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MONOMER–DIMER EQUILIBRIA OF TRIETHYLALUMINIUM

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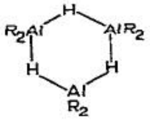
SUMMARY

The association–dissociation equilibria for trimethyl- and triethylaluminium are discussed in order to resolve the apparently anomalous range of values quoted in the literature. Thermodynamic liquid–vapour equilibria data, the temperature dependence of the NMR spectra, and the range of Arrhenius parameters listed for the addition reactions of the tri-n-alkylaluminiums to n-alkenes are considered.

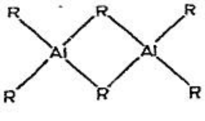
INTRODUCTION

Along with many of the compounds of the Group III elements organoaluminium compounds are electron deficient and exhibit a marked tendency to expand their co-ordination from three to four, either by existing as associated species or by complexing with Lewis bases. Both methods are effective in reducing the reactivity of the aluminium compound.

As a result of this tendency to associate, dialkyl aluminium hydrides are predominantly trimeric[1,2] with bridging hydrogen atoms, *i.e.*,



The nature of the alkyl group has little effect on the degree of association. Tri-n-alkylaluminium compounds are dimeric[2] with a boron hydride structure, *i.e.*,



as determined for trimethylaluminium in the vapour phase by electron diffraction[3], in the solid phase by X-ray diffraction[4], and in solution by IR spectroscopy[5]. The

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dimers are held together by bridging alkyl groups and the bonding produced by the overlap of the sp^3 hybridised orbitals of the aluminium atoms with those of the carbon atom of the alkyl group. This structure is unique for alkylaluminium compounds, since, for example, trialkylboron compounds are monomeric. Progressive substitution of the hydrogen atoms in the diborane molecule with alkyl groups can be accommodated in the terminal positions up to the symmetrical tetraalkylboron hydride, but further substitution, which must take place in the bridge position, cannot be accommodated without the complete collapse of the dimer structure, and it would appear that boron compounds cannot form stable alkyl bridges. It has been proposed that there are four factors which determine the stability of the dimer structure held together by alkyl bridge bonds[4]. Association is favoured by:

(1). a large electronegativity difference between the metal and carbon;
(2). a low energy difference between the *s* and *p* orbitals in the valence shell of the metal;
(3). a strong single bond between the metal and carbon atoms;
(4). low inner shell repulsion between the metal atoms at the molecular separation required by the geometry of the dimer molecule.

The first two effects are unfavourable in the case of the alkylboron compounds while the last two become increasingly unfavourable as the atomic number of the metal increases. Accordingly the trialkyl compounds of boron, gallium, indium, and thallium are monomeric[6], and with aluminium alone does the interplay of all four effects allow dimerisation. Organoaluminium compounds thus occupy a unique position as models for the effect of molecular structure on the strength of the electron deficient bridge bond.

The degree of association and the strength of the bridge bond are very dependent on the nature of the alkyl groups, in that tri-n-alkyl compounds are essentially dimeric[7] but the extent of association decreases as the homologous series is ascended, presumably due to the increased steric interaction. Accordingly methyl groups will preferentially displace ethyl bridges[2], and methyldiisobutylaluminium dimerises entirely through bridging methyl groups[2]. α and β branched trialkyl compounds of aluminium are monomeric[2,7,8].

Triarylaluminium compounds are also associated species. Triphenylaluminium is dimeric[9] with the bridge phenyl groups in a plane perpendicular to that of the aluminium atoms and the terminal phenyl groups. Some distortion of the bridge phenyl groups suggest that there is some π bonding participating in the bridge. Tricyclopropylaluminium also exhibits π bonding and this, it is reported[10], leads to the most stable hydrocarbon bridge known.

Many of the reactions of the alkylaluminium compounds arise from their electron deficient nature and also from the relatively low energy of the Al–C bond (65 kcal/mole) compared with that of Al–O bond (138 kcal/mole). Reactivity reaches a maximum with the uncoordinated species while substitution with groups such as –F, –Cl, –Br, –OMe, $-NR_2$, which are capable of co-ordination within the molecule, reduces it considerably. In an analogous manner the dimerisation of the molecules inhibit certain of their addition reactions, and in all cases the reactive species have been shown to be monomer, and as such only present in equilibrium amounts with the dimer, *i.e.*:

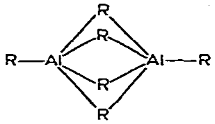
$$Al_2R_6 \rightleftharpoons 2\,AlR_3$$

The importance of the dissociation equilibrium in determining the reactivity of the alkylaluminium compounds is reflected in the detail to which they have been studied[11-20], yet there exists considerable apparent disagreement in the measured thermodynamic constants of the equilibria. Critical evaluation of the data is clearly required.

DISCUSSION

(1). *NMR studies*

NMR spectroscopy has been reasonably successful in investigating the details of the monomer–dimer equilibrium of trimethylaluminium[13,14,21-27]. The spectra show a sharp singlet at room temperature with a chemical shift τ of 10.3, but as the temperature is reduced the line broadens and by $-60°$ it has split into two at τ values 9.50 and 10.65. At room temperature all the methyl groups are equivalent from the time scale of NMR spectroscopy (10^{-3} sec) and only at the lower temperature can a clear distinction be made between terminal and bridge groups. The average life time of each configuration was calculated and used to determine a unimolecular rate constant for the rate determining step in the exchange reaction. An Arrhenius plot of the rate constants, over the temperature range -10 to $-60°$ gave an activation energy of 15.6 kcal/mole for this process[26]. Muller and Pritchard[23], however, have invoked two possible mechanisms for the interchange process which do not involve the monomer–dimer equilibrium mechanism, *i.e.* (*i*) rupture of one bridge bond only followed by it reforming with a different alkyl group, and (*ii*) deformation of the molecule resulting in the formation of a transition state with four methyl bridges, *i.e.*:



These, they considered more likely than the monomeric intermediate since the activation energy of the exchange (6–14 kcal/mole)[23] was considerably less than the heat of dissociation in the vapour phase (20 kcal/mole)[11]. However, a study of the temperature dependence of the interchange of alkyl groups between different trialkylaluminium compounds by Ramey *et al.*[26] suggest that at least one bridge bond must rupture in the rate determining step of the interchange, while a study by Poole *et al.*[27] using ^{27}Al magnetic resonance indicated that it was dependent on the monomer–dimer equilibrium and so involved the rupture of both bridge bonds. This mechanism is exactly that proposed originally by Ziegler[8]. A more detailed and significant kinetic study of the exchange reaction of methyl groups between trimethylaluminium (dimer) and trimethylgallium and -indium (monomer) has been made by Williams and Brown[25] from which it is concluded that the rate determining step in the exchange is the dissociation of the trimethyl dimer into solvent separated monomer units, and that this dissociation is rate determining for the interchange of terminal and bridge methyl groups in trimethylaluminium dimer itself. The heat of dissociation in the liquid phase was determined as 15.4 kcal/mole of dimer.

A similar study, by Mole and his coworkers[28], of the exchange of methyl groups between trimethylaluminium and dimethyl(phenylethynyl)aluminium also indicated that the attack of the trimethyl compound on the dimethyl compound was determined by prior dissociation of the dimer, *i.e.*:

$$Me_6Al_2 \rightleftarrows 2\,Me_3Al \quad \Delta H_d$$

$$Me_3Al + Me_4(PhC{\equiv}C)_2Al_2 \rightarrow \text{Product} \quad \Delta E_a$$

The overall activation energy, ΔE,

$$\Delta E = \tfrac{1}{2}\Delta H_d + \Delta E_a = 14.1 \text{ kcal/mole}$$

was considered consistent with a ΔH_d value of 15.4 kcal/mole of dimer.

NMR studies have also been made on the higher alkyl compounds with same general conclusions about rapid alkyl group interchange at room temperature. However, the resonance lines of the bridge methylene group is obscured at low temperatures by the methyl group resonance and the temperature dependence of their interchange has not been measured. Group interchange has also been observed in triarylaluminium compounds by Mole and coworkers[14], and Yamamoto[22].

(2). *Thermochemical studies*

The amount of thermodynamic information available from the literature on the organoaluminium compounds is sparse and generally what is available is contradictory. Values of -36.5[29], -41.4[30], -51.9[31] and -56.5[32] kcal/mole of monomer have been quoted for the heat of formation of triethylaluminium in the liquid phase. These variations must reflect the extreme difficulties in handling the reactive materials, of obtaining pure samples and ensuring complete reaction in the reaction calorimeter[29]. There is also insufficient detailed spectroscopic information about the rotational and vibrational modes with the dimer and monomer species to enable the thermodynamic parameters of the equilibrium in the ideal gas state to be calculated. Only one set of heat capacity measurements have been made over a wide temperature range and these on trimethylaluminium under conditions where it is predominantly dimeric[33].

Hoffmann[2,13], however, has studied the dimer–monomer equilibrium directly by a calorimeter method in which he measured the interactions of trimethyl- with triisobutylaluminium, and dimethyl- and diethylaluminium hydrides with triisobutylaluminium. He determined that the tri-n-alkyl compounds were dimeric and the isobutyl monomeric, and accordingly on mixing the group interchange which occurred produced more n-alkyl bridges (with terminal isobutyl groups) than were originally present. There is also an increase in the number of alkyl bridges, and so dimerisation, on mixing triisobutylaluminium and the dialkylaluminium hydride, *i.e.*:

$$(AlMe_2H)_3 + 6\,Al\text{-}i\text{-}Bu_3 \rightleftarrows 3\,Al_3Me_2\text{-}i\text{-}Bu_4 + (Al\text{-}i\text{-}Bu_2H)_3$$

Allowing for the heats of dilution of the various reagents, both series of experiments gave a value for the energy of the methyl bridge bond of 6.7 kcal/mole, with 1.0–1.3 kcal/mole less for an ethyl bridge. This would give a value for the heat of dissociation for the trimethylaluminium of 13.4 kcal/mole of dimer which is substantially lower than that determined either by Laubengayer and Gilliam[11], or by Williams and Brown[25]. However, there is an underlying assumption in Hoffmann's treatment that the terminal groups either in the hydride trimer or in the alkyl dimers have no effect on the strength of the bridging bonds. This may be true only as a first approximation and still have a significant effect on the absolute value determined for the bond strengths. Nevertheless, the general conclusion that the methyl bridge is stronger than an ethyl was vindicated by the NMR spectra of mixed methyl and ethyl aluminium compounds which showed conclusively that methyl group preferentially displaced ethyl groups in the bridging positions, *e.g.* in $Al_2Me_2Et_4$ 74% of the methyl groups are in the bridge, and 26% in the terminal positions[2,13]. Also the assumption that triisobutylaluminium is entirely monomeric and has no tendancy to associate has recently been invalidated by M. B. Smith[35]. A value of 8.1 kcal/mole was determined for the heat of dissociation of the isobutyl dimer. This would raise the determined values of the bond strengths, but imposes the complication of an equilibrium between isobutyl groups in the terminal and bridging positions.

M. B. Smith[16], using a precision calorimeter modified for injecting standard amounts of the reactive triethylaluminium into a dilute solution, has measured the heat of dilution as a function of concentration and temperature, from 60–150° in hexadecane. Allowing for the heat of dilution of the dimer (but not monomer) he determined from a computer fit of a four parameter equation a best fit value for the heat of dissociation of 16.93 ± 0.05 kcal/mole of dimer. Unfortunately, the experimental conditions were such that there may be some contribution from the heat of vaporisation of the triethylaluminium (16.5 kcal/mole of vapour) in the measured heat of dissociation. This value is substantially different from 10.2 kcal/mole of dimer determined from the temperature dependence of the equilibrium constant measured by a molecular weight study of the saturated vapour[15,19]. The equilibrium constants for the two systems are also very different, see Table 1(a). Laubengayer and Gilliam[11] also studied the molecular weight of the triethylaluminium vapour as a function of temperature by vapour density measurements, but did not calculate the equilibrium constants, nor list the pressures of vapour used. Nevertheless, for the constant mass system which they describe, and for the equilibrium

$$Al_2Et_6 \rightleftarrows 2\,AlEt_3$$

TABLE 1

DISSOCIATION CONSTANTS

Temp. (°C)	K_d(mole/l)	Ref.	K_d(mole/l)	Ref.
(a). Triethylaluminium				
60	9.7×10^{-4}	15	6.1×10^{-4}	16
90	2.9×10^{-3}		4.9×10^{-3}	
120	0.9×10^{-2}		2.9×10^{-2}	
150	0.3×10^{-1}		1.2×10^{-1}	
(b). Trimethylaluminium				
100.3	2.83×10^{-3}	11	3.24×10^{-3}	12
110.3			$6.43-6.86 \times 10^{-3}$	
115.0	7.67×10^{-3}			
120.5			1.32×10^{-2}	
150.2			8.08×10^{-2}	
155.7	9.23×10^{-2}			

degree of dissociation α then

$$p/(1+\alpha)T \text{ will be constant}.$$

Since

$$K_p = 4\alpha^2 \cdot p/(1-\alpha^2)$$

then at each temperature T_1 and T_2, corresponding to equilibrium constants K_{p1} and K_{p2} and degree of association α_1 and α_2

$$\frac{K_{p1}}{K_{p2}} = \frac{\alpha_1^2 \cdot T_1}{(1-\alpha_1)} \left\{ \frac{\alpha_2^2 \cdot T_2}{(1-\alpha_2)} \right\}^{-1}$$

Accordingly, a plot of log $\alpha^2 \cdot T/(1-\alpha)$ against T^{-1} will be linear with slope equal to $-\Delta H_d/2.3\ R$.

For this particular equilibrium,

$$K_d = K_c \cdot R \cdot T$$

In this way, a value for ΔH_d was estimated[19] at 11.0±2.0 kcal/mole of dimer in good agreement with the 10.2±1.0 kcal/mole of dimer[15]. Laubengayer and Gilliam[11], and more recently Henrickson and Eyman[12], have also used vapour density measurements to determine the equilibrium constants of the dissociation of trimethylaluminium. There is good agreement in the molar heats of dissociation, namely 20.2±1.0 and 20.4±0.3 kcal/mole, and in the dissociation constants, see Table 1(b).

(3). *Vapour pressure studies*

Despite the variable degree of correlation in the thermodynamic parameters of the monomer–dimer equilibrium agreement exists in the literature[11,12,15,33,34], on the temperature dependence of the vapour pressure of trimethyl- and triethylaluminium. This agreement is more obvious if the confidence limits of the experimental measurements are also considered, see Tables 2(a) and (b).

TABLE 2

VAPOUR PRESSURE TEMPERATURE DEPENDENCE

Parameters[a]		Heat of vap. (kcal/mole)	Trouton's Constant (cal/mole·°K)	Temp. range (°C)	Ref.
A	*B*				
(a). Trimethylaluminium					
8.1523	2104	9.60±0.10	24.1	23–70	11
8.3287	2159	9.88±0.06		17–48	12
		10.01±0.05		22–100	33
(b). Triethylaluminium					
10.85	3613	16.5±0.5	35.9	60–120	15
10.784	3625	16.6±0.4	36.2	110–140	11
10.152	3382	15.5	33.3	55–130	34

[a] Parameters A and B are constants in the pressure–temperature relationship, $\log_{10} p = A - B/T$ where p is pressure in mm of Hg, and T in °K.

The Trouton constant for triethylaluminium is higher than for normal liquids, and since the alkyl aluminium compound is more associated in the condensed liquid phase than in the vapour some part of the heat of dissociation is included in the observed heats of vapourisation, $\Delta H_{v(obs)}$. Under the experimental conditions of liquid in equilibrium with vapour the following equilibria, each with their corresponding molar heats, $\Delta H_{x(y)}$, must be established,

$$\begin{tikzcd}
\text{Vapour Phase,(subscript g)} & Al_2R_{6(g)} \arrow[r, leftrightarrows, "\Delta H_{d(g)}"] \arrow[d, shift left, "\Delta H_{v(d)}"'] & 2\,AlR_{3(g)} \arrow[d, shift left] \\
\text{Liquid Phase (subscript l)} & Al_2R_{6(l)} \arrow[r, leftrightarrows, "\Delta H_{d(l)}"] \arrow[u, shift left] & 2\,AlR_{3(l)} \arrow[u, shift left, "\Delta H_{v(m)}"']
\end{tikzcd}$$

(Subscripts d and m denote dimer and monomer respectively) a_g and a_l are the corresponding degrees of dissociation of dimer in the vapour and liquid phases. In practice a simplification can be made with trimethyl- and triethylaluminium in the bulk liquid phase since $a_l \simeq 0$ and the phase can be treated solely as containing dimer. This is not valid, however, for other alkyl compounds or for dilute solution, as for example were used by Smith[16].

On vapourisation, 1 mole of $Al_2R_{6(l)}$ will produce $(1+a_g)$ mole of vapour, *i.e.* $2a_g$ mole of monomer and $(1-a_g)$ mole of dimer. Accordingly the observed heat of vapourisation, $\Delta H_{v(obs)}$, corresponding to the production of 1 mole of vapour, is

$$\Delta H_{v(obs)} = (\Delta H_{v(d)} + a_g \cdot \Delta H_{d(g)}) \cdot (1+a_g)^{-1} \tag{1}$$

$$\Delta H_{v(obs)} = \{\Delta H_{d(l)} + 2\,\Delta H_{v(m)} - [(1-a_g) \cdot \Delta H_{d(g)}]\} \cdot (1+a_g)^{-1} \tag{2}$$

using in eqn. (2) the simplification that $a_l = 0$. Considering:

(*i*). *Trimethylaluminium alone.* The heat of vapourisation of monomer, $\Delta H_{v(m)}$ could not be determined independently but a comparison of the heats of vapourisation of monomeric trimethylboron and trimethylgallium, see Table 3, suggested that it was in the range 6.5 ± 0.5 kcal/mole of monomer. Using this value, $\Delta H_{d(g)} = 20.4 \pm 0.3$ kcal/mole, and a_g values determined from the K_p and the vapour pressures listed by Henrickson and Eyman[12], the heat of dimerisation in the liquid phase was determined as 16.3 ± 1.5 kcal/mole of dimer. This value is in good agreement with that determined by the NMR spectroscopic study of the alkyl group interchange[25] (15.4 kcal/mole).

(*ii*). *Triethylaluminium alone.* $\Delta H_{v(m)}$ was again estimated from the data listed in Table 3 as 9.5 ± 0.5 kcal/mole of monomer. Since an experimental procedure very

TABLE 3

HEAT OF VAPOURISATION OF ALKYL MONOMERS

Compound	$\Delta H_{v(m)}$ (kcal/mole)	Ref.
BMe_3	4.3	29
$GaMe_3$	7.8	6
$InMe_3$	10.0	11
BEt_3	8.3	29
$GaEt_3$	10.2	11

similar to that used by Henrickson and Eyman[12], was also adopted by Hay *et al.*[15], and Laubengayer and Gilliam[11], the observed heat of vapourisation (16.5 kcal/mole) the heat of dissociation in the vapour phase, (10.2 kcal/mole of dimer) and the a_g values listed were used in eqns. 1 and 2. These values gave a heat of dissociation in the liquid phase of 12.5 ± 2.0 kcal/mole of dimer, significantly different to the value determined by Smith[16] (16.9 ± 0.3 kcal/mole of dimer).

To gauge the significant of the difference, and define limits on the value of $\Delta H_{d(l)}$ imposed by eqns. (1) and (2), the higher value of $\Delta H_{d(l)}$ and the corresponding α_g calculated from Smith's recorded K_p values were substituted into eqn. (2). This gave an excessively large value for $\Delta H_{d(g)}$ which in turn gave a negative value for $\Delta H_{v(d)}$ on re-substituting in eqn. (1).

Using the $\Delta H_{d(g)}$ value of 10.2 kcal/mole of dimer an apparently large value of 21.3 ± 1.0 kcal/mole is obtained for $\Delta H_{v(d)}$, when compared with the corresponding value of 8.7 ± 0.7 kcal/mole of dimer obtained for trimethylaluminium dimer. Eqn. (1), however, defines a limit to the range that $\Delta H_{v(d)}$ may have, since for $a_g = 0$, $\Delta H_{v(d)} = 16.5$ kcal/mole of dimer, and for $a_g = 1.00$, $\Delta H_{v(d)} = 23.0$ kcal/mole of dimer. These values in turn define an extreme range for $\Delta H_{d(l)}$ between 8–14 kcal/mole of dimer.

(4). *Addition reactions of organoaluminium compounds to alkenes*

The addition of an Al–C bond to alkenes is probably the most important commercial reaction of organoaluminium compounds because of the relevance of the ethylene "growth" reaction to heterogeneous polymerisations with Ziegler–Natta catalysts, and also of the importance of the alkylation products with n-alkenes. The product of addition of a n-alkyl–aluminium bond to ethylene is also an n-alkyl aluminium compound and so is reactive to further addition. Long n-alkyl chains are thus generated, *i.e.* Ziegler's "Aufbau" reaction[8]:

$$>\text{Al–Et} + \text{CH}_2{=}\text{CH}_2 \rightarrow >\text{AlCH}_2\text{CH}_2\text{Et} \xrightarrow{n\,\text{C}_2\text{H}_4} >\text{Al(CH}_2\text{CH}_2)_{n+1}\text{Et}$$

With n-alkenes, however, the products of the addition are β-branched alkyl aluminium compounds, and the alkyl group is eliminated without further addition. The sole product is then a 2-alkyl-1-alkene. This reaction is commercially exploited in the continuous dimerisation of propylene, *i.e.*:

$$>\text{Al–n-Pr} + \text{CH}_2{=}\text{CHCH}_3 \rightarrow >\text{Al–CH}_2\text{CH(CH}_3\text{)-n-Pr} \xrightarrow{\text{CH}_2=\text{CHCH}_3}$$
$$\rightarrow >\text{Al–n-Pr} + \text{CH}_2{=}\text{C(CH}_3\text{)-n-Pr}$$

(*a*). *Triethylaluminium*

The kinetics of the addition reaction to ethylene[8,17], and to linear[8,18–20], branched[20] and cyclic[20] alkenes have been well studied and there is general agreement on the mechanism of the addition step. Reaction order studies indicate that monomer is the reactive species and that triethylaluminium is present under the reaction conditions as predominantly dimer. Prior dissociation of the dimer is required and the reaction rate is accurately half order (0.51 ± 0.03) in the total triethylaluminium concentration. The reaction is first order in alkene concentration[18–20]. Analysis of the products as a function of reaction extent also indicated that three primary products were involved: 2-ethyl-1-alkene and two aluminium alkyl compounds which on hydrolysis yielded 2-ethylalkane and n-alkane. The formation of the products corresponded with the disappearance of equivalent molar amounts of the alkene. A stationary concentration of the (2-ethylalkyl)aluminium developed from an early stage in the reaction while the yields of the other two increased with the same general rate. Analysis of the reaction products at high conversion indicated the presence of trace amounts of the alkene dimer. This was considered consistent with the following reaction scheme:

(*i*). Dissociation of the triethylaluminium:

$$\mathrm{Al_2Et_6} \rightleftarrows 2\,\mathrm{AlEt_3}$$

for which

$$K_c = \frac{4a^2 \cdot C}{(1-a)}$$

where C is the concentration of triethylaluminium in mol. of dimer/l.

(*ii*). Addition of the monomer to the alkene:

$$\mathrm{AlEt_3 + R{-}CH{=}CH_2 \rightarrow R{-}CH(Et){-}CH_2{-}AlEt_2}$$

rate constant k_1

(*iii*). Elimination of the branched alkyl:

$$\mathrm{R{-}CH(Et){-}CH_2{-}AlEt_2 \rightarrow R{-}C(Et){=}CH_2 + AlHEt_2}$$

rate constant k_2

(*iv*). Hydride addition to alkene:

$$\mathrm{AlHEt_2 + R{-}CH{=}CH_2 \rightarrow Et_2AlCH_2CH_2R}$$

rate constant k_3

(*v*). Alkene dimerisation:

$$\mathrm{Et_2AlCH_2CH_2R + RCH{=}CH_2 \rightarrow Et_2AlCH_2CH(R)CH_2CH_2R}$$

A study of model compounds[36] indicated that $k_3 \gg k_2$ and k_1, and that k_2 was of the order of 10^{-3}–10^{-4} sec^{-1} at the temperatures of the reaction. Accordingly a pseudo-stationary state must develop in diethylaluminium hydride and (2-ethylalkyl)-aluminium, and that

$$\frac{-\mathrm{d}[\mathrm{RCH{=}CH_2}]}{\mathrm{d}t} = k_1 \cdot [\mathrm{AlEt_3}] \cdot [\mathrm{RCH{=}CH_2}] + k_3 \cdot [\mathrm{RCH{=}CH_2}] \cdot [\mathrm{AlHEt_2}]$$

and

$$k_1 \cdot [\mathrm{AlEt_3}] \cdot [\mathrm{RCH{=}CH_2}] = k_2 \cdot [\mathrm{AlEt_2CH(Et)CH_2AlEt_2}] = k_3 \cdot [\mathrm{RCH{=}CH_2}] \cdot [\mathrm{AlHEt_2}]$$

so that

$$\frac{-\mathrm{d}[\mathrm{RCH{=}CH_2}]}{\mathrm{d}t} = 2\,k_1 \cdot [\mathrm{AlEt_3}] \cdot [\mathrm{RCH{=}CH_2}] = 2\,k_1 \cdot K_c^{\frac{1}{2}} \cdot [\mathrm{Al_2Et_6}]^{\frac{1}{2}} \cdot [\mathrm{RCH{=}CH_2}] \quad (3)$$

The overall temperature dependence of the rate of alkene consumption in this system was accordingly,

$$\frac{-\mathrm{d}[\mathrm{RCH{=}CH_2}]}{\mathrm{d}t} = 2A\cdot e^{-\Delta E/(R\cdot T)}\cdot B^{\frac{1}{2}}\cdot e^{-\Delta H_{\mathrm{d(l)}}/(2R\cdot T)}\cdot[\mathrm{Al_2Et_6}]^{\frac{1}{2}}\cdot[\mathrm{RCH{=}CH_2}] \quad (4)$$

where A and B are the corresponding pre-exponential factors, and ΔE the activation energy of the addition reaction.

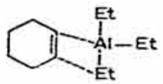
Hay *et al.*[19,20] using $\Delta H_{\mathrm{d(g)}}$ instead of $\Delta H_{\mathrm{d(l)}}$ in eqn. (4) obtained the Arrhenius parameters listed in Table 4. The range of these A factors (10^6–10^7) was considered reasonable for a bimolecular reaction of this complexity, since by comparison Benson[37] has determined values of A in the range 10^6–$10^{8.5}$ for the addition of hydrogen halides to alkenes. It is also possible to account for the relatively low A values in terms of a four centre transition state in which there will be considerable loss of rotational entropy associated with the formation of the ring. This loss will be in the order of that observed, *i.e.*, 25 cal/mole·°K. The further decrease in the value of A observed with the addition to cyclohexene is also consistent with the four centre transition state and the increased strain associated with the four centre fused to the six membered ring, *i.e.*:

TABLE 4

ARRHENIUS PARAMETERS OF THE ADDITION REACTION

Alkene	Activation energy (kcal/mole)	Arrhenius factor ($\log_{10}A$)	Ref.
(a). Triethylaluminium			
n-1-Propene	15.4 ± 1.0	5.5 ± 0.5	15, 19
n-1-Butene	16.4	5.8	
n-1-Pentene	18.4	6.8	
n-1-Hexene	18.2	7.0	
n-1-Hexene	17.1 ± 1.0	6.2 ± 0.3	20
4-Methyl-1-pentene	17.0	5.8	
3-Methyl-1-pentene	18.7	6.5	
2-Methyl-1-pentene	[a]	[a]	
2-Methyl-2-pentene	[a]	[a]	
Cyclohexene	17.8	4.6	
n-1-Octene	18.3 ± 1.0	6.6 ± 0.3	20, 38
(b). Trimethylaluminium			
n-1-Octene	20.3 ± 1.0	6.7 ± 0.3	38

[a] No reaction.



If, however, a value of 16.9 kcal/mole of dimer is used for $\Delta H_{\mathrm{d(l)}}$, as determined by Smith[16], (using the corresponding K_c values quoted), the range of A values and activation energies are substantially reduced to $10^{3.5}$–$10^{5.0}$ and 12.0–15.0 kcal/mole. These values of A are improbable, particularly the values at the lower end of the range, and would suggest in themselves that the reaction mechanism is more complex than suggested by the kinetics.

(*b*). *Trimethylaluminium*

In order to consider this last point further it is useful to compare the kinetics of the addition of trimethylaluminium to n-alkenes. Only one study has been made and that of the addition of trimethylaluminium to n-1-octene[38] (*cf.* the corresponding addition reaction of triethylaluminium). Analysis of the reaction products as a function of the conversion, a study of the reaction order, and the overall temperature dependence of the rate of alkene consumption indicated identical reaction paths for both. Using the equilibrium association–dissociation characteristics listed by Henrickson and Eyman[12] for the vapour phase, Arrhenius parameters very similar to those obtained for triethylaluminium were calculated, see Table 4(b). The small difference observed in the activation energies, *i.e.* 2 ± 2 kcal/mole is either not meaningful or is within the expected difference in the strengths of a metal–ethyl and metal–methyl bonds (~5 kcal/mole)[29]. The former would be consistent with the proposed four centre transition state if the metal–alkyl bond is broken in the rate determining step.

However, in this case substituting the equilibrium characteristics of the trimethylaluminium dimer dissociation, (*i.e.* $\Delta H_{d(l)} = 16.3 \pm 1.5$ kcal/mole of dimer) raised the Arrhenius factor to a more probably value and increased the activation energy to 24 ± 2 kcal/mole.

The trimethyl and triethyl data would then only become consistent (maintaining the expected difference in activation energy, and same A factor) if the $\Delta H_{d(l)}$ for triethylaluminium was substantially less, *i.e.* in the range 10 ± 2 kcal/mole of dimer. A value of this order is similar to that gauged from the vapour pressure measurements[15] but almost half that quoted by Smith[16].

CONCLUSIONS

From vapourisation studies the heat of dissociation of triethylaluminium dimer in the liquid phase is in the range 12.5 ± 2.0 kcal/mole of dimer, with extreme limits 8–14 kcal/mole of dimer. Kinetic studies on the addition reaction to alkenes are compatible only with the lower limit of this range, and both are inconsistent with the only experimental measure of this parameter, i.e. 16.9 kcal/mole of dimer.

For the dissociation,

$$Al_2R_6 \rightleftarrows 2\,AlR_3$$

trimethylaluminium,

$$\Delta H_{d(g)} = 20.2 \pm 0.3 \text{ kcal/mole of dimer}$$

and $\Delta H_{d(l)} = 16.3 \pm 1.5$ kcal/mole of dimer

triethylaluminium,

$$\Delta H_{d(g)} = 10.2 \pm 1.0 \text{ kcal/mole of dimer}$$

and $\Delta H_{d(l)} = 8\text{–}14$ kcal/mole of dimer

summaries the best estimates available.

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