example, see ref. 4.

ficient accuracy. Furthermore, because of the low boiling point of TMA (~127°C), the experimental temperature cannot be extended much above 90°C.

Since direct determination of the monomer–dimer equilibria of liquid TMA is not feasible, indirect methods will be applied. A thermodynamic expression (the "Dissociation–Vaporization Rule") will be introduced which relates the difference $\Delta H^0_{d(g)} - \Delta H^0_{d(l)}$ [or the difference $\Delta S^0_{d(g)} - \Delta S^0_{d(l)}$] to the difference between the heats (or entropies) of vaporization of pure monomer and pure dimer. The latter differences will be approximated from thermodynamic data on compounds analogous in structure to pure monomer and pure dimer. This will permit the calculation of tentative values of $\Delta H^0_{d(l)}$ and $\Delta S^0_{d(l)}$ for TMA from established values of $\Delta H^0_{d(g)}$ and $\Delta S^0_{d(g)}$.

A second value of $\Delta H^0_{d(l)}$ for TMA will be determined experimentally as follows. The difference $\Delta H^0_{d(l)}$ (TMA) $-\Delta H^0_{d(l)}$ (TEA) will be evaluated from heat of mixing experiments described herein. This difference will be added to the previously determined experimental value of $\Delta H^0_{d(l)}$(TEA) to obtain $\Delta H^0_{d(l)}$(TMA). If the two independently determined values of $\Delta H^0_{d(l)}$(TMA) agree well, it will be concluded that the experimental values of $\Delta H^0_{d(l)}$(TEA) and $\Delta H^0_{d(g)}$(TMA) are mutually consistent thermodynamically, and conversely.

The ΔH^0_d and ΔS^0_d values for liquid TMA, along with the established values for gaseous TMA, will be tested by applying them to vapor pressure data. Adjustments will be made, if necessary, so that the final values selected will be thermodynamically consistent with the vapor pressure data.

Values of ΔH^0_d and ΔS^0_d for gaseous TEA will be derived from the corresponding experimental values for liquid TEA, again making use of the "Dissociation–Vaporization Rule" in conjunction with thermodynamic data on analogous compounds. The four values $\Delta H^0_{d(l)}$, $\Delta S^0_{d(l)}$, $\Delta H^0_{d(g)}$ and $\Delta S^0_{d(g)}$ will be tested by applying them to TEA vapor pressure data. Values of these quantities given by Hay, Hooper and Robb[3] (or derived from their measurements where required) will be similarly tested. Preferred values will be selected on the basis of thermodynamic consistency with the vapor pressure data.

RELATIONSHIP BETWEEN $\Delta H^0_{d(g)}$ AND $\Delta H^0_{d(l)}$; $\Delta S^0_{d(g)}$ AND $\Delta S^0_{d(l)}$

The "Dissociation–Vaporization Rule"

The relationship between $\Delta H^0_{d(g)}$ and $\Delta H^0_{d(l)}$ is readily obtained by summing simple equations. At any given temperature*:

$$\begin{array}{lll}
R_6Al_{2(l)} \rightarrow 2R_3Al_{(l)} & \Delta H = \Delta H^0_{d(l)} \\
2R_3Al_{(l)} \rightarrow 2R_3Al_{(g)} & \Delta H = 2\Delta H^0_{v(M)} \\
R_6Al_{2(g)} \rightarrow R_6Al_{2(l)} & \Delta H = -\Delta H^0_{v(D)} \\
\hline
R_6Al_{2(g)} \rightarrow 2R_3Al_{(g)} & \Delta H = \Delta H^0_{d(g)} = \Delta H^0_{d(l)} + 2\Delta H^0_{v(M)} - \Delta H^0_{v(D)}
\end{array}$$

$$\text{Similarly, } \Delta S = \Delta S^0_{d(g)} = \Delta S^0_{d(l)} + 2\Delta S^0_{v(M)} - \Delta S^0_{v(D)}$$

Denoting the difference $\Delta H^0_{d(g)} - \Delta H^0_{d(l)}$ by the symbol δ_H, and the difference $\Delta S^0_{d(g)}$ –

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* Subscripts d and v denote dissociation and vaporization; g and l, gas and liquid; M and D, monomer and dimer.

$\Delta S^0_{d(l)}$ by the symbol δ_S, the following equations are valid at any given temperature:

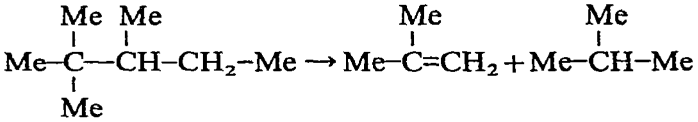
$$\delta_H \equiv \Delta H^0_{d(g)} - \Delta H^0_{d(l)} = 2\Delta H^0_{v\,(M)} - \Delta H^0_{v\,(D)} \tag{1}$$

$$\delta_S \equiv \Delta S^0_{d\,(g)} - \Delta S^0_{d\,(l)} = 2\Delta S^0_{v\,(M)} - \Delta S^0_{v\,(D)} \tag{2}$$

Thus, according to eqn. (1), δ_H (the heat of dissociation of the gas minus that of the liquid) equals twice the molar heat of vaporization of pure monomer minus the molar heat of vaporization of pure dimer, where each substance is in its standard state at the same temperature. For convenience we will refer to the general relationship exemplified by eqns. (1) and (2) as the "Dissociation–Vaporization Rule." (The rule applies equally well to other extensive properties such as free energy.)

Evaluation of δ_H and δ_S

The differences $2\Delta H^0_{v\,(M)} - \Delta H^0_{v\,(D)}$ and $2\Delta S^0_{v\,(M)} - \Delta S^0_{v\,(D)}$, which vary with temperature, will be evaluated at some convenient temperature not too far removed from the experimental range. (δ_H and δ_S also vary with temperature. This variation is ignored since the experimental data are not accurate enough to establish the temperature variation of heat and entropy of dissociation. Thus the derived value for $\Delta H^0_{d(g)}$ of TMA is actually the average value for the experimental temperature range). In view of its relationship to vaporization processes, δ_H (and also δ_S) would be expected to have about the same value for different monomer–dimer systems at comparable temperatures. For actual monomer–dimer systems, heat and entropy of vaporization of pure monomer and pure dimer are not available. One must therefore turn to analogous systems for which the necessary data are available. It is fortunate that a class of compounds exists, not only for which appropriate data are readily available, but which is closely related in its physical chemistry to the aluminum alkyls (aside from the tendency of the latter to dimerize). This class comprises the aliphatic hydrocarbons, both saturated and olefinic. For example, we can write the following equations simulating the dissociation of TMA dimer into monomer:

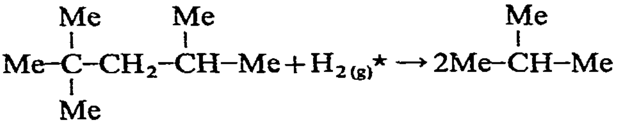


$$\mathrm{Me{-}C(Me)_2{-}CH(Me){-}CH_2{-}Me \longrightarrow Me{-}C(Me){=}CH_2 + Me{-}CH(Me){-}Me} \tag{3}$$

(D) (M1) (M2)

$$\delta_H(25°\mathrm{C}) = \Delta H^0_{v(M1)}(25°\mathrm{C}) + \Delta H^0_{v(M2)}(25°\mathrm{C}) - \Delta H^0_{v(D)}(25°\mathrm{C}) = 0.93\ \mathrm{kcal\cdot mole^{-1}}$$

$$\delta_S(25°\mathrm{C}) = \Delta S^0_{v(M1)}(25°\mathrm{C}) + \Delta S^0_{v(M2)}(25°\mathrm{C}) - \Delta S^0_{v(D)}(25°\mathrm{C}) = 13.26\ \mathrm{cal\cdot K^{-1}\cdot mole^{-1}}$$



$$\mathrm{Me{-}C(Me)_2{-}CH_2{-}CH(Me){-}Me + H_{2\,(g)}{}^{*} \longrightarrow 2Me{-}CH(Me){-}Me} \tag{4}$$

$\delta_H(25°\mathrm{C}) = 1.04\ \mathrm{kcal\cdot mole^{-1}}$

$\delta_S(25°\mathrm{C}) = 13.65\ \mathrm{cal\cdot K^{-1}\cdot mole^{-1}}$

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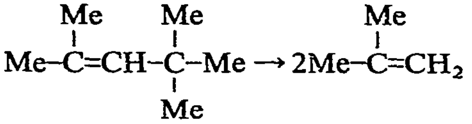
* The H_2(g) was disregarded in the calculation of δ_H and δ_S.



$$\mathrm{Me{-}\overset{Me}{\overset{|}{C}}{=}CH{-}\underset{Me}{\underset{|}{\overset{Me}{\overset{|}{C}}}}{-}Me \rightarrow 2Me{-}\overset{Me}{\overset{|}{C}}{=}CH_2} \qquad (5)$$

$\delta_H (25°\text{C}) = 1.14$ kcal · mole^{-1}
(entropy data not available for gaseous "dimer.")

For 36 such simulated processes, the average δ_H (25°) was 1.04 kcal·(mole of dimer)$^{-1}$ (range 0.75–1.42). For 20 such processes, the average δ_S (25°C) was 13.32 cal·K^{-1}·(mole of "dimer")$^{-1}$ (range 12.80–13.83). The thermochemical data for these calculations were taken from refs. 7 and 8. On the basis of these calculations δ_H(25°C) for TMA was taken as 1.0_4 kcal · (mole of dimer)$^{-1}$ and δ_S(25°C) as 13.3_2 cal · K^{-1} · (mole of dimer)$^{-1}$.

In the case of TEA, thermochemical data were not available on hydrocarbons which closely simulate the dimer. However, after analyzing the effects on δ_H and δ_S of chain length, type of branching (ethyl *vs.* methyl) and amount of branching, δ_H(25°C) for TEA was taken as 1.2_4 kcal · (mole of dimer)$^{-1}$ and δ_S(25°C) as 13.3_2 cal · K^{-1} · (mole of dimer)$^{-1}$.

TRIMETHYLALUMINUM

Heat of dissociation of liquid TMA

From the preceding, δ_H (25°C) for TMA is taken as 1.0_4 kcal · (mole of dimer)$^{-1}$. Using Henrickson and Eyman's[5] value of 20.4_0 for $\Delta H^0_{d(g)}$, we obtain $\Delta H^0_{d(l)} = \Delta H^0_{d(g)} - \delta_H = 20.4_0 - 1.0_4 = 19.4$ kcal · (mole of dimer)$^{-1}$.

In the first paper of this series[1], based on heat of dilution measurements, the $\Delta H^0_{d(l)}$ of TEA was reported as 16.9_3 kcal · (mole of dimer)$^{-1}$. Experiments described herein show that $\Delta H^0_{d(l)}(\text{TMA}) - \Delta H^0_{d(l)}(\text{TEA}) = 2.4_7$ kcal · mole^{-1}* at 25°C. This leads to the value $16.9_3 + 2.4_7 = 19.4_0$ kcal · (mole of dimer)$^{-1}$ for $\Delta H^0_{d(l)}$ of TMA. Since this agrees very closely with the value derived by hydrocarbon simulation, it is concluded that: (1), the experimental value of 16.9_3 kcal·(mole of dimer)$^{-1}$ for $\Delta H^0_{d(l)}$ of TEA is consistent with the experimental value of 20.4_0 kcal·(mole of dimer)$^{-1}$ for $\Delta H^0_{d(g)}$ of TMA; (2), the value of $\Delta H^0_{d(l)}$ for TMA is established as $19.4_0 \pm 0.3_0$ kcal · (mole of dimer)$^{-1}$**.

Equilibrium constant for liquid TMA

Henrickson and Eyman[5] obtained for gaseous TMA: $\log_{10} K_{d(g)}/\text{atm} = 9.4395 - 4457.9/T$, which is rewritten for convenience as:

$$\ln K_{d(g)} = 21.7353 - \frac{10264.7}{T} \qquad (6)$$

$\Delta H^0_{d(g)}$ was calculated from eqn. (6) as 20.4_0 kcal · (mole of dimer)$^{-1}$ and $\Delta S^0_{d(g)}$ as

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* The method of calculation of this value from the heat of mixing data, along with the assumptions made, is included in the Experimental section.

** The significance of this value in relation to the mechanism of bridge–terminal exchange is discussed in part IV (ref. 17).

43.1_9 cal·K^{-1}·mole^{-1}. The $\Delta H^0_{d(g)}$ value, which confirmed the value 20.2±1.0 reported earlier by Laubengayer and Gilliam[9], has a good experimental basis and has received general acceptance. From hydrocarbon simulation, δ_S(25°C) for TMA was estimated as 13.3_2 cal·K^{-1}·(mole of dimer)$^{-1}$. The derived value for $\Delta S^0_{d(l)}$ is then $\Delta S^0_{d(g)} - \delta_S = 43.1_9 - 13.3_2 = 29.9$ cal·K^{-1}·(mole of dimer)$^{-1}$.

Trial values of 29.0, 29.3, 29.6 and 30.0 were selected for $\Delta S^0_{d(l)}$. The equation for the equilibrium constant of liquid TMA based on $\Delta H^0_{d(l)} = 19.4$ kcal·mole^{-1} is then:

$$\ln K_{d(l)} = A - 9762.5/T \tag{7}$$

where $A = \Delta S^0_{d(l)}/R$.

Equations (6) and (7) were applied to the precise vapor pressure data (below 100°C) of McCullough *et al.*[10], as illustrated in Table 1 for $\Delta S^0_{d(l)} = 29.3$ cal·K^{-1}·mole^{-1}. (Vapor pressure readings above 100°C may have been affected slightly by decomposition and are therefore not included here. However, a similar treatment based on all the vapor pressure data gave essentially the same results.) The experimental data are listed in columns 1 and 2 of the Table. Column 3 lists values calculated from an Antoine equation [$\ln P/\text{mmHg} = A - B/(t+C)$] passed through the vapor pressure data (best 3-constant fit).

The following were calculated from eqn. (6): $K_{d(g)}$, α_g (degree of dissociation of the gas, column 4), and the partial pressures of monomer and dimer. From the latter and from eqn. (7), the following were calculated: $K_{d(l)}$, degree of dissociation of the liquid (column 5), mole fraction of monomer in the liquid, "experimental" vapor pressure of pure monomer (column 6), and "experimental" vapor pressure of pure dimer (column 8). Columns 7 and 9 list corresponding values calculated from Antoine equations passed through the "experimental" vapor pressures (best 3-constant

TABLE 1

VAPOR PRESSURES OF PURE TMA MONOMER AND DIMER DERIVED FROM VAPOR PRESSURE DATA OF McCULLOUGH *et al.*[10] USING $\Delta S^0_{d(l)} = 29.3$ cal·K^{-1}·(mole of dimer)$^{-1}$

Calculating eqn.: $\ln K_{d(g)} = 21.7353 - 10264.7/T$; $\alpha_g = \{K_{d(g)}/(K_{d(g)} + 4P/760)\}^{\frac{1}{2}}$; $P_M = 2\ \alpha_g P_{obs}/(1+\alpha_g)$; $P_D = P_{obs} - P_M$; $\ln K_{d(l)} = 14.7444 - 9762.5/T$; $\alpha_l = \{K_{d(l)}/(K_{d(l)}+4)\}^{\frac{1}{2}}$; $X_{M(l)} = 2\alpha_l/(1+\alpha_l)$; $P^0_M = P_M/X_{M(l)}$; $P^0_D = P_D/(1 - X_{M(l)})$.

Temp. (°C)	*P(mmHg)*		α_g	α_l	P^0_M*(mmHg)*		P^0_D*(mmHg)*	
	Obs.	*Calcd.*[a]			*Exp.*	*Calcd.*[b]	*Exp.*	*Calcd.*[c]
63.818	81.64	81.65	0.01943	0.0004069	3824	3824	78.59	78.59
66.779	92.52	92.52	0.02084	0.0004617	4092	4092	88.82	88.83
69.750	104.63	104.63	0.02233	0.0005229	4373	4373	100.17	100.17
72.722	118.06	118.04	0.02391	0.0005909	4667	4667	112.68	112.67
75.707	132.95	132.94	0.02558	0.0006668	4976	4976	126.49	126.48
78.701	149.41	149.42	0.02734	0.0007511	5299	5299	141.67	141.68
84.696	187.57	187.60	0.03116	0.0009476	5987	5987	176.57	176.58
90.712	233.72	233.73	0.03538	0.0011873	6734	6733	218.27	218.26
96.748	289 13	289.10	0.04003	0.0014779	7541	7541	267.66	267.66

[a] $\ln P(\text{calcd.}) = 17.12214 - 3794.98/(t+234.536)$. [b] $\ln P^0_M(\text{calcd.}) = 14.56436 - 1726.11/(t+209.506)$. [c] $\ln P^0_D(\text{calcd.}) = 15.52136 - 2977.55/(t+203.057)$.

fits). In calculating the vapor pressures of pure monomer from the monomer partial pressures, the monomer–dimer mixtures were assumed to be ideal. It is believed that in view of the small magnitude of the heat of mixing of the hydrocarbon analogs of monomer and dimer, the activity coefficients of monomer and dimer do not depart significantly from unity over the temperature range concerned. Although the Antoine-fit is excellent for the raw observed data (columns 2 and 3: RMS % deviation = 0.010), it is even better for the pure monomer (columns 6 and 7: RMS % deviation = 0.003) and the pure dimer (columns 8 and 9: RMS % deviation = 0.005). This reflects both the high precision of the vapor pressure measurements and the fact that dissociation detracts (in this case, only slightly) from the goodness of fit of an Antoine equation passed through raw experimental data. The goodness of fit for the pure monomer and pure dimer is not appreciably different for the other trial values of $\Delta S^0_{d(l)}$ (Table 2).

Antoine constants, boiling points, and thermodynamic properties of pure monomer and pure dimer derived for the four trial values of $\Delta S^0_{d(l)}$ are given in Table 2. ΔH_{vb}, the heat of vaporization at the (normal) boiling point, was calculated as $R \cdot B \cdot \Delta Z_{vb}(t_b+273.15)^2/(t_b+C)^2$, where B and C are Antoine constants [$\ln P/\text{mmHg} = A - B/(t+C)$]. ΔZ_{vb} was calculated from one of two equations developed from data on hydrocarbon analogs (single methyl branching for the monomer, triple methyl branching for the dimer). ΔH_v (25°C) was calculated from the following equation derived from the "Watson correlation"[11]:

$$\Delta H_v(25°\text{C}) = \Delta H_{vb}[(t_c - 25)/(t_c - t_b)]^n.$$

The critical temperature t_c(°C) and exponent n were evaluated from t_b by means of equations developed from data on hydrocarbon analogs. ΔH^0_v (25°C) was obtained from ΔH_v (25°C), and ΔS^0_v (25°C) from ΔS_{vb}, by adding suitable "corrections". These "standard-state corrections" were also based on correlations of data on hydrocarbon analogs. The calculated values of δ_H differ from the input value (1000 cal·mole^{-1}) by at most 24 cal·mole^{-1}. The calculated values of $\Delta S^0_{d(l)}$ agree with the corresponding input values within 0.18 cal·K^{-1}·mole^{-1}. Thus the calculations are reasonably self-consistent.

For the dimer, ΔS_{vb} changes only slightly with $\Delta S^0_{d(l)}$ and is about 0.13 cal·K^{-1}·mole^{-1} below theory*. For the monomer, ΔS_{vb} ranges from 0.19 above theory for $\Delta S^0_{d(l)} = 29.0$ to 0.64 below theory for $\Delta S^0_{d(l)} = 30.0$ cal·K^{-1}·mole^{-1}. It is concluded that the best value for $\Delta S^0_{d(l)}$ is 29.3 ± 0.3 cal·K^{-1}·mole^{-1}. The equation for the equilibrium constant of liquid TMA becomes:

$$\ln K_{d(l)} = 14.7444 - 9762.5/T \tag{8}$$

The corresponding value for the boiling point of pure monomer is 8.1 ± 2.1°C. This appears to fit reasonably well between the boiling points of (monomeric) trimethylboron (−20.5) and (monomeric) trimethylgallium (55.7°C) of the same series. The boiling point of pure dimer is 131.95 ± 0.02°C.

The "observed heat of vaporization," as calculated from the vapor pressure

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* "Theoretical" values of ΔS_{vb} were read from plots (ΔS_{vb} *vs.* t_b) developed for hydrocarbon analogs. Since "pure monomer" and "pure dimer" are hypothetical liquids which boil without associating or dissociating, they are, like their hydrocarbon analogs, "normal" liquids. For a family of normal liquids, ΔS_{vb} is about 20 cal·K^{-1}·mole^{-1} for a t_b near 50° and increases moderately with rising t_b.

TABLE 2

VARIATION OF ΔS_{vb} AND OTHER DERIVED PROPERTIES OF TMA MONOMER AND TMA DIMER WITH VALUE ASSUMED FOR $\Delta S^0_{d(l)}$

Quantity	*Pure monomer*: $\Delta S^0_{d(l)}$ *(cal·K⁻¹·mole⁻¹)*				*Pure dimer*: $\Delta S^0_{d(l)}$ *(cal·K⁻¹·mole⁻¹)*			
	29.0	29.3	29.6	30.0	29.0	29.3	29.6	30.0
Antoine "*A*"	14.62451	14.56436	14.49028	14.37305	15.51107	15.52135	15.53024	15.55213
Antoine "*B*"	1717.58	1726.11	1726.67	1716.58	2972.26	2977.55	2982.10	2993.92
Antoine "*C*"	208.82	209.51	209.54	208.65	202.83	203.06	203.25	203.79
RMS % deviation[a]	0.005	0.003	0.003	0.004	0.004	0.005	0.005	0.005
t_b (°C)	6.12	8.13	10.23	13.14	131.97	131.95	131.95	131.90
ΔH_{vb} (cal·mole⁻¹)	5515	5482	5456	5433	8162	8165	8168	8175
ΔH^0_v (25°C) (cal·mole⁻¹)	5384	5377	5378	5391	9744	9748	9751	9759
δ_H (25°) (calcd., cal·mole⁻¹)	1024	1006	1006	1023				
δ_H (25°) (input, cal·mole⁻¹)	1000	1000	1000	1000				
ΔS_{vb} (calcd.)	19.75	19.49	19.26	18.98	20.15	20.16	20.16	20.18
ΔS_{vb} (theory)[b]	19.56	19.57	19.59	19.62	20.29	20.29	20.29	20.29
ΔS_{vb} (calcd.) − ΔS_{vb} (theory)	0.19	−0.08	−0.33	−0.64	−0.14	−0.13	−0.13	−0.11
ΔS^0_v (25°C)	19.28	19.09	18.94	18.76	24.45	24.46	24.46	24.48
δ_S (25°C) (calcd.)	14.11	13.72	13.41	13.03				
$\Delta S^0_{d(l)}$ (calcd.)	29.08	29.47	29.78	30.16				

[a] Root-mean-square % deviation between "experimental" and calculated vapor pressures. [b] Based on correlation developed for hydrocarbon analogs.

equation for the "real" alkyl (that is, the equilibrium mixture of monomer and dimer), is the net heat absorbed in the production of one mole of equilibrium vapor from equilibrium liquid. It consists partly of true heat of vaporization and partly of heat of dissociation. Since two gram-formula-weights of liquid AlR_3 will produce $(1+\alpha_g)$ moles of vapor [$2\alpha_g$ moles of monomer and $(1-\alpha_g)$ moles of dimer], it is easily shown that the following equations* are valid:

$$\Delta H^0_{v(obs)} = (\Delta H^0_{vD} + \alpha_g \cdot \Delta H^0_{d(g)} - \alpha_l \cdot \Delta H^0_{d(l)})/(1+\alpha_g) \tag{9}$$

$$\Delta H^0_{v(obs)} = [2\Delta H^0_{vM} - (1-\alpha_g)\Delta H^0_{d(g)} + (1-\alpha_l)\Delta H^0_{d(l)}]/(1+\alpha_g) \tag{10}$$

For TMA at 25°C, $\Delta H^0_{v(obs)}$ was calculated from the vapor pressure eqn. (Table 1, footnote *a*) as 9921 cal·(mole of vapor)$^{-1}$. The corresponding values calculated from eqns. (9) and (10), using $\Delta H^0_{vD}(25°C) = 9748$ and $\Delta H^0_{vM}(25°C) = 5377$ (Table 2), are 9820 and 9826 cal·(mole of vapor)$^{-1}$, respectively. The latter values agree well with each other and show reasonable agreement with the former value.

Consistency of K_d equations with other vapor pressure data on TMA

Henrickson and Eyman[5] reported vapor pressure data on TMA covering the range 17.6–47.7°C (mean temperature, $\bar{t}$, $=32.6°C$). They gave the equation:

$$\log_{10} P/\text{mmHg} = 8.3287 - 2159/T$$

which is rewritten for convenience as:

$$\ln P = 19.1775 - 4971.3/T \tag{11}$$

Vapor pressures were calculated from this equation at 5° intervals from 15 to 45°C. For each of these vapor pressures, vapor pressures of pure monomer and pure dimer were calculated using eqns. (6) and (8). Equations of the form $\ln P^0 = A - B/T$ were derived for pure monomer and pure dimer from the vapor pressures (best 2-constant fits). Values of the constants A and B, boiling points, and derived thermodynamic properties for pure monomer and pure dimer are given in Table 3. Heats of vaporization, $\Delta H_{v\bar{T}}$, calculated directly from the vapor pressure equations using estimated values of $\Delta Z_{v\bar{T}}$, were taken as applying at the midpoint of the experimental temperature range. (The heat of vaporization, as calculated from a vapor pressure equation of the form $\ln P = A - B/T$, is temperature independent except for the variation of the correction factor, ΔZ_v.) These heats of vaporization were extrapolated to the boiling points using correlations described earlier. The boiling point (7.1°C) and ΔS_{vb} (19.4 cal·K^{-1}·mole^{-1}) obtained for the pure monomer agree very well with the corresponding values developed from the McCullough data (8.13°C and 19.49 cal·K^{-1}·mole^{-1}), thus tending to confirm the $\Delta S^0_{d(l)}$ value of 29.3 cal·K^{-1}·mole^{-1}. The boiling point (124.7°C) obtained for the pure dimer is well below the value (131.95°C) from the McCullough data, while the ΔS_{vb} (20.9 cal·K^{-1}·mole^{-1}) is somewhat high. This neither confirms nor denies the $\Delta S^0_{d(l)}$ value of 29.3 since, as noted earlier, the derived properties of the dimer are affected only slightly by changes in $\Delta S^0_{d(l)}$. $\Delta H^0_{v(obs)}$ (32.6°C) was calculated from eqn. (11) as 9830 cal·(mole of vapor)$^{-1}$. The corresponding values calculated from eqns. (9) and (10) are 9840 and 9560 cal·(mole of vapor)$^{-1}$, respectively, in reasonable agreement.

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* If α_l is taken as zero, these equations reduce to eqns. (1) and (2) as given by Hay, Hooper and Robb[3].

TABLE 3

PROPERTIES OF TMA MONOMER AND TMA DIMER DERIVED FROM OTHER VAPOR PRESSURE DATA

Quantity	*Henrickson data*		*Laubengayer data*	
	Monomer	*Dimer*	*Monomer*	*Dimer*
A^a	16.3199	19.0239	16.0849	18.5416
B^a	2714.7	4929.8	2641.8	4780.1
RMS % Deviation	0.021	0.054	0.12	0.21
t_b (°C)	7.1	124.7	6.4	128.3
$\bar{t}$ (mean temp.)	32.6	32.6	46.5	46.5
$\Delta H_{v\bar{t}}$(cal·mole^{-1})	5100	9750	4880	9400
$\Delta H^0_{v\bar{t}}$	5230	9750	5060	9400
ΔH_{vb}	5430	8330	5410	8180
ΔS_{vb} (calcd.)	19.4	20.9	19.4	20.4
ΔS_{vb} (theory)	19.6	20.2	19.6	20.3

[a] $\ln P^0 = A - B/T$.

Laubengayer and Gilliam[9] obtained vapor pressure data on TMA over the range 23–70° ($\bar{t}$=46.5°) and gave the equation $\log_{10} P = 8.1520 - 2104/T$ which is rewritten as:

$$\ln P = 18.7707 - 4844.6/T \tag{12}$$

Vapor pressures were calculated from this equation at 10° intervals from 20 to 70°C. Values of the constants A and B, boiling points, and thermodynamic properties for pure monomer and pure dimer, derived as described in the previous paragraph, are listed in Table 3. The boiling point (6.4°C) and ΔS_{vb} (19.4) for the pure monomer again show satisfactory agreement with the corresponding values developed from the McCullough data and are thus consistent with the $\Delta S^0_{d(l)}$ value of 29.3 cal·K^{-1}·mole^{-1}. The boiling point obtained for the pure dimer (128.3°C) is closer to the corresponding value from the McCullough data (131. 95°C) than is the value from the Henrickson data (124.7°C). ΔS_{vb} for the pure dimer (20.4 cal·K^{-1}·mole^{-1}) is very close to theory. $\Delta H_{v(obs)}$, (46.5°C) was calculated from eqn. (12) as 9530 cal·(mole of vapor)$^{-1}$. The corresponding values calculated from eqns. (9) and (10) are 9540 and 9270 cal·(mole of vapor)$^{-1}$, respectively, again in reasonable agreement.

Calculation of $\Delta H^0_{d(l)}$ *from eqn.* (10)

In arriving at their estimate of 16.3±1.5 kcal·(mole of dimer)$^{-1}$ for $\Delta H^0_{d(l)}$ of TMA, Hay *et al.*[3] applied eqn. (10) using the estimated value 6500 cal·mole^{-1} for the heat of vaporization of the monomer. Since the boiling point of the monomer has been shown to be about 8.1°C, this $\Delta H_{v(b)}$ would correspond to a $\Delta S_{v(b)}$ of 23.1 cal·K^{-1}·mole^{-1}, which is well above the value to be expected for a normal liquid of this boiling point (about 19.6 cal·K^{-1}·mole^{-1}). Putting it another way, a normal liquid having a $\Delta H_{v(b)}$ of 6500 cal·mole^{-1} would have a boiling point of about 53°C, which is certainly too high for TMA monomer. Caution should be exercised in the calculation of $\Delta H^0_{d(l)}$ from eqn. (10) since any error in ΔH^0_{vM} is doubled.

For the Henrickson vapor pressure data, eqn. (10) gives $\Delta H^0_{d(l)} = 19.68$ kcal·

TABLE 4

EQUILIBRIUM CONSTANT[a] AND PERCENT DISSOCIATION OF LIQUID TMA

Temp. (°C)	$K_{d(l)}$	*TMA[b] dissociated (%) in aliphatic hydrocarbon solution at TMA mole fraction of:*						
		1	0.5	0.2	0.1	0.01	0.001	0.0001
0	7.613×10^{-10}	0.00138	0.00239	0.00414	0.00601	0.0195	0.0617	0.195
10	2.690×10^{-9}	0.00259	0.00449	0.00778	0.0113	0.0366	0.116	0.366
20	8.720×10^{-9}	0.00467	0.00809	0.0140	0.0203	0.0658	0.209	0.658
30	2.616×10^{-8}	0.00809	0.0140	0.0243	0.0352	0.114	0.361	1.14
40	7.315×10^{-8}	0.0135	0.0234	0.0406	0.0589	0.191	0.603	1.89
50	1.920×10^{-7}	0.0219	0.0379	0.0657	0.0954	0.309	0.975	3.05
60	4.753×10^{-7}	0.0345	0.0597	0.103	0.150	0.485	1.53	4.76
70	1.117×10^{-6}	0.0528	0.0915	0.158	0.230	0.743	2.33	7.20
80	2.499×10^{-6}	0.0790	0.137	0.237	0.344	1.11	3.47	10.6
90	5.350×10^{-6}	0.116	0.200	0.346	0.503	1.62	5.04	15.1
100	1.100×10^{-5}	0.166	0.287	0.496	0.720	2.31	7.14	20.9
110	2.177×10^{-5}	0.233	0.403	0.698	1.01	3.24	9.90	28.0
120	4.161×10^{-5}	0.323	0.558	0.963	1.40	4.45	13.4	36.4
130	7.704×10^{-5}	0.439	0.758	1.31	1.90	6.00	17.8	45.7
140	1.384×10^{-4}	0.588	1.02	1.75	2.53	7.96	23.1	55.5
150	2.420×10^{-4}	0.778	1.34	2.31	3.34	10.4	29.3	65.0
160	4.122×10^{-4}	1.02	1.75	3.00	4.33	13.3	36.2	73.7
170	6.855×10^{-4}	1.31	2.25	3.86	5.55	16.8	43.9	80.9
180	1.115×10^{-3}	1.67	2.86	4.90	7.03	20.9	51.8	86.6

[a] $\ln K_{d(l)} = 14.7444 - 9762.5/T$. [b] TMA was taken as the monomer in computing mole fractions.

(mole of dimer)$^{-1}$ (at 32.6°, $\Delta H^0_{v(obs)} = 9.83$, $\Delta H^0_{v(M)} = 5.23$, $\Delta H^0_{d(g)} = 20.40$ kcal · mole^{-1}, $\alpha_g = 0.00863$, $\alpha_l \approx 1$). For the Laubengayer vapor pressure data, eqn. (10) gives $\Delta H^0_{d(l)} = 19.67$ kcal · (mole of dimer)$^{-1}$ (at 46.5°, $\Delta H^0_{v(obs)} = 9.53$, $\Delta H^0_{v(M)} = 5.06$ kcal · mole^{-1}, $\alpha_g = 0.0126$, $\alpha_l \approx 1$). Both of these values agree well with the value $19.4_0 \pm 0.3_0$ kcal · mole^{-1} developed earlier in the paper.

Tabulation of degrees of dissociation for liquid TMA

Values of the equilibrium constant for liquid TMA calculated from eqn. (8) at 10° intervals are given in column 2 of Table 4. The degree of dissociation of pure liquid TMA was calculated from $K_{d(l)}$ using the equation $\alpha_l = [K_{d(l)}/(4 + K_{d(l)})]^{\frac{1}{2}}$. These values, expressed as percent of TMA dissociated, are listed in column 3. A comparison of these values with corresponding values for TEA[1] shows that TEA is about 17 times as dissociated as TMA at 20, about 13 times at 70, about 10 times at 120, and about 8 times as dissociated as TMA at 170°C. Values of % TMA dissociated at various mole fractions in aliphatic hydrocarbon solution are listed in the remaining columns of Table 4.

TRIETHYLALUMINUM

Equilibrium constant for gaseous TEA

The equilibrium constant for liquid TEA, as reported in the first paper of this series[1], is given by the equation

$$\ln K_{\mathrm{d(l)}} = 16.1973 - 8520.5/T \tag{13}$$

The following values for TEA were derived from this equation: $\Delta H^0_{\mathrm{d(l)}} = 16.9_3 \pm 0.2_3$ kcal·(mole of dimer)$^{-1}$ and $\Delta S^0_{\mathrm{d(l)}} = 32.1_9 \pm 0.6_3$ cal·K^{-1}·(mole of dimer)$^{-1}$. From hydrocarbon simulation, δ_H(25°C) for TEA is taken as 1.2_4 kcal·(mole of dimer)$^{-1}$ and δ_S(25°C) as 13.3_2 cal·K^{-1}·(mole of dimer)$^{-1}$. It follows that $\Delta H^0_{\mathrm{d(g)}} = \Delta H^0_{\mathrm{d(l)}} + \delta_H = 16.9_3 + 1.2_4 = 18.1_7$ kcal·(mole of dimer)$^{-1}$ while $\Delta S^0_{\mathrm{d(g)}} = \Delta S^0_{\mathrm{d(l)}} + \delta_S = 32.1_9 + 13.3_2 = 45.5_1$ cal·K^{-1}·(mole of dimer)$^{-1}$. The following expression for the equilibrium constant of gaseous TEA was derived from these values:

$$\ln K_{\mathrm{d(g)}} = 22.9016 - 9143.5/T \tag{14}$$

Comparison of derived $K_{d(g)}$ expression for TEA with literature values

Laubengayer and Gilliam[9] performed vapor density determinations on TEA over the temperature range 145–200°C and reported molecular weights, but not equilibrium constants, derived from these data. Since their paper does not include the original data, the latter were obtained from Gilliam's thesis[12] and are listed in the first four columns of Table 5. It is noted that the data point at 145.5°C, included in the thesis, was omitted from the paper. The degree of dissociation of gaseous TEA, α_g, (column 5) was calculated from the equation:

TABLE 5

$K_{\mathrm{d(g)}}$ FOR TEA CALCULATED FROM MEASUREMENTS OF LAUBENGAYER AND GILLIAM[9,12]

Temp. (°C)	*Pressure (mmHg)*	*Gas volume (l)*	*Gas weight (g)*	α_g	$K_{d(g)}$
145.5	113.7	0.7098	0.4082	0.7292	0.680
150.6	119.0	0.7101	0.4105	0.7787	0.965
165.5	125.7	0.7098	0.4082	0.8245	1.405
165.5	126.2	0.7101	0.4105	0.8223	1.387
185.2	133.3	0.7101	0.4105	0.8421	1.710
200.0	136.6	0.7101	0.4105	0.8286	1.575

$$1 + \alpha_g = \frac{3.6616\, P \cdot V}{T \cdot W_g} \tag{15}$$

where P = pressure (mmHg), V = volume (l), T = K, and W_g = weight (g). The equilibrium constant, $K_{\mathrm{d(g)}}$, (column 6) was calculated from:

$$K_{\mathrm{d(g)}} = 4P \cdot \alpha_g^2 / 760(1 - \alpha_g^2) \tag{16}$$

The plot of $\ln K_{\mathrm{d(g)}}$ *vs.* $1/T$ (Fig. 1) is not linear but shows a marked downward curvature with increasing temperature, presumably due to decomposition. Since the plot has no linear portion, it is difficult to make a reliable estimate of the slope of the curve and hence of $\Delta H^0_{\mathrm{d(g)}}$. Dashed line A, drawn through the two lowest temperature points, which should have been least affected by decomposition, leads to a $\Delta H^0_{\mathrm{d(g)}}$ value

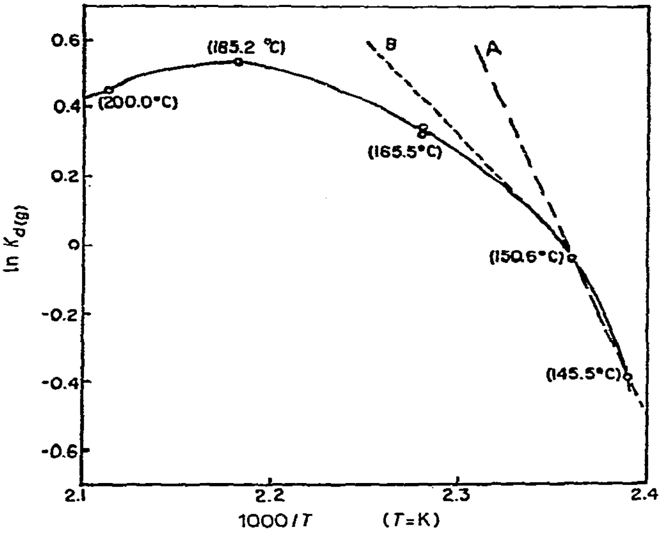

Fig. 1. $K_{d(g)}$ for TEA from measurements of Laubengayer and Gilliam.

of 24.4 kcal · (mole of dimer)$^{-1}$. This should not be considered a good estimate of $\Delta H^0_{d(g)}$, based as it is on two points only 5°C apart. On the whole, however, the data of Laubengayer and Gilliam agree reasonably well with the derived value $\Delta H^0_{d(g)} = 18.1_7$ kcal · mole^{-1}.

Dashed line B in Fig. 1 corresponds to $\Delta H^0_{d(g)} = 11$ kcal · (mole of dimer)$^{-1}$ as estimated by Hay, Hooper, and Robb[2]. Since this estimate was based only on the data included in the Laubengayer and Gilliam paper (Hay *et al.*, did not list Gilliam's thesis among their references), the 145.5°C point was evidently not considered in making the estimate. It is obvious from Fig. 1 that the complete data of Laubengayer and Gilliam do not support a $\Delta H^0_{d(g)}$ as low as 11 kcal · (mole of dimer)$^{-1}$.

Hay, Hooper, and Robb[2] measured the vapor pressure of TEA over the range 60–120° and found it to obey the equation

$$\log_{10} P/\text{mmHg} = 10.85 - 3613/T \tag{17}$$

They also reported vapor density data at saturation pressure for the range 40–100°C, determining $\Delta H^0_{d(g)}$ as 10.2 ± 1.0 kcal · (mole of dimer)$^{-1}$ from a plot of $\log_{10} K_{d(g)}$ *vs.* $1/T$. Although they did not include an equation for $K_{d(g)}$, their equilibrium constants may be represented by the equation:

$$\ln K_{d(g)} = 11.804 - 5173/T \tag{18}$$

Both $\Delta H^0_{d(g)}$ (10.3 kcal · mole^{-1}) and $\Delta S^0_{d(g)}$ (23.5 cal · K^{-1} · mole^{-1}) corresponding to this equation disagree markedly with the derived values [18.1_7 kcal · mole^{-1} for $\Delta H^0_{d(g)}$ and 45.5_1 cal · K^{-1} · mole^{-1} for $\Delta S^0_{d(g)}$]. Degree of dissociation of TEA vapor at saturation pressure, $\alpha_{g(sp)}$, was calculated at several temperatures from the equation $\alpha_g = [K_{d(g)}/(K_{d(g)} + 4P/760)]^{\frac{1}{2}}$. The results are shown in Table 6 where they are compared with similar results calculated from eqn. (14) and with values for TMA. According to eqn. (14), $\alpha_{g(sp)}$ increases gradually with rising temperature. This seems reasonable since $\alpha_{g(sp)}$ for TMA increases with rising temperature, although at a faster

TABLE 6

VARIATION OF α_g (SATURATION PRESSURE) WITH TEMPERATURE

Temp. (°C)	$\alpha_{g(sp)}$ *of TEA from:*		$\alpha_{g(sp)}$ *of TMA*
	Eqn. 18	*Eqn.* 14	
40	0.945	0.794	0.0106
80	0.852	0.835	0.0281
120	0.720	0.863	0.0624
160	0.582	0.883	0.120
200	0.466	0.898	0.208

TABLE 7

$K_{d(g)}$ FOR TEA CALCULATED FROM MEASUREMENTS OF HAY, HOOPER AND ROBB

Temp. (°C)	*Pressure*[a] (*mmHg*)	*Volume* (*l*)	*Weight* (*mg*)	$\alpha_{g(sp)}$	$K_{d(g)}$
40	0.205	0.1658	0.22	0.809	0.00205
50	0.467	0.1660	0.49	0.793	0.00418
60	1.012	0.1662	0.985	0.876	0.0176
70	2.095	0.1664	2.01	0.850	0.0288
80	4.162	0.1666	3.98	0.806	0.0407
90	7.961	0.1668	7.45	0.797	0.0730
100	14.71	0.1670	13.4	0.799	0.136

[a] Calculated from eqn. (17).

rate. According to eqn. (18), however, $\alpha_{g(sp)}$ decreases rather rapidly with rising temperature.

Since it does not seem reasonable that saturated TEA vapor should become more associated with rising temperature, particularly at a rather rapid rate, the vapor density data of Hay *et al.* were recalculated to determine whether a different interpretation of the data is possible. The experimental data are listed in the first four columns of Table 7. For the sake of consistency (α_g is quite sensitive to variations in pressure), pressures were recalculated from Hay's vapor pressure equation and expressed to three decimal places. Values of α_g and $K_{d(g)}$ calculated from eqns. (15) and (16) are listed in the last two columns. Least-squares analysis of the $K_{d(g)}$ values yields the equation:

$$\ln K_{d(g)} = 19.7446 - 8075.7/T \qquad (19)$$

Values of $\Delta H^0_{d(g)}$ and $\Delta S^0_{d(g)}$ calculated from the coefficients, together with their 95% confidence limits, are $\Delta H^0_{d(g)} = 16.05 \pm 3.13$ kcal · (mole of dimer)$^{-1}$ and $\Delta S^0_{d(g)} = 39.24 \pm 9.17$ cal · K^{-1} · (mole of dimer)$^{-1}$. The corresponding derived values [$\Delta H^0_{d(g)} = 18.1_7$ and $\Delta S^0_{d(g)} = 45.5_1$] lie well within these limits. Ln $K_{d(g)}$ is plotted against $1000/T$ in Fig. 2. Solid line C, a plot of eqn. (19), intersects broken line D, representing eqn. (14), near the midpoint of the experimental temperature range. It is concluded that the

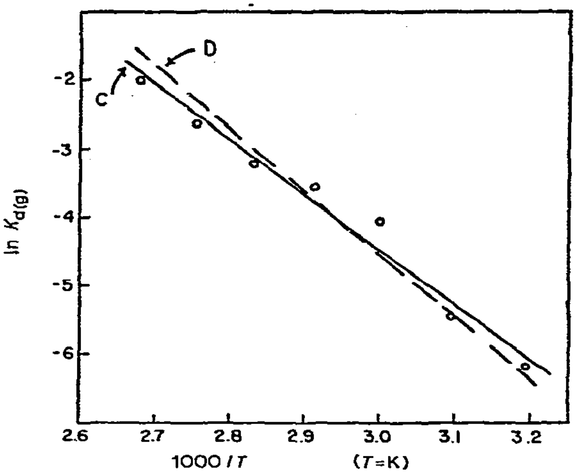

Fig. 2. $K_{d(g)}$ for TEA calculated from measurements of Hay, Hooper and Robb.

recalculated vapor density data of Hay, Hooper, and Robb agree reasonably well with eqn. (14).

Evaluation of $K_{d(g)}$ equations for TEA by means of vapor pressure data

The three candidate $K_{d(g)}$ equations [eqns. (14), (18), and (19)] were tested by applying them to the vapor pressure data of Hay, Hooper and Robb [eqn. (17)]. Values of the constants A and B, boiling point, and thermodynamic properties for pure TEA dimer, derived as described previously for TMA, are listed in Table 8. The value of ΔS_{vb} (entropy of vaporization at the normal boiling point) derived from eqn. (14) agrees closely with theory (as based on hydrocarbon analogs) while the boiling point of 267.1°C is reasonable (the boiling point of TEA dimer was estimated independently as 275 ± 10°C). The ΔS_{vb} of 26.3 from eqn. (19) is too high by a considerable margin and the boiling point (236.8°C) too low. The ΔS_{vb} of 39.1 derived from

TABLE 8

COMPARISON OF PROPERTIES OF TEA DIMER DERIVED FROM HAY'S VAPOR PRESSURE EQUATION FOR VARIOUS $K_{d(g)}$ EQUATIONS

	$K_{d(g)}$ equation		
	Eqn. (18)	*Eqn.* (19)	*Eqn.* (14)
$\Delta H^0_{d(g)}$ (cal·mole^{-1})	10280	16050	18170
$\Delta S^0_{d(g)}$ (cal·K^{-1}·mole^{-1})	23.46	39.24	45.51
$K_{d(l)}$ eqn. used	[a]	[a]	[b]
A^c	30.0021	23.4781	20.9641
B^c	10981	8590.4	7742.0
t_b (°C)	196.8	236.8	267.1
ΔH_v (90°C) (cal·mole^{-1})	21820	17070	15385
ΔH_{vb}	18385	13435	11465
ΔS_{vb} (calcd.)	39.1	26.3	21.2
ΔS_{vb} (theory)	20.7	21.1	21.4

[a] $\ln K_{d(l)} = 7.9759 - 5535.0/T$. [b] See eqn. (13). [c] $\ln P^0_D = A - B/T$.

eqn. (18) is almost twice the theoretical value while the boiling point (196.8°C) is much too low. Equation (14), therefore, shows excellent thermodynamic consistency with the Hay vapor pressure equation while eqn. (19) shows only a fair consistency, and eqn. (18) is thermodynamically inconsistent with the Hay equation. These conclusions are unaltered if the $K_{d(l)}$ equation used in the derivation is changed. Table 9 lists values derived from eqn. (18) using four different $K_{d(l)}$ equations. Despite the fact that $\alpha_l(90°)$ is varied over a ten-fold range, ΔS_{vb} remains in the narrow range 38.8 to 40.2 while t_b varies only between 193.6 and 197.8°C. It is evident that the properties of TEA dimer are primarily related to the values of the constants $\Delta H^0_{d(g)}$ and $\Delta S^0_{d(g)}$. It has also been determined that the properties of TEA monomer are primarily related to the values of $\Delta H^0_{d(l)}$ and $\Delta S^0_{d(l)}$.

TABLE 9

EFFECT OF USING DIFFERENT $K_{d(l)}$ EQUATIONS ON PROPERTIES OF TEA DIMER DERIVED FROM HAY'S VAPOR PRESSURE EQUATION [$K_{d(g)}$ GIVEN BY EQN. (18)]

	$K_{d(l)}$ Equation			
		$\ln K_{d(l)} = A_l - 5535.0/T$		
	Eqn. (13)	$A_l = 5.6733$	$A_l = 7.9759$	$A_l = 10.2799$
$\Delta H^0_{d(l)}$ (cal·mole^{-1})	16930	11000	11000	11000
$\Delta S^0_{d(l)}$	32.19	11.27	15.85	20.43
α_l (90°)	0.0132	0.00418	0.0132	0.0418
A^a	30.1237	29.8438	30.0021	30.5026
B^a	11024	10931	10981	11140
t_b (°C)	196.2	197.8	196.8	193.6
ΔH_v (90°C) (cal·mole^{-1})	21905	21720	21820	22140
ΔH_{vb}	18475	18270	18385	18750
ΔS_{vb} (calcd.)	39.4	38.8	39.1	40.2
ΔS_{vb} (theory)	20.7	20.7	20.7	20.7

[a] $\ln P^0_D = A - B/T$.

Laubengayer and Gilliam[9] measured vapor pressures of TEA over the range 110–140°C ($\bar{t}$ 125°C) and gave the equation $\log_{10} P = 10.784 - 3625/T$ which is rewritten as:

$$\ln P = 24.8311 - 8346.9/T \tag{20}$$

Application of the three $K_{d(g)}$ equations to this vapor pressure equation gave results similar to those obtained with the Hay equation: ΔS_{vb} and t_b for TEA dimer are 22.0 cal·K^{-1}·mole^{-1} and 276.7°C for eqn. (14); 27.3 cal·K^{-1}·mole^{-1} and 245.0°C for eqn. (19); and 39.4 cal·K^{-1}·mole^{-1} and 205.3°C for eqn. (18). It is concluded that on the basis of thermodynamic consistency with vapor pressure data, eqn. (14) is much to be preferred over eqn. (19) while eqn. (18) is completely unacceptable.

Hay *et al.*[3] applied eqn. (9) to TEA using their $\Delta H^0_{d(g)}$ value of 10.2 kcal·(mole of dimer)$^{-1}$ and obtained 21.3 kcal·mole^{-1} for the heat of vaporization of the dimer (at 90°C). They observed that this value of $\Delta H^0_{vD}(90°)$ is "apparently large" but did not pursue the matter further. Calculations show that a "normal" liquid whose ΔH_v

is 21.3 kcal · mole^{-1} at 90°C will have a boiling point (at 760 mmHg) of about 345°C. Since this is surely too high for the boiling point of TEA dimer, the $\Delta H^0_{d(g)}$ value of 10.2 kcal · mole^{-1} cannot be correct. By contrast, when the $\Delta H^0_{d(g)}$ value of 18.1_7 kcal · (mole of dimer)$^{-1}$ is used in eqn. (9), the resulting value of ΔH^0_{vD}(90°) is 15.35 kcal · mole^{-1}. This corresponds to a boiling point of about 265°C which is reasonable. (In these calculations, account was taken of the decrease of ΔH^0_{vD} with increasing temperature.)

Consistency of derived $K_{d(l)}$ and $K_{d(g)}$ equations for TEA with vapor pressure data

Values of the constants A and B, boiling point, and thermodynamic properties for pure TEA monomer and pure dimer were derived from preferred eqns. (13) and (14) as described earlier for TMA. The results obtained using two different vapor pressure equations (Hay, Laubengayer) are listed in Table 10. For the monomer, the ΔS_{vb} values of 18.9 and 19.7 cal · K^{-1} · mole^{-1} are reasonably close to theory, although both are on the low side. The monomer boiling points of 124.5 and 132.1°C, while somewhat high*, are also reasonable. For the dimer, as already mentioned, the ΔS_{vb} values are close to theory and the boiling points are reasonable. For the Hay vapor pressure data, $\Delta H^0_{v(obs)}$(90°) was calculated as 16520 from eqn. (17), 16540 from eqn. (9), and 16340 cal · mole^{-1} from eqn. (10). For the Laubengayer vapor pressure data, $\Delta H^0_{v(obs)}$(125°) was calculated as 16530 from eqn. (20), 16590 from eqn. (9), and 16210 cal · mole^{-1} from eqn. (10). For each of the vapor pressure equations, the agreement among the three values of $\Delta H^0_{v(obs)}$ is reasonably good. It is concluded that eqns. (13) and (14) show satisfactory agreement with both the Hay and the Laubengayer vapor pressure equations.

Vapor pressure data on TEA of precision comparable to the McCullough data on TMA are lacking. Of the available data, the Hay and Laubengayer equations appear to be most nearly correct. The $\Delta H_{v\bar{T}}$ (molar heat of vaporization at the mean

TABLE 10

PROPERTIES OF TEA MONOMER AND DIMER DERIVED FROM VAPOR PRESSURE EQUATIONS USING PREFERRED[a] $K_{d(l)}$ AND $K_{d(g)}$ EQUATIONS

Quantity	*Hay equation*[b]		*Laubengayer equation*[c]	
	Monomer	*Dimer*	*Monomer*	*Dimer*
A[d]	17.1502	20.9641	17.2200	21.1038
B[d]	4182.5	7742.0	4290.1	7957.2
t_b (°C)	124.5	267.1	132.1	276.7
$\bar{t}$ (mean temp.)	90	90	125	125
$\Delta H_{v\bar{T}}$	8089	15385	8104	15810
$\Delta H^0_{v\bar{T}}$	8129	15385	8172	15810
ΔH_{vb}	7528	11465	7976	12090
ΔS_{vb} (calcd.)	18.9	21.2	19.7	22.0
ΔS_{vb} (theory)	20.4	21.4	20.5	21.4

[a] $\ln K_{d(l)} = 16.1973 - 8520.5/T$; $\ln K_{d(g)} = 22.9016 - 9143.5/T$. [b] $\ln P = 24.983 - 8319/T$ ($t_b = 180.2$°C). [c] $\ln P = 24.831 - 8347/T$ ($t_b = 185.5$°C). [d] $\ln P^0 = A - B/T$.

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* The normal boiling point of TEA monomer was independently estimated as 120±7°C.

experimental temperature) values agree well (both are about 16.5 kcal·mole^{-1}). Although $t_{b(\text{extr.})}$ (extrapolated boiling point at 760 mmHg) is somewhat low (180.2°C) for the Hay equation, the $t_{b(\text{extr.})}$ for the Laubengayer equation (185.5°C) agrees well with an experimental value of the boiling point (186.6°C) determined in this laboratory[13]. Other vapor pressure equations from the literature show ΔH_{vT}-values ranging from 15.5 down to 12.9 kcal·mole^{-1} and $t_{b(\text{extr.})}$ values ranging from 192 to 206°C. These equations are believed to be less representative of TEA and were not considered in the present treatment.

Calculation of $\Delta H^0_{d(l)}$ from eqn. (10)

In applying eqn. (10) to TEA, Hay *et al.*[3] used the low $\Delta H^0_{d(g)}$ value of 10.2 kcal·mole^{-1} and the estimated value of 9.5 kcal·mole^{-1} for ΔH_v of the monomer to obtain $\Delta H^0_{d(l)} = 12.5$ kcal·(mole of dimer)$^{-1}$. This value of ΔH_v is too large since a normal liquid having $\Delta H_v(90°) = 9.5$ kcal·mole^{-1} would have a boiling point of about 142° which is too high for TEA monomer (for example, TEA monomer must surely boil lower than TMA dimer whose boiling point is ~132°C).

Using $\Delta H^0_{d(g)} = 18.17$ kcal·mole^{-1}, eqn. (10) gives, for the Hay vapor pressure data, $\Delta H^0_{d(l)} = 17.27$ kcal·(mole of dimer)$^{-1}$ (at 90°C, $\Delta H_{v(\text{obs})} = 16.52$, $\Delta H^0_{vM} = 8.13$ kcal·mole^{-1}, $\alpha_g = 0.8427$, $\alpha_l = 0.0132$). For the Laubengayer vapor pressure data, eqn. (10) gives $\Delta H^0_{d(l)} = 17.55$ kcal·(mole of dimer)$^{-1}$ (at 125°, $\Delta H_{v(\text{obs})} = 16.53$, $\Delta H^0_{vM} = 8.17$ kcal·mole^{-1}, $\alpha_g = 0.8881$, $\alpha_l = 0.0371$). Both values of $\Delta H^0_{d(l)}$ agree reasonably well with the experimental value of 16.93 ± 0.23 kcal·(mole of dimer)$^{-1}$.

EXPERIMENTAL

TMA of 98.0% purity was supplied by Ethyl Corporation. The TEA, also supplied by Ethyl Corporation, was shown by chemical analysis to contain 95.1% $(C_2H_5)_3Al$, 1.4% $(C_2H_5)_2AlH$, and 3.5% $(C_4H_9)_3Al$. n-Hexadecane (Humphrey Chemical Co.) of 99+ % purity was deoxygenated by bubbling dry nitrogen through it for two hours and was stored over molecular sieves.

The apparatus used in the heat of mixing experiments has been described elsewhere[14]. Solutions of TMA and TEA in hexadecane, each about 2.9 molal, were prepared accurately by weight. At 25°C, 6 ml of the TEA solution was added to 35 ml of the TMA solution in the calorimeter (the exact weights used were determined) and the temperature rise (about 0.3–0.4°C) measured accurately. The heat evolved per mole of TEA dimer added was calculated from the temperature rise, the total heat capacity, and the weight of TEA solution added.

Despite the preponderance of methyl groups in the mixture, some ethyl groups continued to occupy bridging positions. Yamamoto and Hayamizu[15] determined from PMR measurements that, in TMA–TEA mixtures at room temperature, the tendency of the methyl group to occupy the bridge position is six times as large as that of the ethyl group. Utilizing this "bridge-bonding factor" in conjunction with a detailed analysis of the different dimeric species present in the mixture, the net conversion of ethyl bridges to methyl bridges for the experiment (typically about 72%) was calculated. The heat evolved per mole of TEA dimer added divided by the net fraction converted gave the heat evolved per mole of ethyl bridges converted to methyl bridges. Duplicate values thus obtained are 2.44 and 2.50 kcal·(mole of dimer)$^{-1}$.

Thermal effects accompanying the mixing other than changes in bridging (heats of dilution, physical mixing, and exchange of terminal groups) were considered to be quite small and were neglected. It was also assumed that one mole of "mixed methyl–ethyl bridges" is thermally equivalent to 1/2 mole of "ethyl bridges" plus 1/2 mole of "methyl bridges." It follows that in n-hexadecane solution, $\Delta H^0_{d(l)}$ (TMA) − $\Delta H^0_{d(l)}$ (TEA) = 2.47 kcal·(mole of dimer)$^{-1}$. This result is assumed to apply also to the pure alkyls since solvation effects between aluminum alkyls and saturated hydrocarbons are believed to be negligible. This result agrees with the statement by Hoffmann[16], based on calorimetric experiments in benzene solution, that "the energy of association across ethyl bridges must be lower (than that across methyl bridges) by 1.0–1.3 kcal·(mole of monomer)$^{-1}$"; that is, $\Delta H^0_{d(l)}$ (TMA) − $\Delta H^0_{d(l)}$ (TEA) = 2.0–2.6 kcal·(mole of dimer)$^{-1}$.

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