KINETICS OF THE REACTIONS BETWEEN TRIETHYLALUMINIUM AND UNSATURATED HYDROCARBONS

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Abstract

The literature concerning the physical and thermodynamic properties of trialkylaluminiums and the reaction of triethylaluminium with terminal alkenes has been critically reviewed.

A detailed kinetic study of the reaction of triethylaluminium with styrene and 2-methyl-1-heptene has been performed using a p.m.r. technique. The kinetic parameters obtained have been compared with others available for 1-alkenes and a co-ordinated mechanism involving two rate determining steps to account for the observed parameters is postulated.

Previous studies of the reactions between triethylaluminium and alkynes have been reviewed and a kinetic study of the reaction of triethylaluminium with phenylacetylene performed, using p.m.r. and manometric techniques. The existence of a donor complex between alkynes and triethylaluminium has been established. Previously this had only been postulated. Finally the kinetics of the reaction of two amine complexes of triethylaluminium with phenylacetylene have been investigated and a mechanism proposed to explain the observed kinetic parameters.

This thesis is a record of research undertaken in the Department of Physical and Inorganic Chemistry at the University of Adelaide between March 1971 and September 1973.

To the best of my knowledge and belief no material contained herein has been accepted for the award of any other degree or diploma in any university, or been previously published or written by another person except when due reference is made in the text.

Roger M. Lough.

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SECTION I

TRIALKYLALUMINIUMS

Synopsis

General - The historical background and industrial uses of organoaluminiums are briefly reviewed and their relationships to Ziegler-Natta catalyst systems are discussed.

Preparation - A very brief outline of the methods of preparation of trialkylaluminiums is given.

Structure and Bonding - Some aspects of the x-ray crystallographic, p.m.r., and mass spectroscopic evidence for association are discussed. As a result, two orbital descriptions of the three-centre, electron deficient bond have been proposed.

Thermodynamic Properties - The merits of the various values put forward for the enthalpies and entropies of dissociation of Al_2Et_6 and Al_2Me_6 in the liquid and vapour phase are discussed.

Chemical Properties - A very brief outline of the more important chemical properties of trialkylaluminiums is given.

I.1.

1. GENERAL

Although an organoaluminium compound was synthesized by Hallwachs and Schafarik[1] in 1859, the study of the chemistry of these compounds remained static until about 1950. At this time Professor Karl Ziegler and his co-workers utilized alkylaluminiums to greatly increase the rate of polymerization of ethylene,[2] while simultaneously developing a cheap synthesis for alkylaluminiums directly from aluminium, olefins and hydrogen.[3]

As a result, the scope of usefulness of organoaluminiums in general, and alkylaluminiums specifically, has broadened considerably, with the consequent dramatic increase in the quantities used in industry and research.

Most organoaluminiums are used as components in the various Ziegler-Natta polymerization catalysts. These catalysts, formed by combining aluminium with a transition metal compound, are used in preparing nearly all of the commercial polyolefin produced in the world today. Their main advantages over other polymerization catalysts are the stereoregularity of the resulting polymer - which can be readily changed - and the increased rate of reaction when compared to other catalysts. Organoaluminiums, alone, are used extensively for the oligermization and polymerization of the simpler olefins. Trialkylaluminium catalysts, for example, are used for the dimerization of propylene to 2-methylpent-1-ene.[46] This latter compound is often used as a precursor for isoprene, which is extensively used in the synthetic rubber industry.

I.1.

In spite of this vast use, comparatively little is known of the chemistry of the organoaluminiums, in part due to their reactive nature. The explanation for stereoregular polymerization by Ziegler-Natta catalysts has been particularly confused, as many theories have been proposed over the last decade,[4-6] but recently a clearer picture seems to be emerging.[7] Many patents concerning olefin polymerization appear each year, but as yet there does not seem to be any correlation between the myriad of catalysts and conditions used, with the resulting polymer. Thus an understanding of the basic reactivity factors and the mechanisms that are operating when organoaluminiums react with unsaturated hydrocarbons could conceivably throw some light on the situation.

The purpose of this thesis is to provide some information towards this end. Trialkylaluminiums are one of the simplest classes of organoaluminiums, and the results derived from these compounds have, up to the present, been interpreted with less ambiguity than other organoaluminiums. For this reason, they have been used in this study. The particular trialkylaluminium used- triethylaluminium - was selected mainly on its ready availability and widespread use as a catalyst and a co-catalyst.

Before examining the detailed kinetics of the reactions of triethylaluminium with unsaturated hydrocarbons, however, it is necessary to review the structure and properties of trialkylaluminiums, so that the subsequent kinetic results can be correctly interpreted.

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2. PREPARATION OF TRIALKYLALUMINIUMS

Trialkylaluminiums can be prepared from olefins by direct synthesis,[3] displacement or by a growth reaction. They can also be prepared from alkyl halides, dialkyl mercury compounds, Grignards, organolithiums, trialkyl boranes, tetraalkylaluminates, and diazomethane. Substantial literature[8] is available on these methods and so further elaboration seems unnecessary.

3. STRUCTURE AND BONDING IN TRIALKYLALUMINIUMS

Trialkylaluminiums are unusual in the fact that all of the lower homologues are associated to a greater or lesser extent in solution ($AlEt_3$, $AliBu_3$) or even in the vapor phase ($AlMe_3$). This discovery caused confusion in the early days of the valence theory (1940s), as association in these compounds necessitates the postulate of an electron deficient bond. However, since then many other compounds have been prepared that also require an electron deficient bond as part of their structure, and thus this concept, no longer unique to the alkylaluminiums, is now widely accepted.

In all cases, the bridging has been found to be through a carbon atom, although recently Byram *et al*[9] attempted to re-interpret the x-ray crystallographic data on trimethylaluminium collected by Vranka and Amma[10] in terms of a hydrogen bridge, but this has been refuted recently by Huffman and Strieb[19] who determined, unequivocally, the structure of trimethylaluminium (Fig.I.1.) at 443K. It can be seen that the hydrogen atoms are in no position to bond strongly to the aluminium atom.

The presence of dimer formation has also been demonstrated by p.m.r. spectroscopy. At 230K, the p.m.r. spectrum of triethyaluminium in toluence or cyclopentane shows two sharp resonances having area ratios of 1:2.[26-27] These peaks are respectively assigned to the six mutually equivalent protons of the two methyl bridging groups and the twelve protons of the terminal methyl groups. This observation can be interpreted in terms of a hydrogen bridge only if there is rapid intramolecular rearrangement of the bridging group at 203K.

No such rearrangement is necessary if carbon atoms bridge. As the temperature is increased, the two peaks coalesce; this is ascribed to the rate of exchange between bridging and terminal methyls becoming faster, because the single peak appears at the weighted average of the two at low temperature.[47]

Williams and Brown[22] studied the coalesence in trimethylaluminium and trimethylaluminium/trimethylgallium mixtures and concluded that bridge-terminal equilibration takes place by a first order dissociation of the dimer to trimethylaluminium monomer, followed by fast recombination of

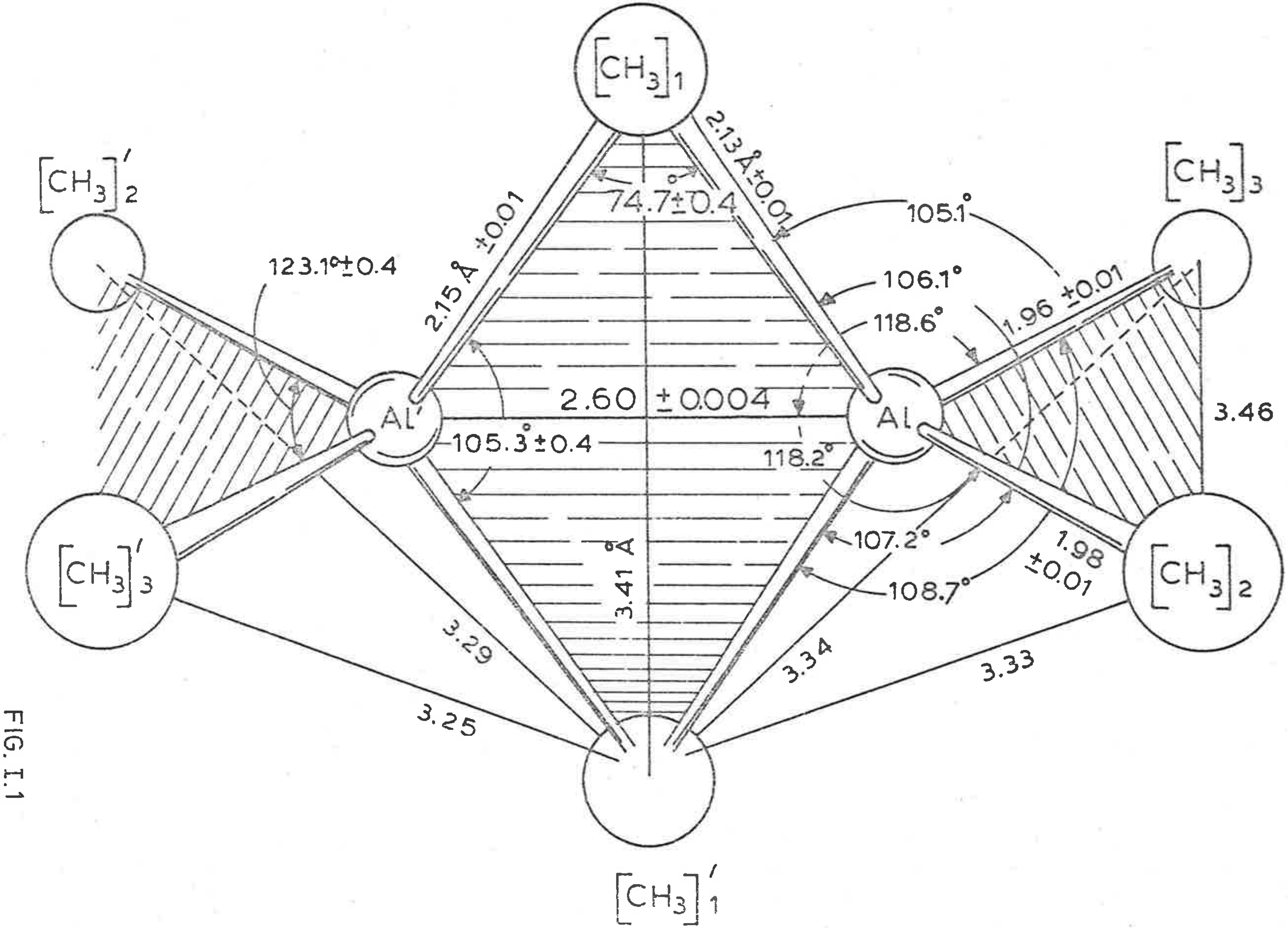
[CH3]1
[CH3]'2
[CH3]3
[CH3]'3
[CH3]2
[CH3]'1
Al'
Al
2.13 Å ±0.01
74.7±0.4
2.15 Å ±0.01
123.1°±0.4
105.1°
106.1°
118.6°
1.96 ±0.01
2.60 ±0.004
105.3°±0.4
118.2°
3.46
107.2°
108.7°
1.98 ±0.01
3.41 Å
3.29
3.25
3.34
3.33

FIG. I.1

the monomer leading to scrambling of the methyl groups. They also determined a value for the enthalpy of activation in cyclopentane which will be discussed later. The dissociation was observed to proceed about ten times faster in toluene than in cyclopentane.

Ramey *et al*[29] found a similar situation to exist when they investigated the low temperature p.m.r. spectrum of triethylaluminium in cyclopentane. The methylene quartet (Fig. II.5) broadens as the temperature is lowered, finally emerging at 223K as two quartets at 0.08 and 1.08 p.p.m., corresponding to terminal and bridging methylene groups respectively. An exact ratio of 2:1 was not observed due to resonance overlap, but the result is nevertheless definitive. A similar investigation in toluene confirmed this result.[30]

The infra-red and Raman spectra of trimethylaluminium have also been interpreted in terms of a carbon bridged dimer. Hoffman[31] did the original work on the I.R. spectra of trialkylaluminiums and dialkylaluminium chlorides, either as pure liquids or in cyclohexane. His assignments of carbon-aluminium vibrations and rocking modes of the methyl groups were questioned in 1963[32] and 1964,[33] but later they were shown, by complete analysis of the spectra, to be correct.[20]

Two peaks at 1255 cm^{-1} and 1200-1 cm^{-1} (I.R. and Raman) have been assigned to methyl symmetrical bending modes in the bridging and terminal positions respectively, while three peaks (768 cm^{-1}, 697 cm^{-1}, 608 cm^{-1} -I.R.; 725 cm^{-1}, 683 cm^{-1}, 632 cm^{-1} -Raman) have been assigned to three methyl rocking modes: bridge in plane, terminal, and bridge out of plane respectively. Most of the low frequency peaks can be assigned to skeletal vibrations of the Al_2Me_6 molecule.

Mass spectroscopic data is inconclusive. Trimethylaluminium shows a weak $Al_2Me_5^+$ peak, but all other peaks appear to be derived from the $AlMe_3$ monomer.[28] Triethylaluminium, however, shows no peaks derived from a dimeric species, presumably because the dimer is not stable, and this is supported by the fact that more strongly associated organoaluminium compounds such as dimethylaluminium hydride (trimer) and diethylaluminium ethoxide (dimer) show evidence of association in their mass spectra.[34~35]

Other related organoaluminiums have been demonstrated to be associated. For example, an x-ray crystallographic study of triphenylaluminium reported bridging by two phenyl groups, inclined at an angle to the Al-C-Al plane, presumably because of steric hindrance.[36] The p.m.r. spectrum of dimethyl(phenylethynyl)aluminium shows only one methyl peak at all temperatures.[37] As ebulliometry has shown the compound to exist as a dimer, the bridging groups must be phenylethynyl. This configuration probably results from the stability of the three centred bond being enhanced by the π orbital system of the phenylethynyl group.

Branching at the α or β carbon atom of the alkyl group usually causes the trialkylaluminium to be monomeric. Cryoscopic measurements show triisopropylaluminium,[38] triisobutylaluminium,[39,40] tri-t-butyaluminium[41] and tribenzylaluminium[42] to be monomeric. Thermochemical measurements, on the other hand, indicate that triisobutylaluminium is significantly associated in pure liquid and in n-tetradecane,[43] but I.R. data also dispute this.[31]

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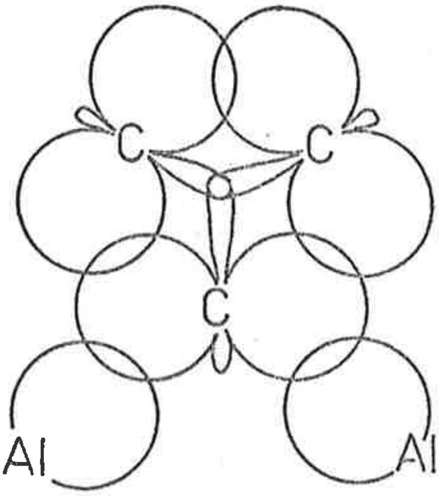
Tricyclopropylaluminium is so strongly associated that its p.m.r. spectrum clearly shows two cyclopropyl resonance sets even at room temperature and not until the temperature has been increased to 343K does coalesence occur to give a single cyclopropyl pattern. Sanders and Oliver[44] proposed that the stability of the tricyclopropylaluminium dimer is due to the facile transfer of electrons from the bridging cyclopropyl group into a non-bonding three centred orbital that is suggested to form the electron deficient bridge. This is most readily understood using the Walsh model for cyclopropane, in which the cyclopropane skeleton is derived from sp^2 and p orbital overlap. The bridging carbon atom of the cyclopropyl group has a p orbital of the correct symmetry to overlap with the non-bonding molecular orbital of the Al-C-Al bridge, as shown.



Bonding in Tricyclopropylaluminium

This concept can be extended to include bonding in trialkylaluminiums: the bridge is formed from overlap of the vacant aluminium p

orbitals and the sp^3 orbital of the alkyl group. sp^2 hybridization on the aluminium also leaves open the possibility of a sigma bond between the aluminiums. This is not possible in a second explanation which proposes that the bridge is derived from overlap of sp^3 orbitals of aluminium and carbon to give two three centre bonds. These three orbitals (two aluminium, one carbon) combine to form a bonding, a non-bonding, and an anti-bonding orbital, analagous to the accepted orbital description for diborane. The former view is supported by the fact that in trimethylaluminium there is a slight distortion from D_2h to C_2h,[10] and the value of the Al-Al stretching constant suggests significant Al-Al bonding.[20]

I.4.

4. PROPERTIES OF TRIALKYLALUMINIUMS

4.1. Thermodynamic Properties

The basic physical properties of trialkylaluminiums are well documented elsewhere[21] and will not be given here, but some thermodynamic properties, especially those of triethylaluminium are the subject of controversy at present, and, as these properties have an important bearing on conclusions derived later, they will be discussed here in some detail.

The main areas of contention are the enthalpies and entropies of dissociation and vaporization. Under liquid-vapor equilibrium, the following equilibria exist:

$$\begin{tikzcd}
\text{Vapour (g)} & Al_2R_6(g) \arrow[r, shift left, "\Delta H^o_{d(g)}"] \arrow[d, shift left] & 2AlR_3(g) \arrow[l, shift left] \arrow[d, shift left] \\
\text{Liquid (1)} & Al_2R_6(1) \arrow[r, shift left] \arrow[u, shift left, "\Delta H^o_{VD}"] & 2AlR_3(1) \arrow[l, shift left, "\Delta H^o_{d(1)}"] \arrow[u, shift left, "\Delta H^o_{VM}"]
\end{tikzcd}$$

Laubengayer and Gilliam[17] determined the vapour phase dissociation parameters for both triethylaluminium and trimethylaluminium from saturated vapour density measurements. However, it can be seen (Fig. I.2) that the temperatures of measurement for triethylaluminium were generally too high because the change of $\Delta H^o_{d(g)}$ with temperature is probably due to decomposition. Thus only the lower values are of any use. Hay, Hooper and Robb[11] performed saturated vapour density measurements on triethylaluminium between 313K and 373K. They also determined the Antoine equation for triethylaluminium. Smith,[13] in 1967, determined values for $K_{d(l)}$, the equilibrium constant for liquid phase dissociation, over the temperature range 333K-423K, by a calorimetric technique, while Allen and Byers[14] determined values of the same parameter over the range 354K-399K by an ebullioscopic method. Van't Hoff plots of the equilibrium constants, as determined by each worker are shown in Fig. I.2. It should be emphasized at this stage that these are the only values that have been determined directly for triethylaluminium. In the case of trimethylaluminium, parameters for dissociation in the vapour phase have been determined by vapor density measurements[16,17] and those for the liquid phase by p.m.r. measurements,[22] although the latter are held by some to be in error.[23] The Antoine equation is also known.[16,18]

It can be seen from the liquid-vapor equilibrium relationships detailed above that if ideal mixing between monomer and dimer is assumed, various derived values can be determined. Thus using the observed heat of vaporization:

$$\begin{aligned}\Delta H^{o}_{V,obs} &= \Delta H^{o}_{VD} + \alpha_g . \Delta H^{o}_{d(g)} - \alpha_l . \Delta H^{o}_{d(l)}/(1+\alpha_g) \\ &= [2\Delta H^{o}_{VM} - (1-\alpha_g)] . \Delta H^{o}_{d(g)} + (1-\alpha_l) . \Delta H^{o}_{d(l)}/(1+\alpha_g)\end{aligned} \qquad ....(5)$$

where α_l = degree of dissociation of dimer in the liquid phase

and α_g = degree of dissociation of dimer in the vapor phase.

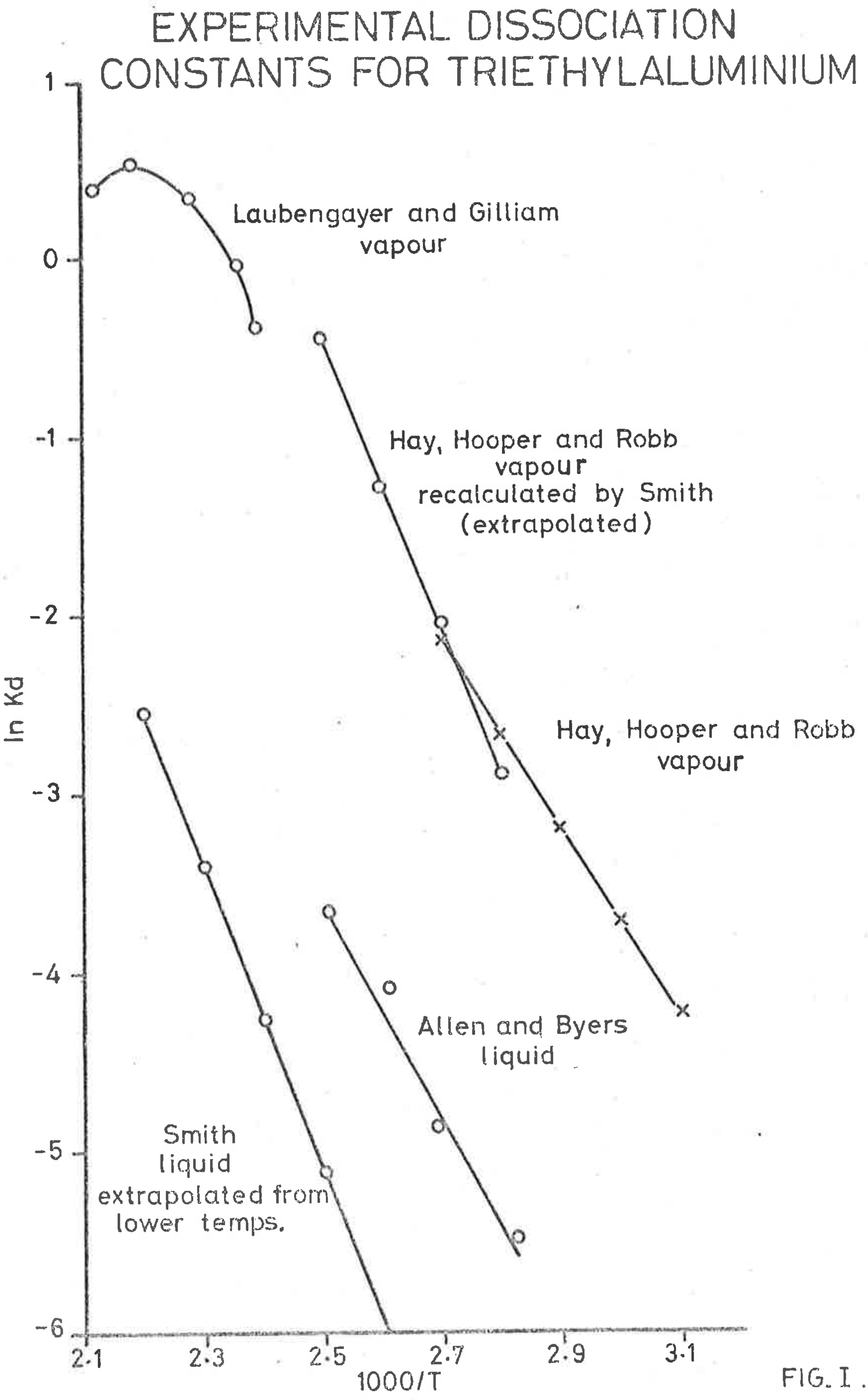

EXPERIMENTAL DISSOCIATION
CONSTANTS FOR TRIETHYLALUMINIUM
Laubengayer and Gilliam
vapour
Hay, Hooper and Robb
vapour
recalculated by Smith
(extrapolated)
Hay, Hooper and Robb
vapour
Allen and Byers
liquid
Smith
liquid
extrapolated from
lower temps.
ln Kd
1
0
-1
-2
-3
-4
-5
-6
2·1
2·3
2·5
2·7
2·9
3·1
1000/T

FIG. I . 2

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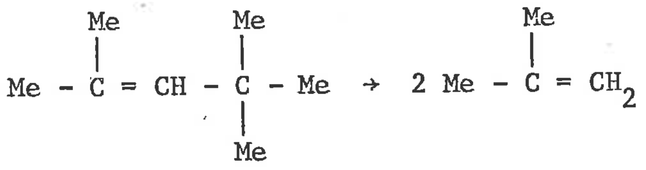
In practice, $\alpha_1 \simeq 0$ so the equations are somewhat simplified.

Hay, Hooper and Robb[12] estimated the heat of vaporization of the trialkylaluminium monomer (ΔH^o_{VM}) by assuming it was the median of the heats of vaporization of the monomeric trialkyl compounds of the elements above and below aluminium in Group IIIb. They then derived a value for $\Delta H^o_{d(1)}$ from their $\Delta H^o_{d(g)}$. Smith,[15] on the other hand, derived the difference in dissociation enthalpies from the estimated difference in vaporization enthalpies. Thus:

$$\delta_H = \Delta H^o_{d(g)} - \Delta H^o_{d(1)} = 2\Delta H^o_{VM} - \Delta H^o_{VD} \qquad \text{....(6)}$$

A similar argument obviously applies to other extensive properties. The aliphatic saturated and olefinic hydrocarbons were chosen as analogues of the trialkylaluminium monomer-dimer systems. An average of 36 simulated processes of the type



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

was used to determine δ_H and the corresponding entropy term δ_S, for trimethylaluminium. Values for triethylaluminium were estimated from the effects of chain lengthening and branching on the compounds used for trimethylaluminium. Table I.1. shows the determined, derived and estimated enthalpies and entropies for trimethylaluminium and triethylaluminium.

TABLE I.1. Thermodynamic properties of Trialkylaluminiums

	$\Delta H^o_{d(l)}$	$\Delta H^o_{d(g)}$	$\Delta S^o_{d(l)}$	$\Delta S^o_{d(g)}$	δ_H	ΔH^o_{VD}	ΔH^o_{VM}	δ_S	ΔS^o_{VD}	ΔS^o_{VM}
	kJ mol dimer^{-1}		J mol^{-1}K^{-1}		kJ mol dimer^{-1}			J mol^{-1}K^{-1}		
$AlMe_3$	$68.2\pm6^{12}_{der}$ 81.1^{15}_{b} 82.3^{15}_{c} 82.3_{d}	$85.3\pm1^{16}_{det}$ $84.5\pm4^{17}_{det}$	122.6^{15}_{der}	180.7^{16}_{det}	4.34^{15}_{est}	$36.4\pm3^{12}_{est}$ 36.8^{15}_{c} 34.3^{15}_{d} 40.6^{15}_{b}	$27.2\pm2^{12}_{est}$ 22.6^{15}_{c} 22.6^{15}_{b}	55.7^{15}_{est}	87.4^{15}_{b} 85.3^{15}_{d} 87.4^{15}_{c}	81.1^{15}_{c} 81.5^{15}_{c}
$AlEt_3$	$52.3\pm8^{12}_{der}$ $51.5\pm5^{14}_{der}$ $70.7\ 1^{13}_{det}$ 72.2^{15}_{c} 73.4^{15}_{d}	42.6^{11}_{det} 76.0^{13}_{der} 67.1^{15}_{a}	134.7^{13}_{det} 115.9^{14}_{f}	190.4^{15}_{der} 98.3^{11}_{det} 164.0^{15}_{a}	5.2^{15}_{est}	89.1^{12}_{der} 64.2^{15}_{der}	39.7^{12}_{est}	55.7^{15}_{est}	163.6^{15}_{e} 110.0^{15}_{a} 88.6^{15}_{der}	79.1^{15}_{c} 82.4^{15}_{d}

<u>Footnotes</u>: Standard states: gas: 101325 Nm^{-2} (1 atm) : liquid: pure substance at 1 atm except when specified

det: Determined directly from experimental results : est: Estimated by analogy with related compounds.

der: Derived from directly determined and estimated values.

a: Calculated by Smith[15] from the Hay, Hooper and Robb[11] vapor density data.
b: Derived by Smith[15] from the McCullough[8] vapor pressure data.
c: Derived by Smith[15] from the Henrickson and Eyeman[16] vapor pressure data.
d: Derived by Smith[15] from the Laubengayer and Gillian[17] vapor pressure data.
e: Derived by Smith from the Hay, Hooper and Robb[11] vapor pressure data.
f: Calculated on a 1 molar standard state.

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In the case of trimethylaluminium, Smith[15] argues that the $\Delta H^o_{d(1)}$ value derived by Hay *et al*[12] is too low as they have used an unrealistic value for ΔH^o_{VM}, because, using their ΔH^o_{VM}, a normal liquid obeying Trouton's rule (the pure monomer or dimer can be classified as such) would have a boiling point of about 306K. Smith separated the observed vapor pressure data from various sources into two component equations of the form

$$\ln P = A - B/T \qquad ....(7)$$

using a computer best fit program and determined the boiling point of pure trimethylaluminium monomer as 281K. The $\Delta H^o_{d(1)}$ value that he calculated from triethylaluminium-trimethylaluminium heat of mixing experiments is consistent with the series of vapor pressure data available and trimethylaluminium being a normal Trouton liquid. However, the value obtained from the n.m.r. study of the alkyl group interchange is closer to Hay *et al's* figure.[22]

The discrepency between Smith and Hay *et al* is more marked for triethylaluminium. Smith has recalculated the dissociation constants from the raw vapor density data displayed in Hay *et al's* paper and obtained substantially different results. It appears that these recalculated results agree reasonably well with those obtained by Smith from heat of dilution experiments modified for dissociation in the gas phase.[15]

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The degree of dissociation α_{sp} of triethylaluminium at saturation pressure appears to decrease with temperature if it is calculated from the $K_{d(g)}$ given by Hay *et al.*[11] This is unusual since, even if the pressure has not remained constant, it means that triethylaluminium is more associated at higher temperatures. Using Smith's $K_{d(g)}$ calculated from the data of Hay *et al*,[11] the value of α_{sp} does increase with temperature.

In deriving the value $\Delta H^o_{d(1)} = 52.3$ kJ mol dimer^{-1}, Hay *et al*[12] used an estimated enthapy of vaporization of monomer (ΔH^o_{VM}) of 39.7 kJ mol dimer^{-1}. Smith[15] argues that this is too high, as a Trouton liquid with this ΔH^o_V would have a boiling point of 415K, which is higher than that of the trimethylaluminium dimer. The derived value for ΔH^o_{VD}, the enthapy of vaporization of pure triethylaluminium dimer as calculated by Hay *et al* is 89.1 kJ mol dimer^{-1}. This is surely too high as a Trouton liquid with this enthalpy of vaporization will have a boiling point of 608K. The ΔH^o_{VD} derived from Smith's estimate of $\Delta H^o_{d(g)}$ is 64.2 kJ mol dimer^{-1}. This corresponds to a more reasonable 538K for the boiling point of the pure dimer. Smith[15] also demonstrates that vaporization parameters derived from his vapor dissociation parameters are compatible with those obtained from both the Hay *et al*[11] and the Laubengayer and Gilliam[17] vapor pressure data.

Smith determined the thermodynamic properties for triethylaluminium dissociation in the liquid phase by a heat of dilution method,[13] covering a wide temperature range, obtaining substantially larger values

I.4.

($\Delta H^{o}_{d(1)}$ = 70.7 kJ mol dimer^{-1}, $\Delta S^{o}_{d(1)}$ = 134.7 J mol^{-1}K^{-1}) than those derived by Hay *et al*, whose values do agree with those presented by Allen and Byers.[14] Allen and Byers do, however, admit that the values which they obtained for the enthalpies and entropies of dissociation; $\Delta H^{o}_{d(1)}$ = 51.0 kJ mol dimer^{-1}, $\Delta S^{o}_{d(1)}$ = 102 J mol^{-1}K^{-1} (when converted from a 1 molar standard state to a pure substance (mole fraction = 1)) by an ebullioscopic method are not reliable. This is because

a) apparent molecular weight measurement is not reliable,

b) only four data points were obtained, and these were in the narrow temperature range 354K-399K, and

c) one of these points was determined using toluene as the solvent. This has been found to complex with triethylaluminium.[24]

In summary, the parameters determined by Hay *et al* for the triethylaluminium vapor are miscalculated, and those calculated from the data presented by Laubengayer and Gilliam are not valid due to decomposition. The liquid phase values as determined by Smith are to be preferred to those of Allen and Byers on the grounds of method reliability and temperature range covered. The use of hydrocarbon analogues by Smith to determine enthalpy and entropy differences between liquid and vapor dissociations also appears to have a sounder base than the periodic trend method used by Hay *et al*, as demonstrated by the compatability of derived and experimental parameters. Consequently, the liquid phase dissociation parameters used in future discussion in this treatise will be those of Smith. The correct values for the gas phase, of which we fortunately have no cause to use, are still open to conjecture.

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4.2. CHEMICAL PROPERTIES

The aluminium-carbon bond is a highly reactive co-valent one, as expected from the Pauling electronegativity of the aluminium atom (1.50). However, the reactivity is not as high as that of the alkali metal alkyls (electronegatively about 0.8) and thus the reactions of trialkylaluminiums and alkyl compounds of elements of similar electronegativity (Si, Be, Mg) are able to be controlled to some degree by manipulating solvents and temperatures. This property of the Al-C bond - high reactivity, together with an element of control - is the reason for the widespread use of organoaluminiums throughout all fields of chemistry.

The chemical reactions of trialkylaluminiums may be grouped in the following way:

a) Reaction to form complexes with electron donors not containing acidic hydrogen.

b) Reaction to form complexes with electron donor compounds containing acidic hydrogen.

c) Reaction to form anionic complexes.

d) Thermal rearrangement and decomposition.

f) Addition-Elimination reactions.

- (i) with alkenes
- (ii) with alkynes
- (iii) with nitriles
- (iv) with oxygen containing compounds

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A full description of the chemical properties not studied here (b,c,d,e,f(iii) and f(iv)) are available in any one of several excellent texts[8, 21, 25] and so will not be discussed further.

The reactions of trialkylaluminiums with alkenes and alkynes is by far the most important and these will be discussed fully in Sections II and III respectively. In Section IV, the reactions of two co-ordination complexes ($Et_3Al{\leftarrow}NEt_3$ and $Et_3Al{\leftarrow}NBu_3$) will be discussed and so the full description of these types of compounds will be left until then. Suffice it to say at this stage that trialkylaluminiums are strong Lewis acids complexing with electron donors to form, in most cases, thermally stable compounds.

With electron donor compounds containing acidic hydrogen, the trialkylaluminiums again complex, but usually the complexation is accompanied by the evolution of alkane (the aluminium carbon bond reacts with the acidic proton), and association to dimers or trimers of the complex results.[45]

For example:

$$AlMe_3 + NHMe_2 \rightarrow Me_3Al{\leftarrow}NHMe_2$$

$$2Me_3Al{\leftarrow}NHMe_2 \rightarrow (Me_2Al{\leftarrow}NMe_2)_2 + 2CH_4$$

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SECTION II

THE REACTION OF TRIETHYLALUMINIUM WITH ALKENES

Synopsis

Introduction - Ethylene undergoes growth and displacement reactions, but only dimerization is observed with n-alk-1-enes. Kinetic evidence shows that rate determining step for displacement is alkene elimination and that the monomer is reactive in addition to alkenes. To date, kinetics have been explained in terms of one or two of the Dessy mechanisms.

Reaction with 2-methylhept-1-ene - No vinyl π complex could be found by p.m.r. spectroscopy. Kinetic parameters were evaluated between 398K and 423K, using p.m.r. spectroscopy and were found to be high when compared with other alkenes.

Reaction with styrene - An aromatic π complex was found and confirmed by showing complexing in other aromatic solvents. Kinetics of addition were evaluated at low conversion due to simultaneous polymerization. Kinetic parameters were determined for the preferred mechanism, which does not include an aromatic π complex as an intermediate.

Discussion of mechanism - All kinetic parameters are explained in terms of two alternative rate determining steps - formation of a vinyl π complex or a four-centre transition state. Entropy calculations show this to be plausible.

II.1.

1. INTRODUCTION

1.1. General

Ziegler's original growth or "aufbau" reaction[1,2] involves the combination of triethylaluminium with ethylene under comparatively mild conditions. (373K, 100 atm).

$$AlR_3 + 3nC_2H_4 \rightleftarrows (R(C_2H_4)_n)_3Al \qquad ....(1)$$

This reaction, however, is in competition with the displacement or "verdrangung" reaction.

$$R'_2Al\text{-}CH_2\text{-}CH_2R \rightleftarrows R'_2Al\text{-}H + CH_2 = CH_2R \qquad ....(2)$$

$$R'_2Al\text{-}H + CH_2{=}CH_2 \rightleftarrows R'_2AlC_2H_5 \qquad ....(3)$$

If a second alkene is present the additional equilibrium

$$R'_2Al(CH_2)_2R + CH_2{=}CR''R''' \rightleftarrows R'_2AlCH_2CHR''R''' + CH_2{=}CH_2R \qquad ....(4)$$

is also present. Straight chain alkylaluminiums are more stable than branched alkylaluminiums so the equilibrium position of reaction (4) lies on the left hand side. In general, the ease of displacement of an alkyl group from an alkylaluminium compound decreases in the series

$$RR'CH\text{-}CH_2\text{-} > RCH_2\text{-}CH_2\text{-} > CH_3\,CH_2\text{-}$$

II.1.

The equilibrium constants

$$K = \frac{[\text{n-alkyl-Al}]\ [\text{isoalkene}]}{[\text{isoalkyl-Al}]\ [\text{n-alkene}]}$$

$$K = \frac{[\text{ethyl-Al}]\ [\text{n-alkene}]}{[\text{n-alkyl-Al}]\ [\text{ethylene}]}$$

$$K = \frac{[\text{ethyl-Al}]\ [\text{isoalkene}]}{[\text{isoalkyl-Al}]\ [\text{ethylene}]}$$

have been estimated as approximately 40,40 and 1600 respectively.[3,4]

In spite of this displacement, however, the growth reaction is capable, under suitable conditions, of producing trialkylaluminiums containing 4-30 carbon atoms. There are a number of technical difficulties. At low temperatures the growth is slow, while at higher temperatures unwanted side reactions predominate. Growth is exothermic to the extent of 84 kJ per mol of ethylene uptake and the reaction consequently becomes explosive at high pressures and temperatures. Zosel[5] solved these problems by conducting the reaction in thin heated copper tubes, whereby the residence time is shortened permitting an increased temperature of reaction (433K) and eliminating side reactions such as double bond isomerization and dimerization. A narrow range of alkene chain lengths is obtained using Zosel's technique, if a smaller amount of ethylene is reacted first, to produce small alkenes, which are then recycled.[6]

II.1.

When trialkylaluminiums react with alkenes other than ethylene, the reaction rarely proceeds beyond the first adduct before displacement, reaction (2), resulting in the formation of 2-alkylalk-1-enes

$$\begin{aligned} AlR_3 + H_2C{=}CHR' &\rightleftarrows R_2AlCH_2CHRR' \rightleftarrows R_2AlH + H_2C{=}CRR' \\ R_2AlH + H_2C{=}CHR' &\rightleftarrows R_2AlCH_2CH_2R' \qquad \ldots.(5) \end{aligned}$$

An important example of this reaction is the addition of tripropylaluminium to propene eliminating 2-methylpent-1-ene which is in turn isomerized to 2-methylpent-2-ene. On pyrolysis this yields isoprene and methane.

Perry and Ory[7] did force the reaction of triethylaluminium and n-1-octene beyond the first adduct stage, but even under their extreme conditions they only managed to dimerize octene to give 2-hexyldec-1-ene in addition to the first adduct.

II.1.

1.2. Previous Kinetic Studies

1.2.1. Displacement

Evidence suggests that the rate determining step for alkene displacement from trialkylaluminiums is the decomposition to dialkylaluminium hydride and alkene. Firstly, the rates of addition of dialkylaluminium hydrides to alkenes are in the same order as rates of alkene displacement,[8] i.e.

$$CH_2{=}CH_2 \; > \; RCH_2{=}CH_2 \; > \; R_2C{=}CH_2 \; > \; RCH{=}CHR$$

Secondly, when tridecylaluminium reacts with ethylene, the growth reaction appears dependent on ethylene pressure, while the displacement reaction does not.[1] Thirdly, the nature of the alkyl group in n-alk-1-enes does not affect the rate of displacement of propene from tripropylaluminium.[4]

Unfortunately the kinetic studies were performed at either high concentrations in the liquid phase or high temperatures in the gas phase, and so it is impossible to decide whether the monomer or dimer is reactive. Mole and Jeffery[9] have proposed that the order of reactivity observed[10]

$$AliBu_3 \; > \; Aln\text{-}alkyl_3 \; > \; AlEt_3$$

indicates that the monomer is reacting. This implies that the reactivities of each monomer are either the same or in the reverse order to that above, and that the varying concentrations of each monomer determine the reactivity order. (Triisobutylaluminium is the least associated.) This is not so. The ease of elimination from each alkyl is determined by the lability of the β hydrogen on the alkyl group, and observed reactivities can be accounted for on this basis, because the hydrogen lability is increased in more substituted alkyls. A reactive monomer does, of course, accentuate the reactivity differences between the alkylaluminiums due to the varying concentrations, but this fact can in no way be used as an *apriori* reason to account for the observed order.

Egger has determined the kinetics of gas phase alkene elimination from several trialkyl compounds of Group III metals including aluminium, and has interpreted his data in terms of a four-centre, polar, transition state as the rate determining step for alkene elimination.[11-13,21] A four-centre transition state was postulated for alkene additions by triethylaluminium by Allen, Allison, Majer and Robb in 1963[14] and has since gained wide acceptance. Egger's results reinforce some of the points made later in this treatise, and a full discussion of his kinetic data is in Section II.4.

1.2.2. Addition

The first kinetic determination of the addition reaction appears to be that of Natta *et al*[15] who studied the triethylaluminium/ethylene system, but their results were inconclusive. Ziegler *et al*[1,16] also studied the triethylaluminium/ethylene system, but under their conditions

(383K, decalin solvent), the displacement reaction to give but-2-ene was suppressed and only the addition reaction occured. They found that the rate of ethylene uptake was proportional to the square root of the triethylaluminium concentration, thereby implying the monomer to be reactive, as the dimer is predominant in solution at 383K.

$$Al_2Et_6 \quad \overset{K_{d(1)}}{\rightleftarrows} \quad 2AlEt_3 \qquad \text{....(6)}$$

Allen, Allison, Majer and Robb[14] investigated the reaction between triethylaluminium and hex-1-ene by following the formation of products using gas chromatography. Their data seemed to indicate dimeric triethylaluminium as the reacting species. However, their experimental technique is suspect on two grounds. A sampling method, unsuitable for such air-sensitive reagents as triethylaluminium was used to follow the reaction, and secondly, quantitative extraction from such a complex reaction mixture is a long and tedious procedure. Both of these reasons could explain in part the low precision of their work. In addition, their quoted Arrhenius parameters (which appear to rule out monomer participation) are not valid as Laubengayer and Gilliam's data were used (see Section I.4).

A consequent re-investigation by Allen, Hay, Jones and Robb[17] of the reaction of triethylaluminium with prop-1-ene, but-1-ene, pent-1-ene as well as hex-1-ene, using gas absorption techniques for the first three and dilatometry for the latter, resulted in the conclusion that the monomer only was reacting. The Arrhenius parameters quoted do take into account the heat of dissociation of the dimer, and thus their relative rate parameters should be correct, but the absolute values are still incorrect because the dissociation parameters used were again those of Laubengayer and Gilliam. In addition, dilatometry is not a very sensitive method for following these reactions, and it is also potentially ambiguous because column changes may arise from shifts in the position of association equilibria during the course of the reaction, as well as from the addition reaction.

More recently, Hay *et al* have extended their dilatometric study to include 4-methylpent-1-ene, 3-methylpent-1-ene, 2-methylpent-1-ene, 3,3-dimethylbut-1-ene, n-oct-1-ene and cyclohexene, as well as restudying hex-1-ene.[18] In spite of the availability of dissociation parameters calculated for the liquid phase, they persisted in using the uncorrected vapour phase values to determine Arrhenius parameters.

Allen and Byers studied in detail the kinetics of the triethylaluminium/n-oct-1-ene system by the superior experimental technique of p.m.r. spectroscopy.[19] This is a direct method whereby the actual concentration of each species in the reaction mixture is followed, and is to be preferred to blind methods such as dilatometry which depend on a bulk property. In their results, the slope of the log-log plot of initial rate against total triethylaluminium concentration was 0.5±0.1

and the integrated rate plots gave straight lines for the integrated form of equation (7)

$$v = -d[\text{oct-1-ene}]dt = kC_{Al}^{\frac{1}{2}}[\text{oct-1-ene}] \qquad \text{....(7)}$$

The reaction order is thus again indicative that monomeric $AlEt_3$ is the reactive species. Allen and Byers and Lough confirmed this result whilst establishing the mechanism of the triethylaluminium/n-oct-1-ene system in diphenyl ether solutions.[20]

A study of the kinetics of the gas phase addition of ethylene to triethylaluminium[12] and trimethylaluminium[11] and the addition of propene to the latter[22] has been recently published by Egger. The study was made at temperatures ranging from 478.1K to 587.2K and at these temperatures the trimethylaluminium was assumed to be exclusively monomeric. From the accepted dissociation parameters[23]

$$\log_{10} K_{d(g)} = 9.4395 - 4457.9/T$$

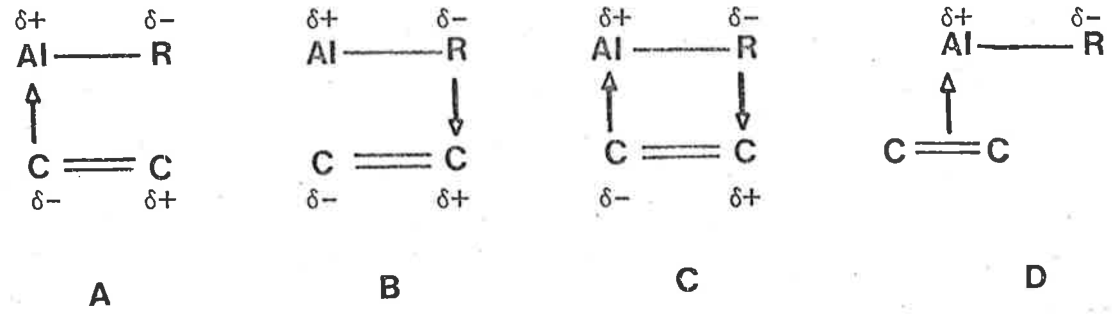
the dissociation constant at 478K is 1.3 atm. and 70.3 atm. at 578K. Most of the determinations appear to have been carried out at approximately 0.3 atm. At this pressure, trimethylaluminium has a degree of association of 0.28 at 478K, and thus the assumption is unjustified, especially at the lower temperatures. The quoted kinetic coefficients are therefore only a first order approximation, but this will have little effect on the rate equation except at high pressures, and so the mechanistic conclusions remain.

In summary, it can be stated that present evidence is overwhelmingly in favour of a reactive trialkylaluminium monomer in addition to alkenes. The low *A* factors determined have consistently been interpreted in terms of a four-centre transition state, and most workers postulate a π complex between the unsaturated bond and the aluminium to precede the transition state.

Only Arrhenius parameters for the addition to alkenes of the type $RCH=CH_2$ are available. The one kinetic study of addition with an alkene of the type $R_2C=CH_2$ attempted was 2-methylpent-2-ene/triethylaluminium and this was reported not to react.[18] This seems singularly unusual because internal olefins have been shown to dimerize with triethylaluminium at 473K, although the resulting product appears to have been produced from an olefin not present in the original solution, but one formed from double bond migration.[24] When the reactivities of n-alk-1-enes and alk-2-enes with diethylaluminium hydride are compared with the reactivity of n-alk-1-enes with triethylaluminiums, it appears that alk-2-enes should react with triethylaluminium, although at a reduced rate.

Possible mechanisms for the nucleophilic addition of covalent organometallic components were first proposed by Dessey.[25] The crucial factor is the role of the metal atom. Specifically for aluminium, the mechanisms are

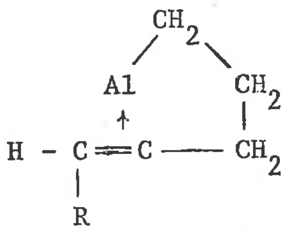
II.1.



Extreme cases are the nucleophilic attack of an electron rich carbon on the metal (A), a nucleophilic attack of a carbanionic like alkyl group to an electropositive atom (B), and the formation of a complex (D). The intermediate case (C) involves concerted nucleophilic attacks and is usually postulated as a transition state.

As mentioned previously, low *A* factors for the addition of triethylaluminium to n-alk-1-enes have, since 1963, been interpreted in terms of a four-centre transition state (C), preceded by a π complex (D). Reasons for preferring the formation of D to mechanism B are based on the effect of complexing solvents and will be discussed in Section V. The formation of D in preference to the reaction proceeding via mechanism A is based on the fact that, in alkenes, no significant charge localization occurs in the double bond. With compounds such as nitriles, which have significant charge separation along the unsaturated bond, mechanism A is much more likely.

In 1968, Hata[26] reported evidence of an intramolecular complex formed between an olefinic double bond and aluminium. Infra-red and p.m.r. determinations indicated that such an interaction is present in alk-4-enyldiisobutylaluminiums, but absent in the corresponding alk-6-enyl and alk-7-enyl compounds. Intramolecular complexing was claimed because the observed spectroscopic changes were independent of concentration. They also disappeared in diethylether solution.



Two points about this work need to be made. Firstly, all p.m.r. spectra appear to be determined in benzene. This is known to complex with trialkylaluminiums, therefore some spectroscopic changes could be due to this complex rather than intramolecular complexing. Secondly, models show that alk-5-enylaluminium compounds should form a more stable intramolecular complex than alk-4-enylaluminium compounds, due to the formation of a six membered ring. The conclusions presented would be more convincing if the spectroscopic changes had also been demonstrated to be present in alk-5-enyl but absent in alk-3-enyl aluminium compounds.

While the overall mechanism for alkene addition is generally accepted as a π complex, followed by a four-centre transition state, several reactivity factors affecting this mechanism remain obscure. Specifically, data on the effect of steric and electronic factors are very slight. Hay *et al*[18] have reported kinetic results on the addition of 3,3dimethyl-but-1-ene with triethylaluminium, but their interpretation of the high kinetic parameters observed (Table II.4) in terms of a methyl shift is unattractive because methyl shifts in hydrocarbons are rare at 400K.

In order to try and evaluate some of the steric and electronic factors, it was decided to investigate the kinetics of the addition of triethylaluminium to 2-methylhept-1-ene (bulky, slightly electron donating) and styrene (bulky, electron withdrawing), and at the same time, try and establish the presence of the π complex.

2. REACTION OF TRIETHYLALUMINIUM WITH 2-METHYLHEPT-1-ENE

2.1. Material Handling

The extreme reactivity of triethylaluminium with air and moisture necessitates special handling and dispensing techniques. In this study a vacuum line technique was used, but other workers have successfully performed experiments using an inert-gas purged glove box. This can be clumsy, however, when physical measurements need to be taken, and is always susceptible to contamination due to the practical impossibility of obtaining a completely airtight seal. Evacuation, and sealing with glass eliminates all of these disadvantages, but has its own disadvantage in being tedious. Some workers also claim that, under high vacuum, triethylaluminium reacts with the glass walls to evolve ethane,[27] but this has never been a problem in this laboratory. Before describing in detail the purification techniques, a brief description of the vacuum line used will be given.

The vacuum apparatus employed in this work, shown schematically in Fig. II.1, consists of two separate lines that can be interconnected in order to optimize the available pumping capacity. An Edwards single stage rotary oil pump was used as the backing pump, and this was connected to two three stage mercury diffusion pumps, which in turn led into the two manifolds. One manifold was reserved exclusively for evacuating vessels that contained no frozen solvent. Springham Viton "A" greaseless taps were used throughout this "exclusive" manifold to eliminate any grease

VACUUM LINE

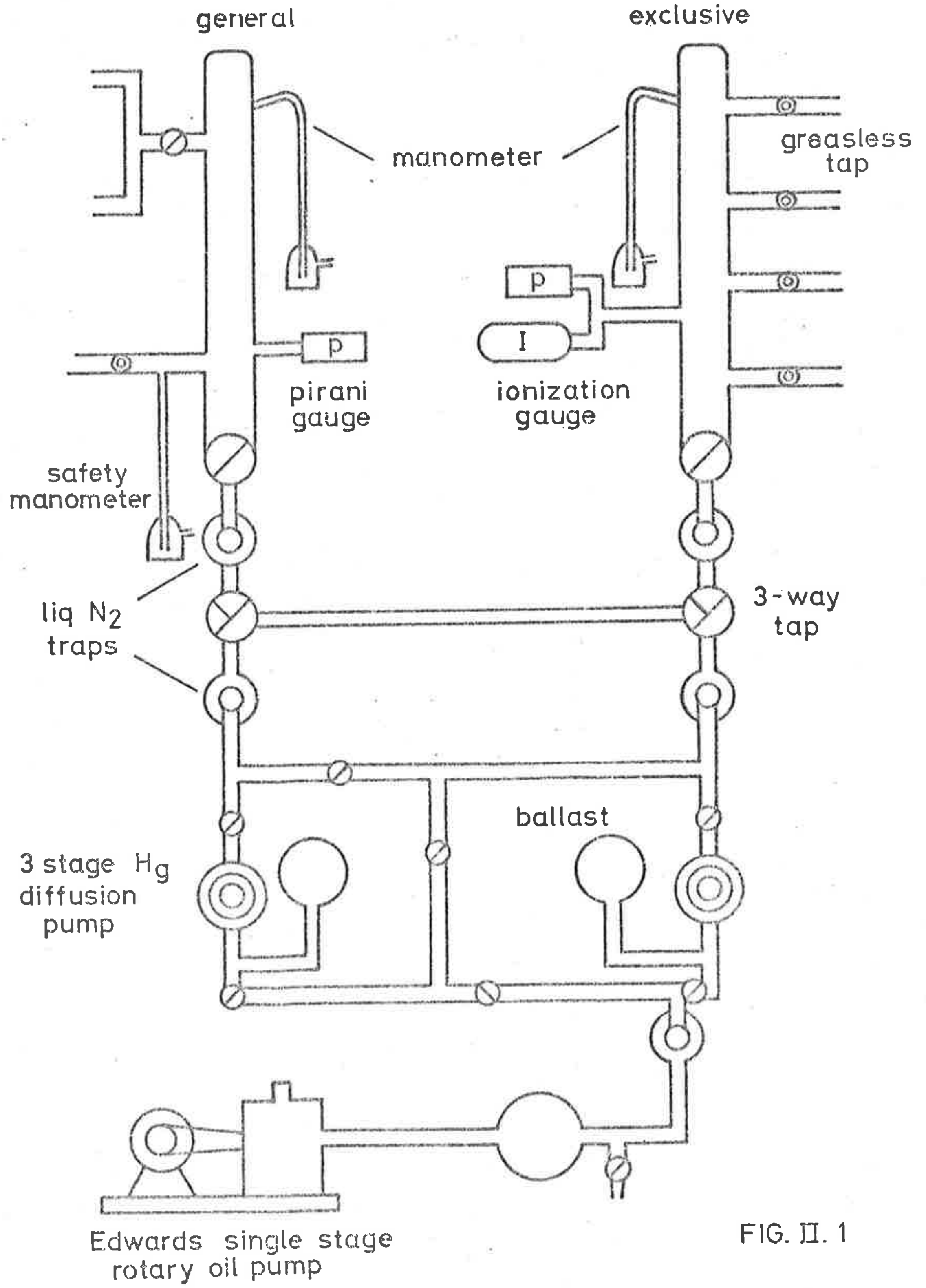


FIG. II. 1

contamination and to minimize leaks from grease streaks. The other manifold contained greased taps (Dow Corning High Vacuum grease), and was used for general purposes such as distillation of solvents and evacuating vessels containing solvents that were liable to contaminate the line. As can be seen from Fig. II.1, the diffusion pumps can pump each line separately, or both can be connected to a single manifold, either in parallel, or in series if high capacity pumping was needed.

Evacuation was assisted by using electrical heating tape to heat the manifolds and liberal use of liquid nitrogen traps. Pressures were generally measured with Edwards Pirani gauges, but for a high vacuum in the exclusive line a G.E.C. Ionization gauge was used. By these methods, the average evacuation time of a vessel was reduced by up to 50% when compared to less elaborate apparatus.

Purification of Triethylaluminium

Triethylaluminium was obtained from Ethyl Corporation, Texas, U.S.A., in lecture bottles containing 200 gms of the alkyl under about 5 psi of nitrogen, from which it has to be removed, purified and sealed in glass breakseals before it can be used further. The triethylaluminium purification apparatus is shown in Fig. II.2. The lecture bottle, supported in an upright position, was connected to a 100 ml. receiving vessel by a length of high density polyethylene tubing. This vessel was in turn connected to a dispenser for either nine or ten breakseals. The

$AlEt_3$ PURIFICATION

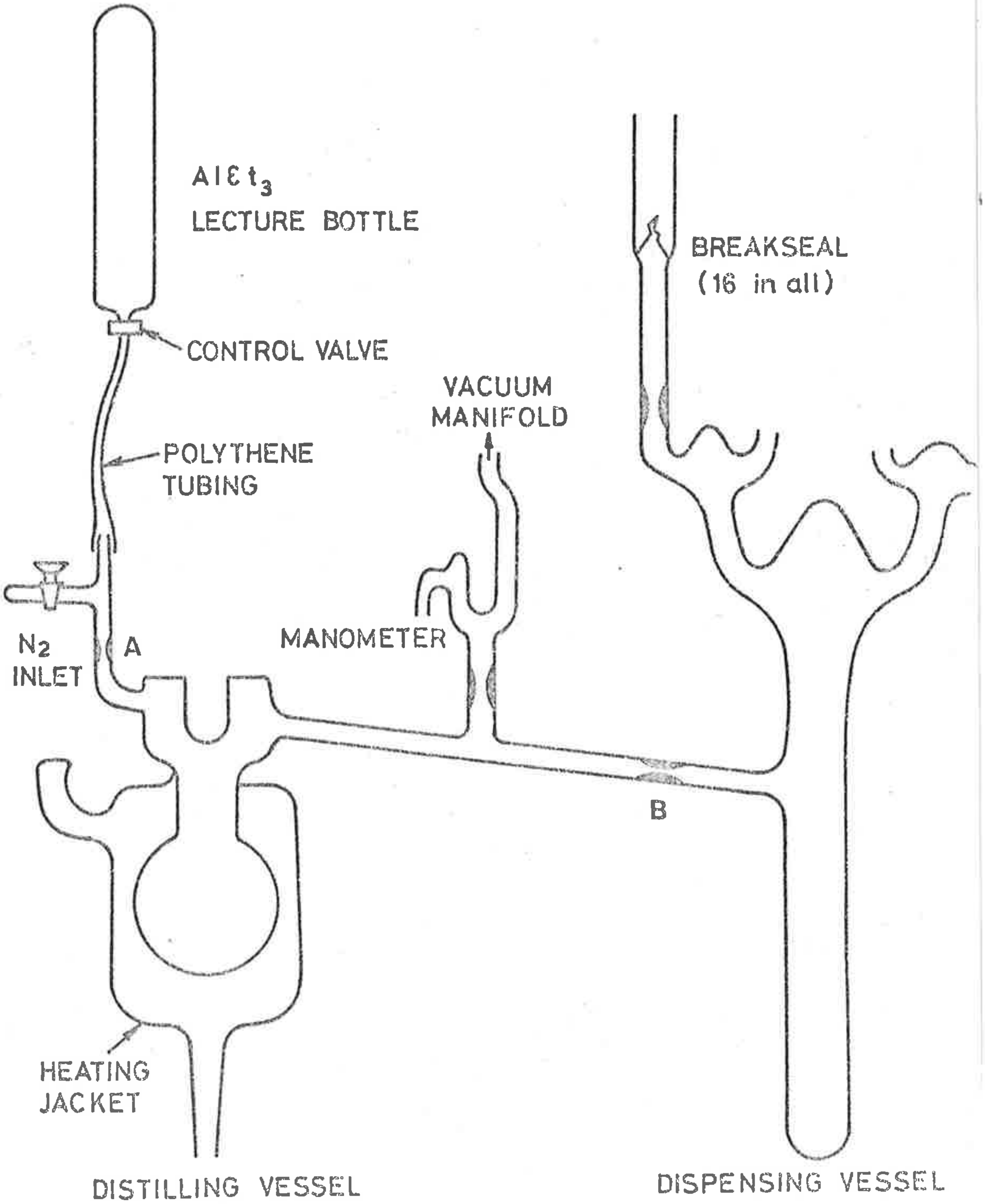


FIG. II 2

vacuum takeoff was provided with a safety manometer for emergencies. After one hour of evacuation ($10^{-1}Nm^{-2}$), the tap to the line was shut and the control valve of the lecture bottle opened *very* slowly and carefully, allowing about 75 ml. of triethylaluminium to run into the receiving vessel. The lecture bottle valve was then closed and the constriction at A sealed to form a complete glass apparatus. This was done as molten glass seals are infinitely more reliable than polythene/glass, metal/polythene or metal/metal seals.

The major impurity formed during the commercial synthesis of triethylaluminium is diethylaluminium hydride.[28] Since this has a higher boiling point than triethylaluminium ($AlEt_2H$ exists as a trimer), it was felt that distillation under reduced pressure would purify the triethylaluminium sufficiently for our purpose. In order to accomplish this, heptane vapour (b.p. 371K) was introduced into the outer jacket, after first outgassing the alkyl by opening the vessel to the line for about half an hour. (The vapour pressure of triethylaluminium at room temperature is negligible.) To assist in distillation the dispenser was frozen with liquid nitrogen (b.p. 77K). The distillation was stopped when the residue started to discolour (approximately 80% distilled) and the dispenser was sealed at constriction B. The distilled alkyl was then thawed and tipped into breakseals which were then sealed from the main dispenser.

The average amount in each breakseal (7-10 mls.) was generally far too much as the kinetic experiments required usually 1 ml. or less per run, and so it was necessary to divide each prepared triethylaluminium breakseal into smaller quantities. This was accomplished using the apparatus in Fig. II.3. After evacuation (1hr, $< 10^{-1} Nm^{-2}$), the constriction at A was sealed and the large breakseal broken by moving the nickel steel breaker against the capillary with a magnet. The triethylaluminium was then tipped to the mark in the precalibrated breakseals, which were then sealed from the dispenser. Up to 20 calibrated breakseals could be filled using this type of apparatus. As triethylaluminium is rather a viscous liquid with a long drain time, the filling procedure could be very tedious, but this was overcome by slightly overfilling the breakseal and back distilling the excess, using a very small, very cool flame. The extreme reactivity of triethylaluminium with air and moisture necessitated several special safety precautions that were observed during its manipulation. These were:

(1) Sealing of breakseals was never carried out with the contents at 77K, as volatile compounds, which may be formed during the procedure, will be condensed and on thawing will subject the breakseal to a dangerously high pressure. Such volatile compounds are ethylene, from the pyrolysis of triethylaluminium (formed if sealing is carried out whilst there is still a trace of alkyl on the glass walls), and ethane (formed if traces of moisture are still in the apparatus or in the lecture bottle).

(2) Water was never used for thawing any solution containing triethylaluminium and a "dry chemical" type of fire extinguisher was always standing by when manipulating large quantities of reagent.

BREAKDOWN APPARATUS

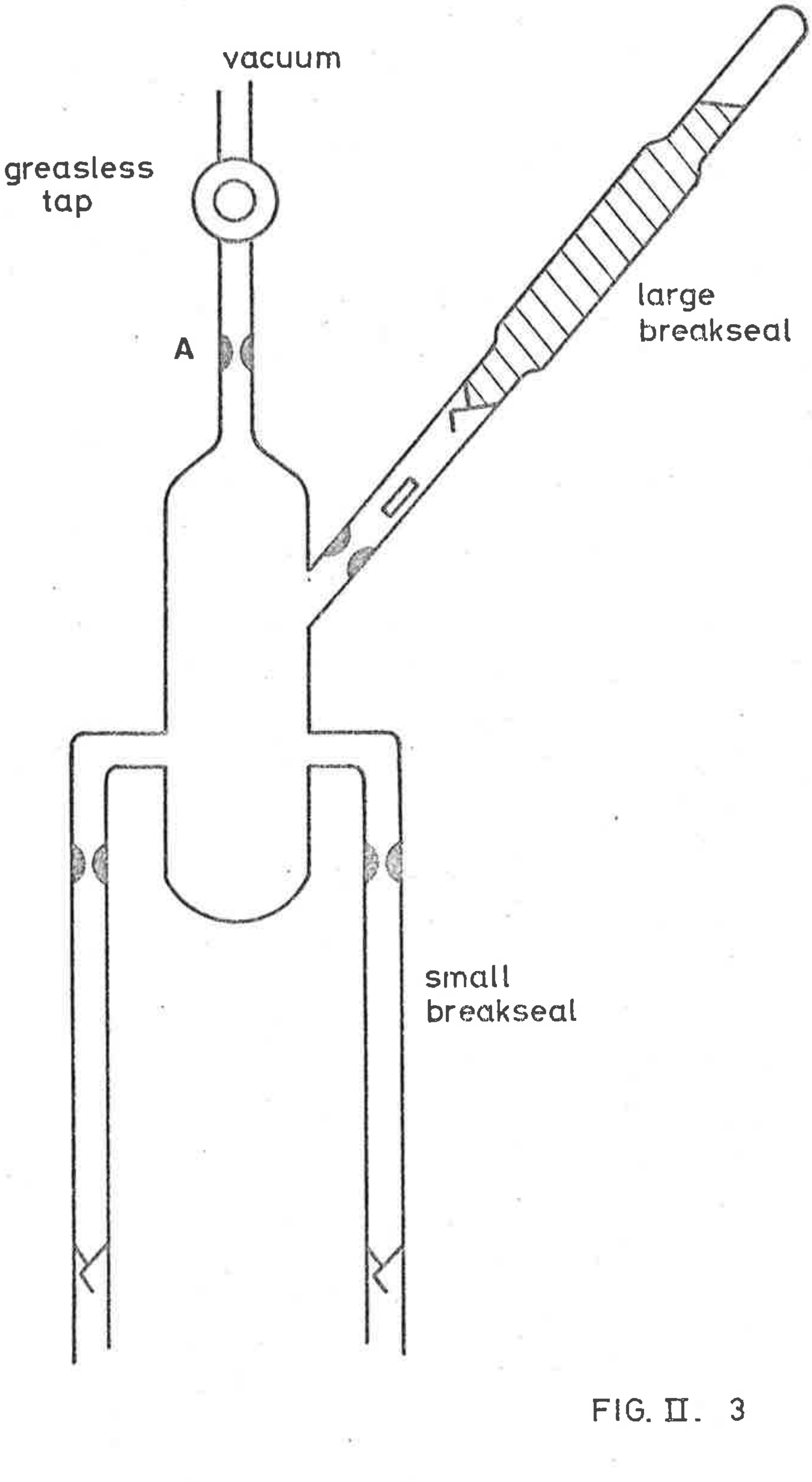


FIG. II. 3

II.2.

(3) Large scale (10 mls.) manipulation of triethylaluminium was never carried out without the presence of at least one other person in the laboratory.

(4) Deactivation of unwanted triethylaluminium solutions was achieved by dilution with commercial petroleum spirit (b.p. 413-433K) and left in a fume hood for slow reaction with the atmosphere.

(5) Breakseals of triethylaluminium were stored in vermiculite in a sealed, non-inflammable plastic container in a fume hood. The lecture bottles were stored in containers in a fire-proof room.

Purification of other compounds

(a) *2-Methylhept-1-ene* ("Purum" grade, Aldrich. Chem. Co. U.S.A.)

The alkene was dried over fresh calcium hydride for 48 hours, degassed (freeze, pump, thaw) four times and vacuum distilled into breakseals using the apparatus in Fig. II.4. Samples of the purified alkene, checked by gas chromatography, were shown to contain less than 0.3% impurity.

(b) *Phenylcyclohexane* (A.R. grade, Pfaltz and Baur, N.Y., U.S.A.)

A similar procedure to that used for 2-methylhept-1-ene was used, except that because phenylcyclohexane adheres strongly to glass, the freezing mixture was dry ice/acetone (196K). Due to contraction, cooling to 77K invariably fractured the flask. The purified compound was stored in glass ampoules.

VACUUM DISTILLATION APPARATUS

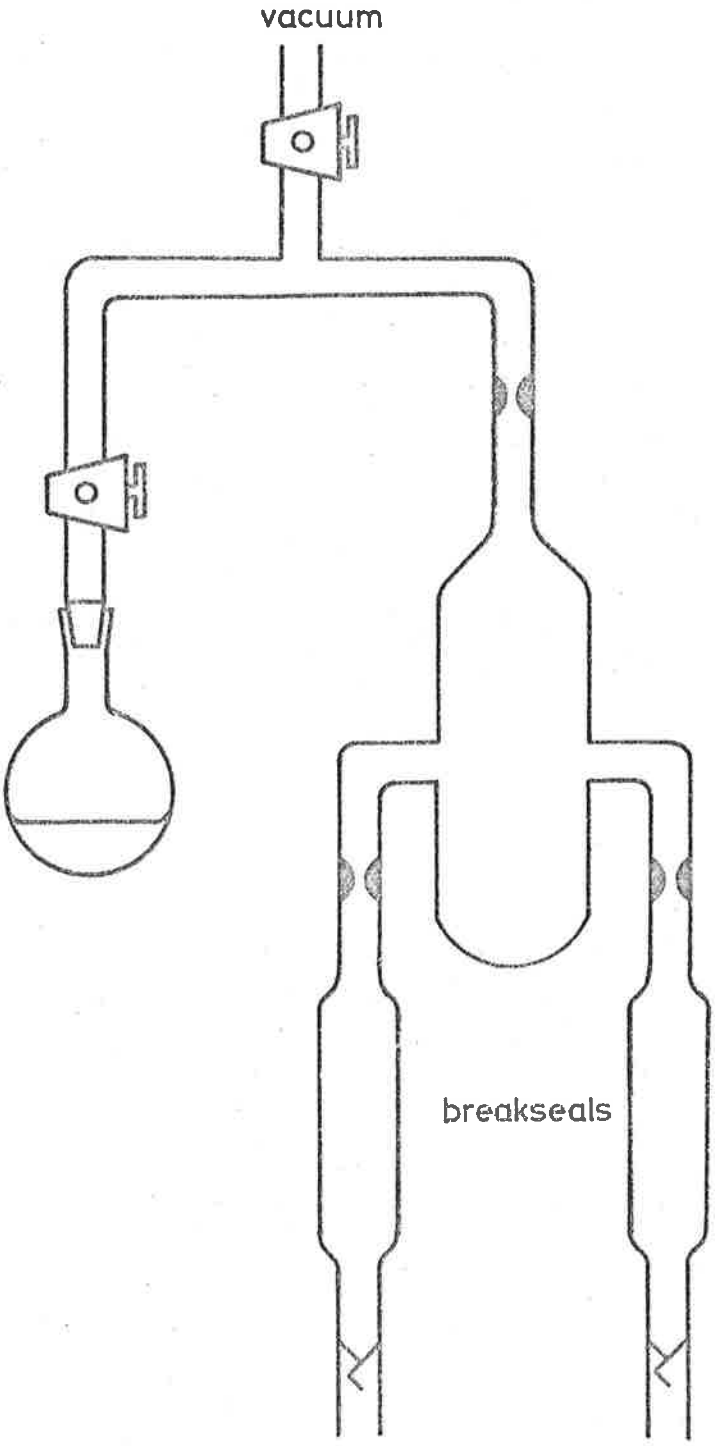


FIG. II. 4

(c) *Cyclohexane* ("Spectroscopic" grade, Fluka, Swtzld.)

The solvent was dried over calcium hydride, degassed five times, and vacuum distilled on to more calcium hydride. It was stored under vacuum over calcium hydride, and vacuum distilled into breakseals when necessary, using the apparatus in Fig. II.4.

2.2. P.m.r. Measurements

P.m.r. spectroscopy is by far the best experimental technique available to follow reactions such as the addition of triethylaluminium to alkenes. The disadvantages of a gas chromatographic sampling method and dilatometry have been outlined before. Infra-red spectroscopy is possible but cannot be preferred to p.m.r. spectroscopy because resolution of each component in the system is much better in the latter. Practical difficulties associated with obtaining a cell consisting of an inert material also are present. P.m.r. is preferred to Al^{27} n.m.r. because the line widths in Al^{27} n.m.r. are so much wider (1.5 g. for $AlEt_3$ in Al^{27} n.m.r. compared with 10^{-3}-10^{-4} g. for p.m.r.), due to the aluminium nuclear spin of 5/2 and the attendant large electric dipole moment.

We used p.m.r. spectroscopy very successfully in studying the reaction of triethylaluminium in hydrocarbon and diphenylether solution. P.m.r. spectroscopy can also be used in the investigation of the complex because there is a spectroscopic parameter that changes with the magnetic, and hence chemical, environment of the aluminium atom.

2.2.1. Triethylaluminium-Alk-1-ene π Complex

The p.m.r. spectrum of triethylaluminium in cyclohexane is shown in Fig. II.5. Formation of a complex such as a π complex will have the effect of decreasing the electronegativity of the aluminium atom and thus altering the internal shift (δ_{int}) between the methylene quartet and the methyl triplet.

P.M.R. SPECTRUM OF $AlEt_3$
in cyclohexane

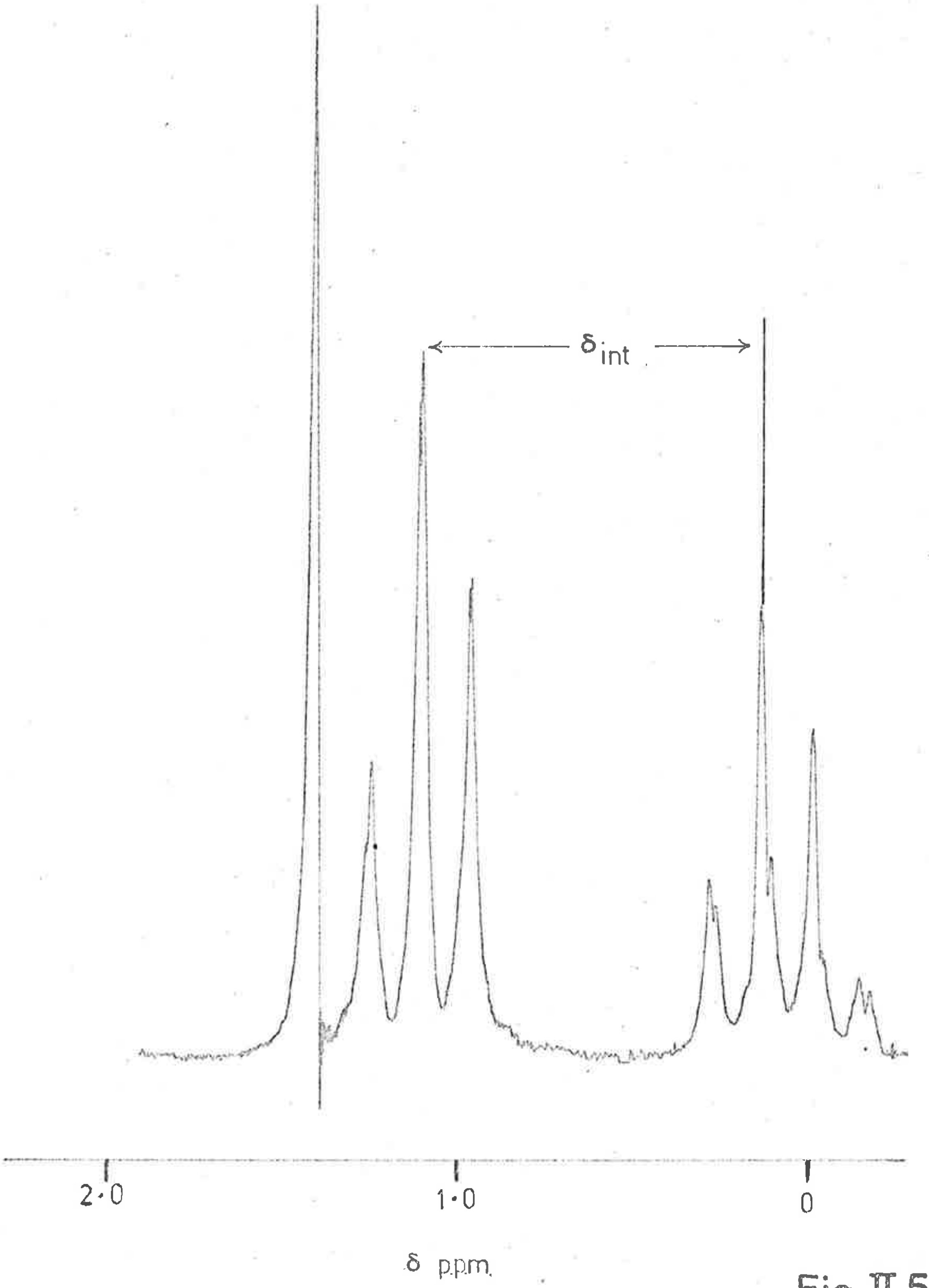


Fig II.5

II.2.

$$\delta_{int} = \delta_{CH_3} - \delta_{CH_2}$$

The dependence between electronegativity and internal proton shifts of ethyl derivatives was first recognized in a quantitive manner by Shoolery[29] and modified by Narashimhan[30] to give the relation

$$\text{Electronegativity} = 0.62\ \delta_{int} + 2.07$$

As the electronegativity of aluminium is less than 2.07, δ_{int} must be negative, inferring that the methyl protons are less shielded than the methylene protons, as observed. On complexing, the group electronegativity of aluminium is decreased, therefore the absolute value of this internal shift will increase. Thus the experiment consisted of measuring δ_{int} in a 1:1 ratio of alkene to triethylaluminium at various concentrations in cyclohexane.

The n.m.r. samples were prepared using the apparatus shown in Fig. II.6, which incorporated three input sidearms and three ouput sidearms (two n.m.r., one "dump"). After evacuation (1 hr, $< 10^{-1}\text{Nm}^{-2}$) the apparatus was sealed from the line and the alkene and triethylaluminium breakseals, each containing 0.007 mol were broken. The mixture was tipped to a predetermined height in each n.m.r. tube and the residue tipped into the "dump" tube, after which the cyclohexane was dispensed in a similar fashion to give a total volume in each n.m.r. tube of 1.6 ml.

PREPARATION OF NMR TUBES

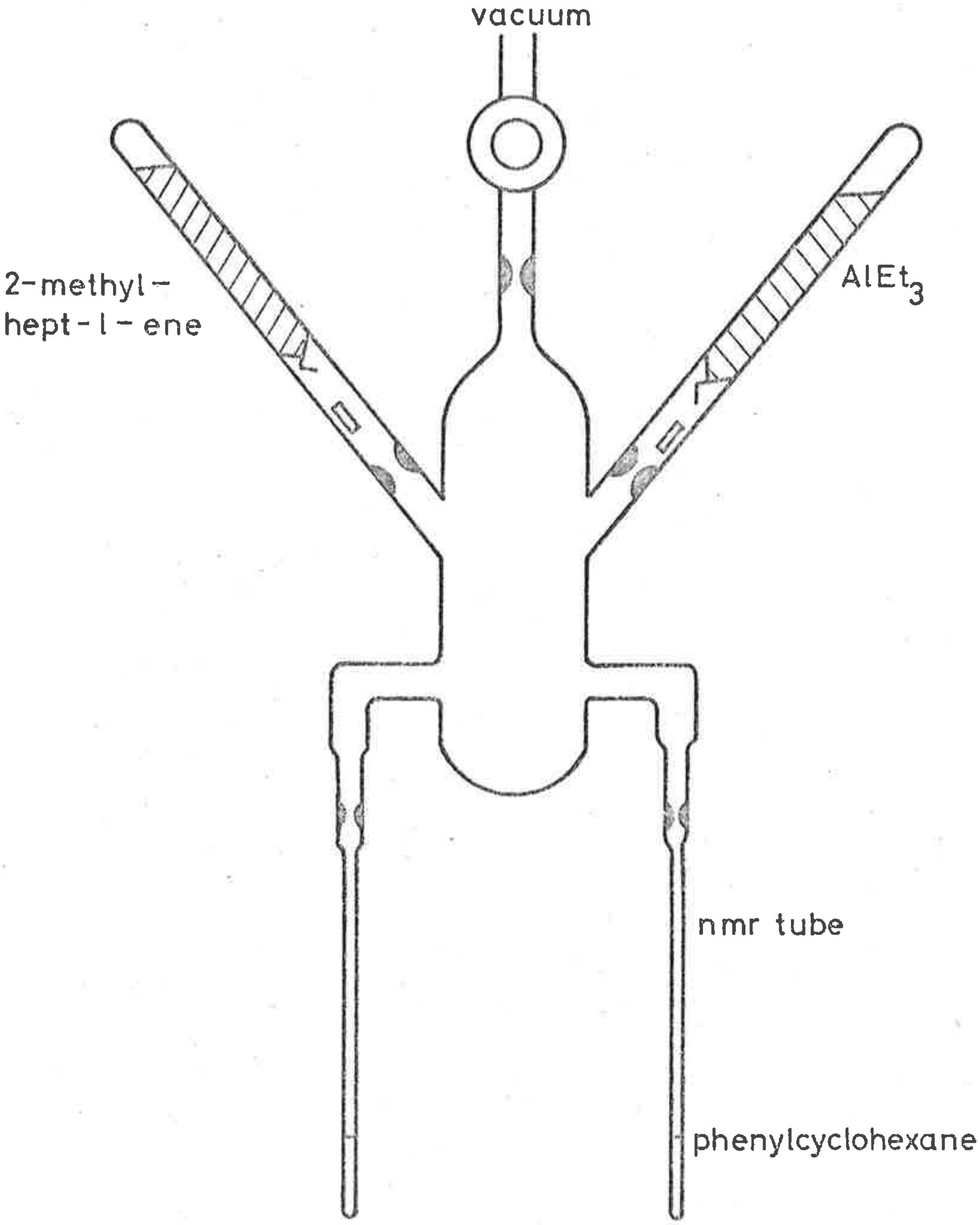


FIG. II. 6

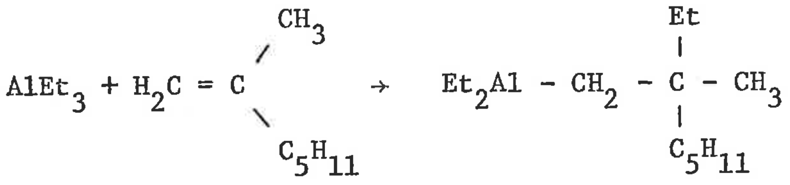
Vapour pressure calculations show that a negligible amount of reactant and solvent are present in the vapour space above the liquid. The n.m.r. tubes were then sealed off very carefully to give a symmetrical head in order to avoid precession and subsequent shattering when spun in the p.m.r. probe. After mixing, the tubes were stored at 253K, to suppress any reaction, until they were required. The two tubes so prepared contained triethylaluminium and alkene at 2.3M and 1.1M.

Values of δ_{int} were recorded for the two tubes at temperatures ranging from 302K to 213K on a Varian Associates DA-IL 60MHz.N.M.R. spectrometer. If the formation of the complex is exothermic, the concentration of the complex will increase with decreasing temperature. No significant change in δ_{int}, however, could be detected over the temperature range covered. As the temperature decreased, the only effect observed was the broadening, followed by coalescence of the methylene quartet, due to the fact that the life-time of the alkyl groups in the bridging and terminal positions was becoming longer. The study proved inconclusive because, while no significant concentration of π complex was found, it could still be present as a reaction intermediate, at very small concentration.

2.2.2. Addition of Triethylaluminium to 2-Methylhept-1-ene

The reaction to be followed is:

II.2.



$$\mathrm{AlEt_3 + H_2C = C(CH_3)(C_5H_{11}) \rightarrow Et_2Al - CH_2 - C(Et)(C_5H_{11}) - CH_3}$$

....(8)

Trans-elimination of diethylaluminium hydride to give a product alkene, as is observed in n-alk-1-enes, is not possible in this case.

The disappearance of the peak due to the vinyl proton resonance of 2-methylhept-1-ene, was selected as the means of following the reaction. A high resolution p.m.r. spectrum shows the vinyl peak to be split, due to the fact that the carbon-carbon double bond is rigid, and that there are two different alkyl groups attached, thus creating slightly different magnetic environments for the two protons.

The main advantage of using the vinyl peak to follow the reaction is that its resonance is well away ($\delta = 5.1$) from other peaks in an alkene spectrum ($\delta = 1\text{-}2$), and is thus easily distinguished and integrated. Its main disadvantage lies in the fact that the ratio of vinyl protons to other types of protons in the system is small, and thus only a small resonance is observed.

To obtain meaningful integrals, the integrator gain on the instrument has to be high, resulting in a less accurate value than would be the case with other protons, but this was partly overcome by careful tuning of the instrument and averaging several integral determinations. To relate one integral to another at a different time, it is necessary to have an integral standard in the n.m.r. tube whose concentration does not change with time. While the peaks of the standard and reactant must not overlap it is advisable that their chemical shifts shall be as close as possible in order to reduce phasing errors in the instrument. Aromatic protons are ideal for this purpose, but aromatic solvents generally complex with the triethylaluminium altering the position of the monomer-dimer equilibrium. An investigation (Section II.3.3.1.) revealed that the aromatic compounds containing large substituents complexed to a lesser degree than small or no substituents, and it was found that phenylcyclohexane altered the value of δ_{int} the least of the aromatics investigated. The small change in δ_{int} that did occur, indicated that the monomer-dimer equilibrium of triethylaluminium is not changed to a measureable extent in the presence of a small concentration of phenylcyclohexane. Therefore the aromatic proton resonances of phenylcyclohexane were chosen as the integration standard.

Preparation of tubes

N.m.r. tubes (five for each temperature) each had a set amount of phenylcyclohexane weighed into them prior to sealing on to the outlet arms of an apparatus similar to Fig. II.6. Triethylaluminium and 2-methylhept-1-ene were contained in breakseals on the input arms.

Triple de-gassing of the phenylcyclohexane followed, using a dry ice/acetone freezing mixture for the reasons mentioned previously. (II.2.1.) The apparatus was then sealed off from the vacuum line, the phenylcyclohexane thawed and the triethylaluminium breakseal broken. Following this the alkyl was dispensed into each n.m.r. tube to a predetermined height, with the residue being tipped into a "dump" tube. This was an n.m.r. tube if a triethylaluminium purity check was necessary, (e.g. first batch of a new lecture bottle) and sealed off from the apparatus. The alkene breakseal was then broken and the alkene dispensed to a predetermined height. Each n.m.r. tube contained different volumes of alkyl and alkene, but the total volume remained constant (1.4 ml.). When draining was complete, the tubes were sealed carefully, allowed to cool, mixed, and stored at 253K until measured.

Kinetic measurements

P.m.r. spectra were determined for each tube using a Varian Associates DA-IL 60 MHz spectrometer at a probe temperature of 302K. The initial (zero time) spectrum was recorded with the centre resonance of the triethylaluminium methyl triplet or one of the non-aromatic resonances of the phenylcyclohexane as the internal lock, offset 105Hz downfield. A 500Hz sweep thus scanned from 395Hz downfield of the lock to 105Hz upfield. A composite spectrum, i.e. two spectra combined to eliminate the lock signal, is shown in Fig. II.7. At least three integral sweeps in the same direction were made over the aromatic, vinyl,

P.M.R. SPECTRUM OF

$AlEt_3$–2-METHYLHEPT-1-ENE

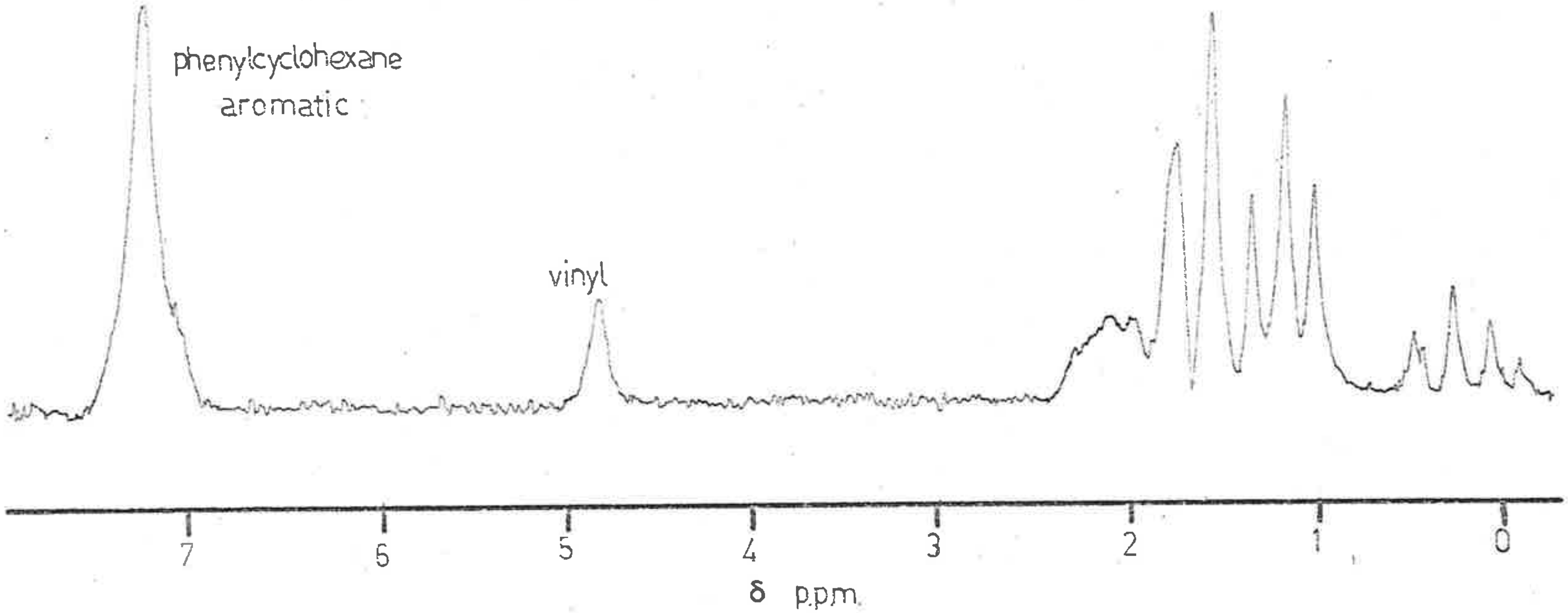


Fig II.7

and triethylaluminium methylene resonances and the initial concentrations calculated from the relationships;

$$[\text{alkene}]_o = [\text{phenylcyclohexane}]\ \frac{\text{alkene vinyl integral}}{\text{phen. cycl. integral}} \cdot \frac{5}{2}$$

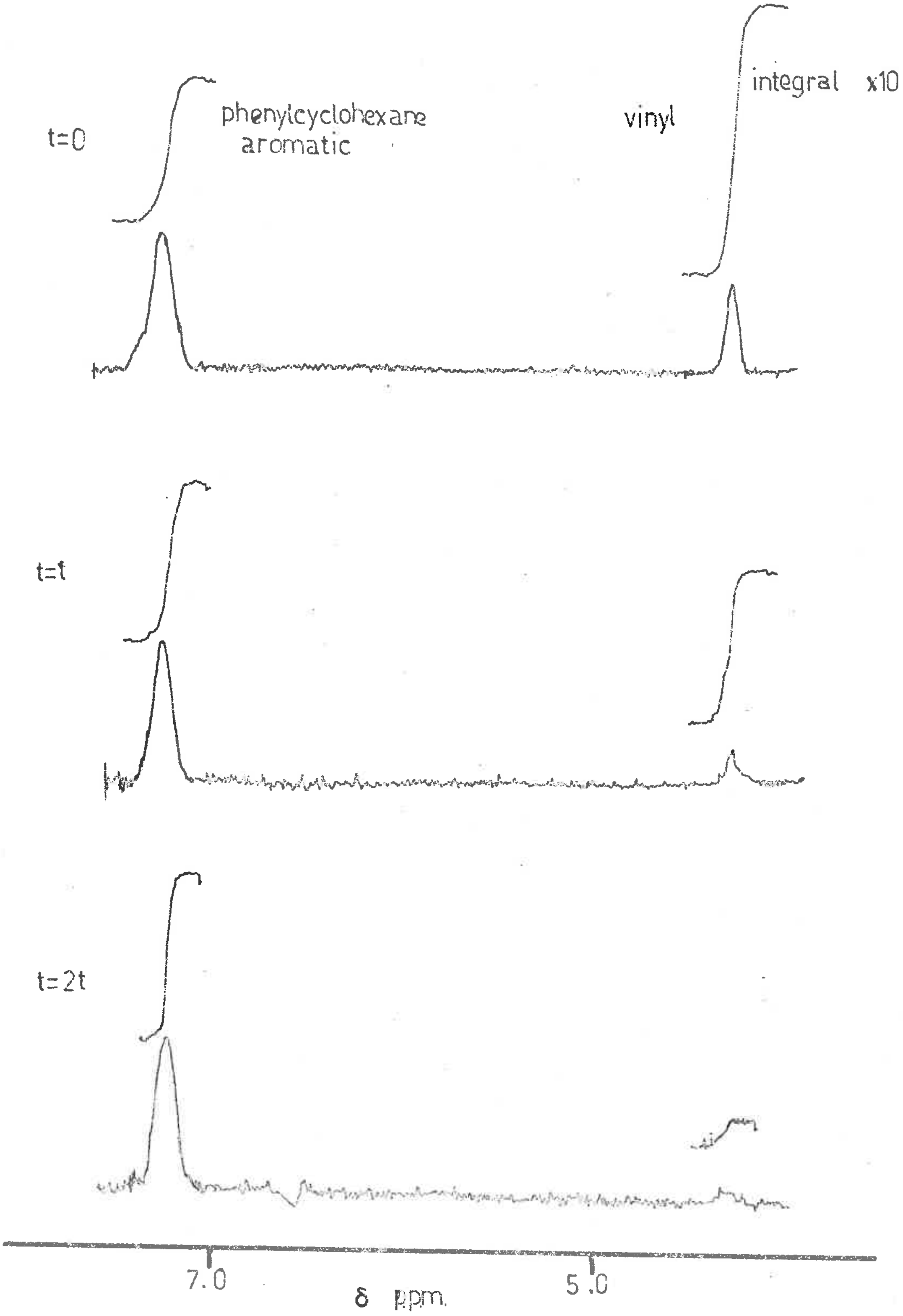
$$[\text{Al}_2\text{Et}_6]_o = [\text{phenylcyclohexane}]\ \frac{\text{Al methylene integral}}{\text{phen. cycl. integral}} \cdot \frac{5}{12}$$

The n.m.r. tubes were then placed in an oil bath (Voluta 45) at the required temperature for a set time, depending on the temperature, cooled, and stored at 253K until measured. As it was not necessary to measure the concentration of triethylaluminium throughout the reaction, subsequent spectra were recorded slightly differently. The internal lock (central Al methyl or phenycyclohexane alkyl) was offset 150 Hz upfield and a 250 Hz scan recorded. This resulted in the aromatic and vinyl resonances being spaced further apart with the integrals more sharply defined. The tubes were then replaced in the oil bath and the procedure repeated until a satisfactory kinetic curve of [alkene] vs time was obtained. At low [alkene], the vinyl integral was too small to provide accurate integrals when run on the same gain as that used to determine the aromatic integrals, and so the gain was increased by a supposed factor of 10. Accurate calibration of the decade switch with the aromatic resonances revealed, however, that the actual factor was 11.42. A typical gradation of the spectrum with time is shown in Fig. II.8 and a representative plot of the alkene decay is shown in Fig. II.9.

2.3. Results

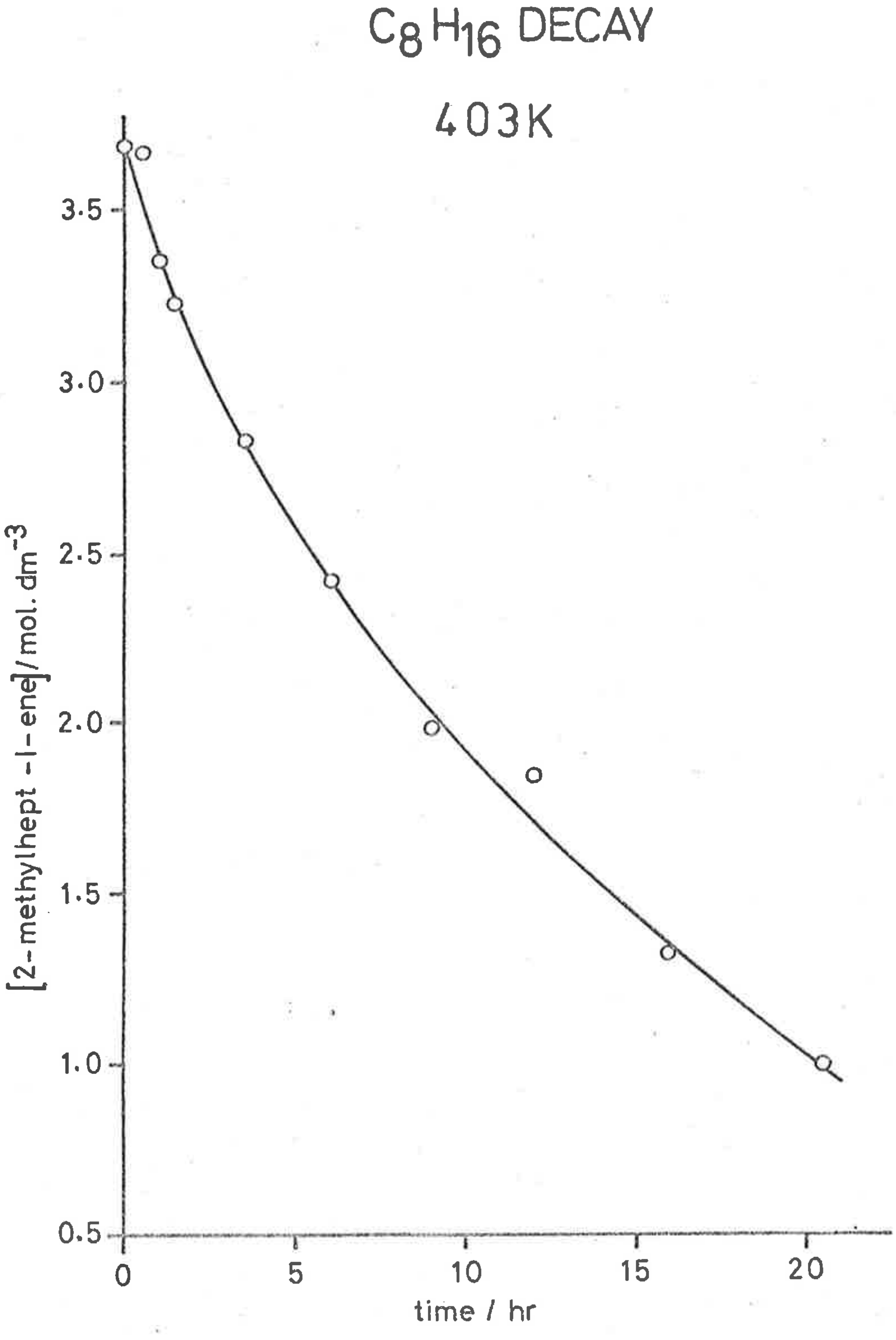
In the case of alk-1-enes, the product of reaction (8) undergoes alkene elimination and the dialkylaluminium hydride formed rapidly adds a second molecule of reactant alkene. The rate of reaction in these cases can be followed by observing the appearance of the vinyl resonances of the product alkene or the disappearance of the reactant alkene ones. In the latter case, a stoichiometric co-efficient of two must be allowed for. With 2-methylhept-1-ene, no vinyl resonances of an unsaturated product appeared at any stage and thus reaction (8) represents the total reaction. After very long reaction times at 423K (one week), the vinyl resonances could no longer be observed. This was taken as indicating that the reaction goes effectively to completion under the conditions used. The absence of vinyl resonances, other than those of the reactant, indicates that no isomerization occurred during the course of the reaction. Isomerization of 2-methylpent-1-ene has been reported in both the presence and absence of triethylaluminium at 406K.[18] This is unusual because, although such reactions are well known, they normally occur only at temperatures much higher than 400K-450K, or in the presence of specific catalysts. Samples of 2-methylhept-1-ene

CHANGE OF P.M.R. SPECTRUM WITH TIME



$AlEt_3$—2-METHYLHEPT-1-ENE

Fig II.8



C_8H_{16} DECAY
403K
3.5
3.0
2.5
2.0
1.5
1.0
0.5
[2-methylhept -1-ene]/mol. dm^{-3}
0
5
10
15
20
time / hr

FIG. II. 9

were held at 423K for three days in both the presence and absence of triethylaluminium. After hydrolysis, the samples were analysed by gas chromatography but no isomerization products could be detected, thus confirming the evidence of the p.m.r. spectra that 2-methylhept-1-ene does not isomerize under our conditions.

In the absence of side, subsequent, or back reactions, the rate equation where the extent of triethylaluminium dissociation is slight, may be taken to be:

$$v = -\mathrm{d}\,[\text{alkene}]/\mathrm{d}t = k_1 . K_\mathrm{d}^{\frac{1}{2}} . \ [\mathrm{Al_2Et_6}]^{\frac{1}{2}} \ [\text{alkene}]$$

where K_d is the equilibrium constant for the dissociation of dimeric triethylaluminium ($K_{\mathrm{d}(1)}$ in Section I). This rate equation was confirmed by the external order of reaction with respect to total triethylaluminium concentration. The plot of log $v^\mathrm{o}/[\text{alkene}]_\mathrm{o}$ against log $[\mathrm{Al_2Et_6}]_\mathrm{o}$ at 423K had a slope of 0.58± (s.e.)0.1 (Fig. II.10).

The stoichiometric relationships are:

$$\tfrac{1}{2}\mathrm{Al_2Et_6} \overset{K_\mathrm{d}^{\frac{1}{2}}}{\rightleftarrows} \mathrm{AlEt_3} \quad + \quad \mathrm{C_8H_{16}} \xrightarrow{k_1} \text{Product}$$

	$\tfrac{1}{2}\mathrm{Al_2Et_6}$	$\mathrm{AlEt_3}$	$\mathrm{C_8H_{16}}$	Product
$t = 0$	a	b	m	o
$t = t$	$a-x/2$	$b+x-y$	$m-y$	y

and the kinetic equation is:

EXTERNAL ORDER WITH RESPECT TO
TRIETHYLUMINIUM
423 K

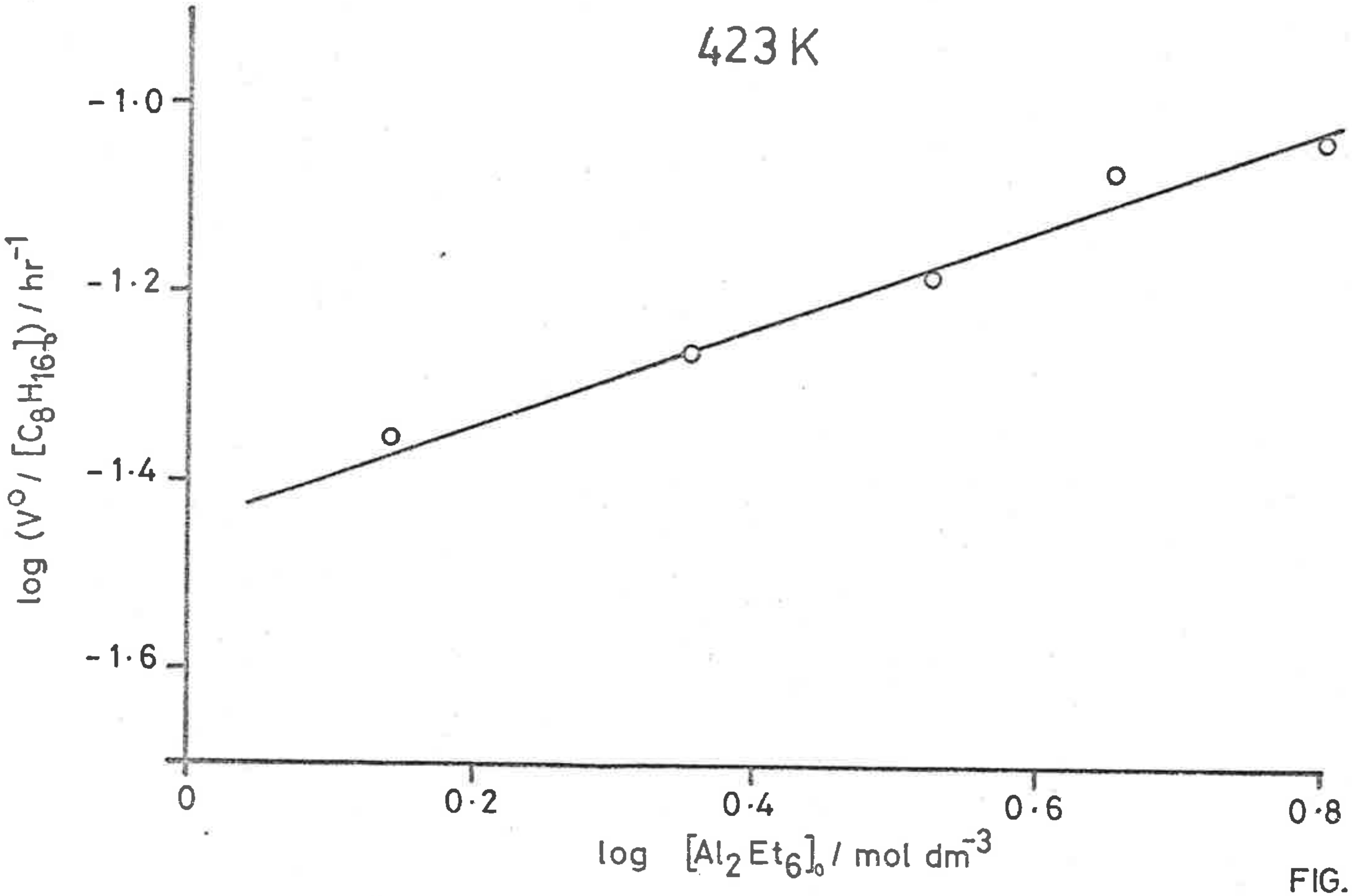


FIG. II. 10

II.2.

$$dy/dt = -d[C_8H_{16}]/dt = k_1(b+x-y)(m-y)$$

The relationship between x and y is given by:

$$K_d = (b+x-y)^2/(a-x/2) \qquad \text{....(9)}$$

The variables in equation (9) cannot be separated to give $x = f(y)$, so the following procedure was used. For each experimental value of y the cubic in x was solved using Smith's value of K_d (see Section I), resulting in a series of points $(x_n y_n)$. Cursory examination showed that while the slope of a plot of x vs y was approximately unity up to 10% conversion, after this, significant deviation occurred, preventing any simplification of the calculations obtained by assuming $x = y$. Up to 60% conversion the points could satisfactorily be described as a parabola and were fitted to a second degree polynomial, using an orthogonal iteration technique (Appendix I) on a CDC 6400 computer to give

$$x = py^2 + qy + r$$

The kinetic equation thus becomes:

$$-d[C_8H_{16}]/dt = dy/dt = k_1(a+py^2+(q-1)y+r)(m-y)$$

which on rearrangement becomes a standard integral of the type:

$$dy/(fy+g)(ay^2+by+c) = k\,dt$$

A computer programme was written in Fortran IV to accomplish the integration (Appendix II), yielding plots of which Fig. II.11 is a typical example. The line, which is weighted to pass through the origin, is shown with its 90% confidence limits. For all runs, the data fitted well with few points outside the 90% confidence limits. These limits were computed from the relationship:[37]

$$y_{cl} = y_i \pm t_{\frac{1}{2}a(n-2)} \cdot S_o \left[\frac{1}{n} + \frac{(x_i - \bar{x})^2}{\sum_{i=1}^{n} (x_i - \bar{x})^2} \right]^{\frac{1}{2}} \qquad \ldots.(10)$$

y_{cl} = values of the confidence limits at point $x_i y_i$

$\bar{x}$ = mean x value

S_o = Standard error of y_i from the linear regression line

t = t test parameter

a = probability parameter (in this case 0.9)

Calculated values of the rate co-efficients determined at five temperatures between 398K and 423K are shown in Table II.1. As can be seen, the

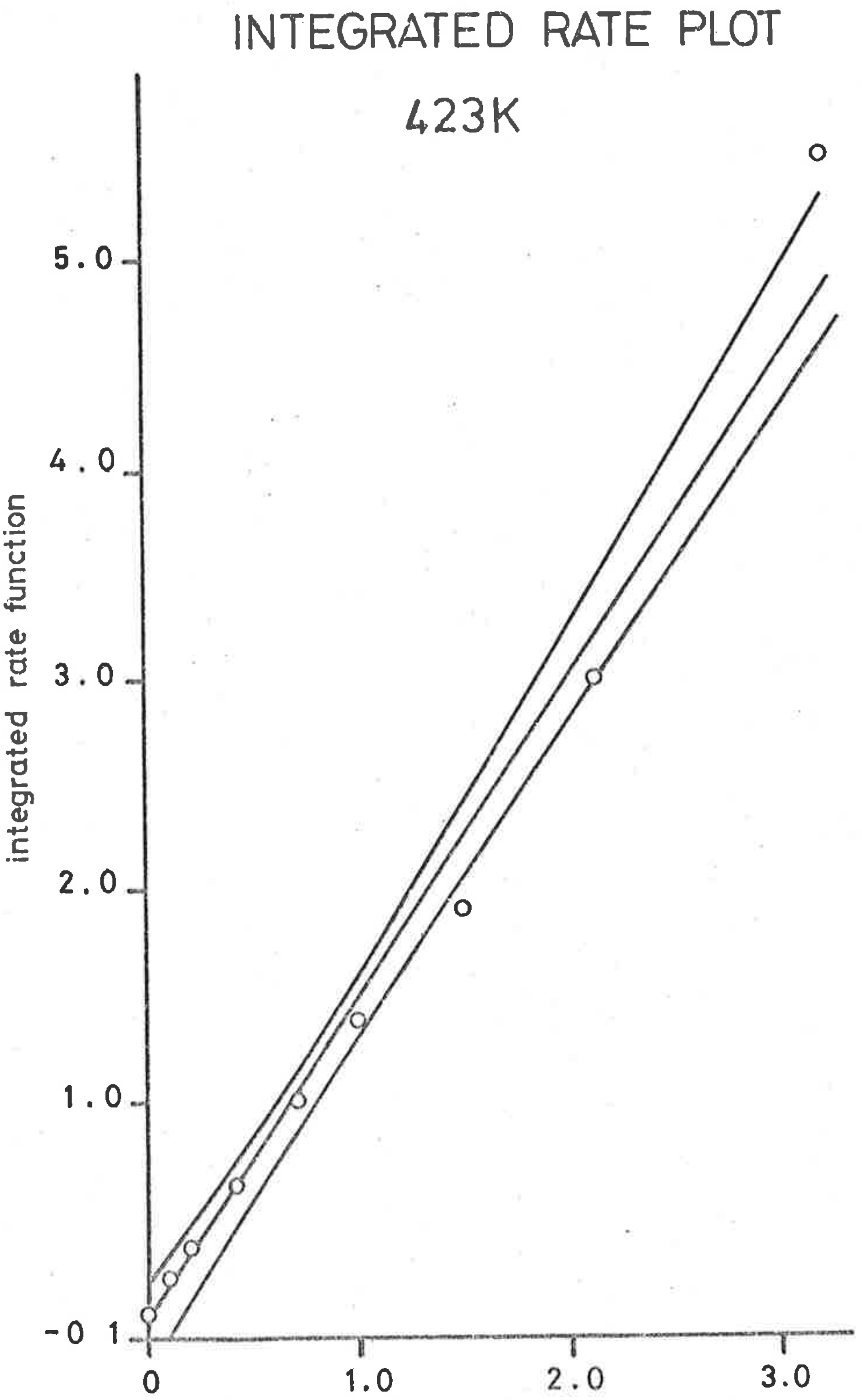

INTEGRATED RATE PLOT
423K
integrated rate function
5.0
4.0
3.0
2.0
1.0
-0 1
0
1.0
2.0
3.0
time / hr

FIG. II.11

II.2.

TABLE II.1.

2-Methylhept-1-ene rate data

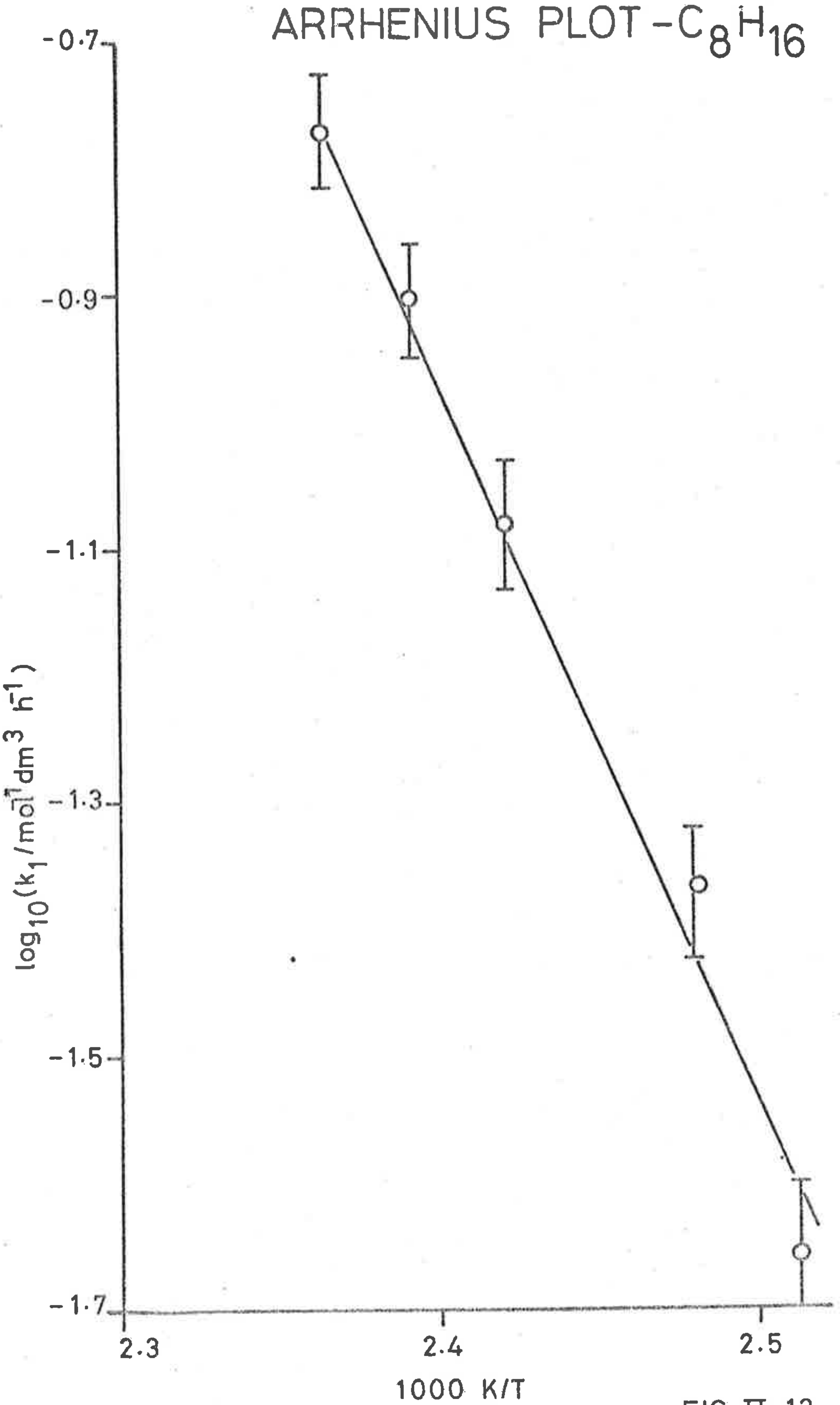
Temp/K	concentrations/M		k_1/dm^{3}mol^{-1}hr^{-1}	Ave k_1
	alkene	Al_2Et_6		
398	4.092	1.500	.0284	$.03_{74}$ ± .007
	3.062	1.428	.0283	
	2.189	1.235	.0515	
	2.923	1.824	.0368	
	1.849	1.529	.0418	
403	3.174	1.315	.1168	$.10_{43}$ ± .009
	3.478	0.941	.1133	
	2.264	0.898	.1043	
	2.393	1.990	.0802	
	1.586	1.706	.1067	
413	3.880	1.567	.1792	$.12_{96}$ ± .030
	3.591	1.923	.0964	
	3.483	1.609	.1134	
	2.048	2.026	.1558	
	3.020	2.000	.1033	
418	3.916	1.210	.1278	$.17_{21}$ ± .022
	3.312	1.220	.1893	
	1.875	1.991	.1921	
423	4.190	0.658	.2520	$.28_{33}$ ± .047
	3.473	0.910	.2059	
	3.661	1.440	.3370	
	2.932	1.276	.3474	
	2.169	1.631	.2744	

the rate co-efficients show only a small random scatter while the concentration ratio varied from 0.5 to 2.0.

The Arrhenius plot is shown in Fig. (II.12), and the determined kinetic parameters are

$$A = 10^{7.6\pm0.2(\mathrm{s.e.})}\,\mathrm{dm^3\ mol^{-1}s^{-1}}$$

$$E = 95.0\pm1.3(\mathrm{s.e.})\,\mathrm{kJ\ mol^{-1}}$$



ARRHENIUS PLOT - C_8H_{16}

FIG. II. 12

3. REACTION OF TRIETHYLALUMINIUM WITH STYRENE

3.1. Preparation of N.M.R. Tubes

Triethylaluminium and cyclohexane were purified as mentioned previously. Styrene (A.R. grade, B.D.H. (Aust.) Ltd.,) was purified using a similar technique to that used for 2-methylhept-1-ene. The n.m.r. tubes used for kinetic runs were also prepared using a similar technique to that used for 2-methylhept-1-ene, except that the amount of styrene in each tube was known accurately by tipping the styrene in first and measuring the height in each n.m.r. tube with a cathetometer. Triethylaluminium and cyclohexane (if needed) were then dispensed and the tubes sealed off from the main dispenser. The actual volume of liquid in each tube was calculated from the total height of liquid and the diameter of the n.m.r. tube.

During preparation of the tubes for determining the characteristics of the triethylaluminium-styrene complexes, the volumes added were not accurately measured, as the only concentration parameter required - [styrene]/[$AlEt_3$] - was determined directly from the p.m.r. spectra.

3.2. P.m.r. measurements

3.2.1. Triethylaluminium-Styrene Complex

Ten tubes were prepared containing [styrene]/[Al] ratios ranging from 0.1/1 to 13.5/1 and their p.m.r. spectra measured. The triethylaluminium methyl triplet, offset 105Hz was used as the internal lock, and a 500Hz scan recorded. Integration over the styrene aromatic resonances and triethylaluminium methylene resonances yielded the concentration ratio:

$$\frac{[\text{Styrene}]}{[\text{AlEt}_3]} = \frac{\text{styrene aromatic integral}}{\text{Al methylene integral}} \cdot \frac{6}{5}$$

When this had been recorded, the internal lock was shifted to the aromatic styrene resonances, offset 500Hz, and the triethylaluminium methyl and methylene resonances recorded on a 250Hz sweep, giving values for the internal chemical shift, δ_{int} (see Fig. II.5.)

3.2.2. Addition of Triethylaluminium to Styrene

In most of the kinetic runs, only the reactants (styrene and triethylaluminium) were present in the tube and their volumes were known accurately from height measurements. The only exception was the run at 408K which needed the styrene concentration constant to determine the order with respect to triethylaluminium, and so cyclohexane was used to bring the volume of each tube to 1.6 ml. It was assumed by analogy with the triethylaluminium/diphenylether/n-oct-1-ene system, that cyclohexane would have no effect on the rate of reaction and this seemed to be justified in retrospect when the Arrhenius plot was examined.

II.3.

During the course of the reaction the number of aromatic protons in the system does not change, and so their integral provided a convenient reference. The kinetic run was performed in a similar fashion to that already described for 2-methylhept-1-ene, except that, in this case, a product vinyl resonance appeared (Fig. II.13). This resonance was consistent with the product being β-ethylstyrene. At higher conversions a second product resonance very close to the first, became apparent. This was assigned to the other β-ethylstyrene stereoisomer. From the chemical shifts of the two resonances it was inferred that the major product was cisβ-ethylstyrene. This cannot be confirmed by measuring the coupling constants between components of each resonance, as by the stage of the second peak is apparent, the reaction has proceeded to such a degree that the reaction mixture is slightly viscous and p.m.r. resolution is low (see below).

Concentrations throughout the reaction were obtained using the following relationships:

$$[\text{styrene}]_t = [\text{styrene}]_o \frac{\text{react. vinyl integral}}{\text{aromatic integral}} \cdot \frac{5}{2}$$

$$[\beta\text{-ethylstyrene}]_t = [\text{styrene}]_o \frac{\text{product vinyl integral}}{\text{aromatic integral}} \cdot \frac{5}{2}$$

Only the upfield quartet of vinyl resonances (terminal protons) was used to calculate the concentration of styrene. Plots of reactant decay and

CHANGE OF P.M.R. SPECTRUM WITH TIME

$AlEt_3$ – STYRENE

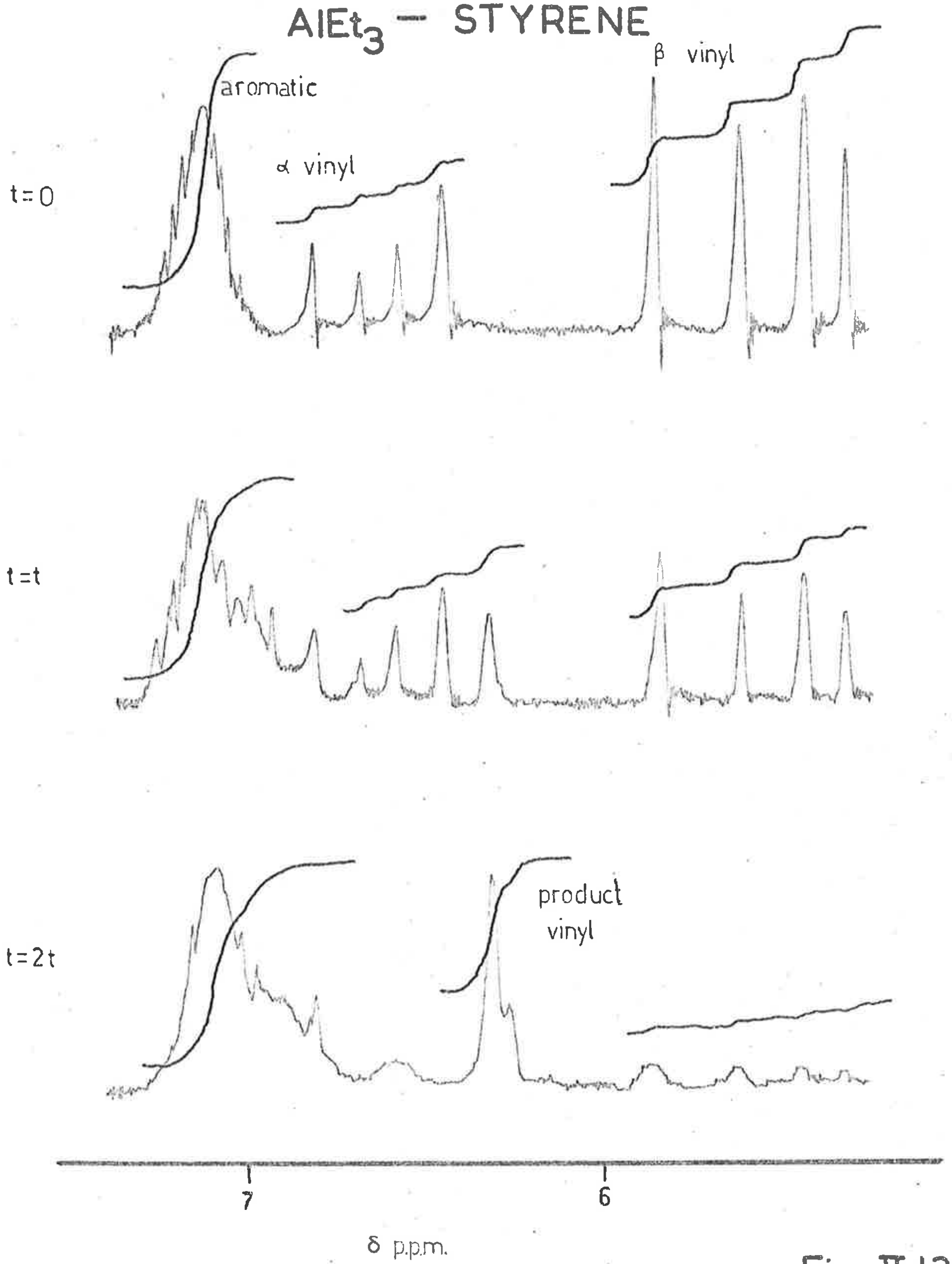
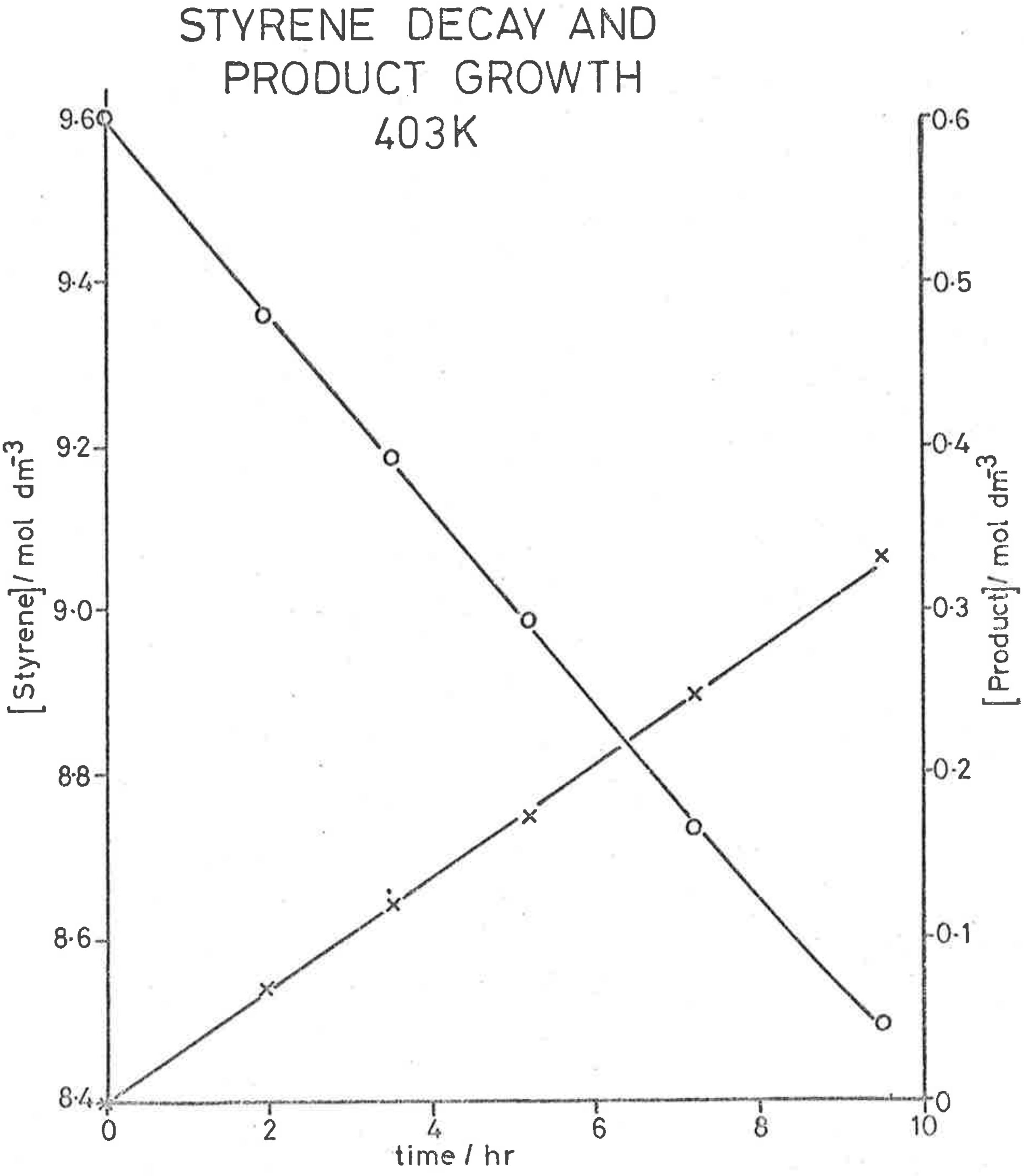


Fig II.13

product appearance are shown on Fig. II.14. If the mechanism presented above is the only one operating, the ratio of reactant decay to product appearance should approach 2. An examination of Fig. II.14 shows, however, that this ratio is greater than 2. This fact, as well as the increased viscosity noted earlier, is because styrene undergoes thermal polymerization at the temperatures of reaction, (373K-408K). Reactant decay, therefore, is not a reliable indicator of the rate of addition and consequently product concentrations were used in calculating kinetic results. In addition, to minimize the effect of polymerization, all kinetic data were calculated from reaction data collected below 20% conversion.



STYRENE DECAY AND PRODUCT GROWTH 403K

FIG. II. 14

3.3. Results

3.3.1. Triethylaluminium-Styrene Complex

Fig. II.15 shows the plot of the internal shift of triethylaluminium proton resonances (δ_{int}) versus the concentration ratio [styrene]/[$AlEt_3$] at 302K and at 323K before any reaction occurred. It is apparent that a 1:1 complex between triethylaluminium and styrene is formed, although the equilibrium constant for its formation (K_S) is probably not large at any particular ratio. The magnitude of δ_{int} is determined not only from the value of K_S, but also from the change of the electronegativity of the aluminium that complexing brings about. The latter can be found by determining the limiting internal chemical shift at high [donor]/[$AlEt_3$] ratios (see Section III). Unfortunately, in this case, the magnitude of δ_{int} is very small, magnifying any instrumental measuring errors, and it is impossible to determine if the high [styrene]/[$AlEt_3$] ratios measured, approach δ_{∞} or are still increasing due to a low K_S. In any case, the method developed for determining K_S from δ_o (free Al_2Et_6), δ_{int}, and δ_{∞} (as described in Section III) is not accurate enough with internal chemical shift changes of the magnitude presented here, because small errors in δ_{int} are greatly exaggerated. A preliminary calculation showed that a K_S value estimated using δ_{int} values could not be determined closer than 2 orders of magnitude, viz. 10^{-2} – 1.

A better estimate of K_S, and at a reaction temperature, was made from the observed order with respect to total triethylaluminium concentration at 408K. The equilibrium concentration of uncomplexed monomer, [$AlEt_3$], is very small, and so the equilibrium concentrations of Al_2Et_6

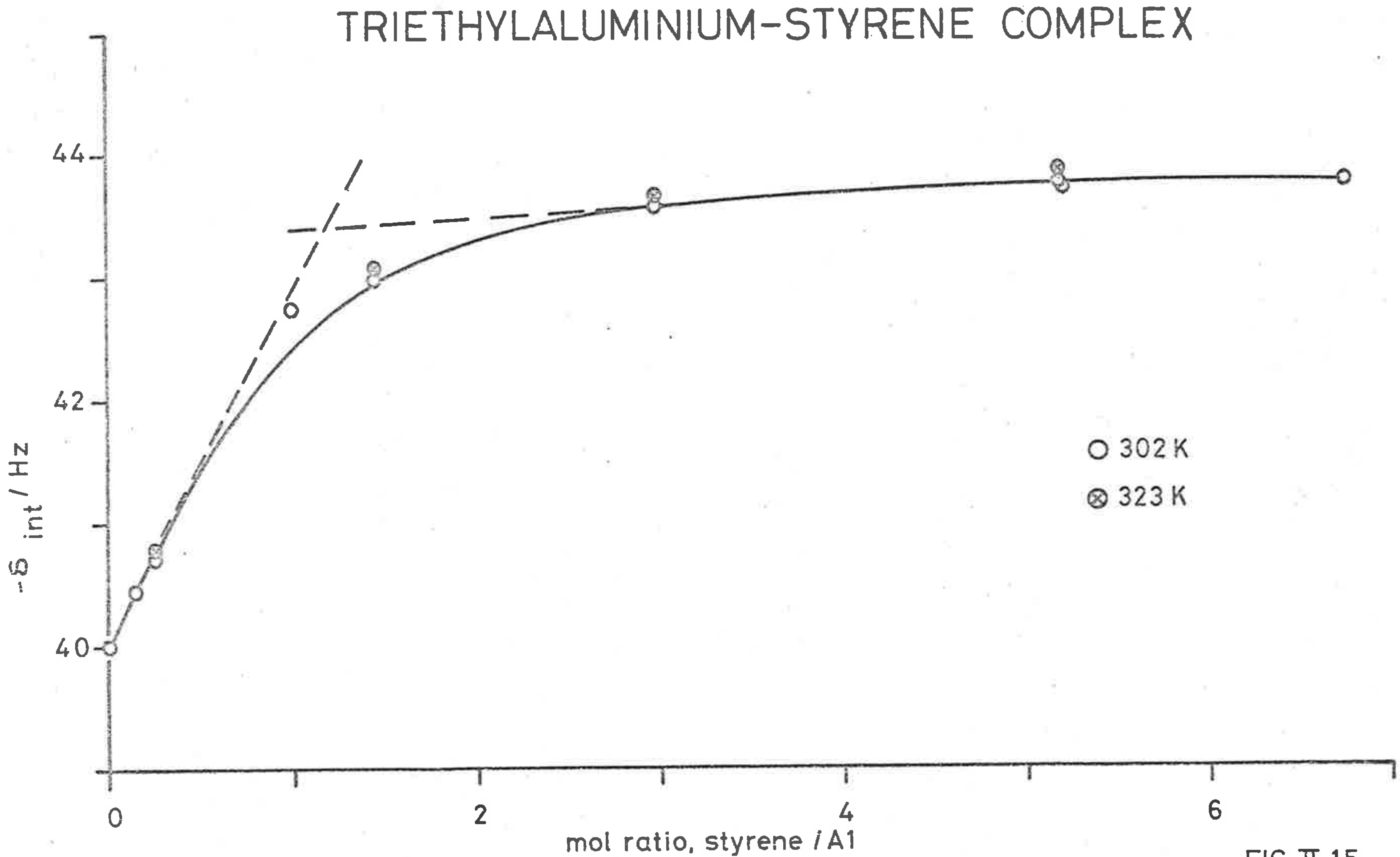

TRIETHYLALUMINIUM-STYRENE COMPLEX

FIG. II.15

and complex ($AlEt_3:C_8H_8$) may be taken as

$$\underset{a/2}{\tfrac{1}{2}\,Al_2Et_6} + \underset{e+\alpha}{C_8H_8} \overset{K_S}{\rightleftarrows} \underset{a-\alpha}{AlEt_3:C_8H_8}$$

where a is the total concentration of triethylaluminium compounds calculated as monomer, and e is the concentration of styrene in excess of a. The equilibrium constant is given by

$$K_s = \frac{a-\alpha}{(a/2)^{\frac{1}{2}}\,(e+\alpha)} \qquad \ldots.(11)$$

The external order of reaction with respect to total triethylaluminium concentration was estimated from a plot of log initial rate (v^o) against a at constant styrene concentration. The initial rate was found to be given by

$$v^o = k_{app}\ a^{0.73}$$

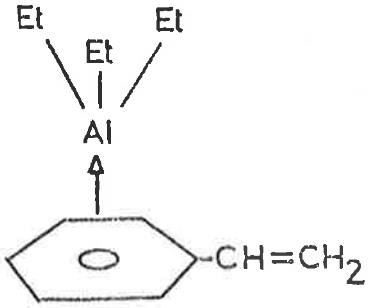
As the reaction proceeds via the complex or the unassociated monomer, (a reactive dimer can be discounted immediately), the order with respect to total concentration of triethylaluminium, depends on the relative concentrations of monomeric and dimeric forms. When $a \to \alpha$, the reaction is half order, with respect to total triethylaluminium concentration. The simplest of the family of phenomenological equations representing this behaviour is

$$\frac{\alpha^{\frac{1}{2}}}{2} + (a-\alpha) = a^{n} \qquad \ldots.(12)$$

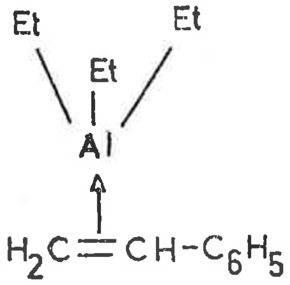
Equations (11) and (12) were solved numerically for n = 0.73 by testing 100 values of K_S between 10^{-2} and 1 with the data obtained at 408K. The best fit was obtained with $K_S = 0.17$ dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$. The sensitivity of the kinetic parameters ultimately calculated to the value of K_S was also tested. It was found that a tenfold change in K_S induced only a 12% change in the rate co-efficient of the rate determining step. The rate parameters are obviously well screened from uncertainties and errors in the value of K_S. As is the case with other weak π complexes (Section III.2), K_S is relatively insensitive to temperature changes (Fig. II.15). Consequently, the value of 0.17 dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$ was used in calculating the rate parameters over the temperature range employed (373K-408K).

Two possibilities as to the structure of the complex exist. It may be either an aromatic π complex (I) or a vinyl π complex (II)

II.3.



I



II

When compared with the same concentration of pure styrene, the vinyl resonances of a 0.1/1 ratio of [styrene] [Al] shifted 2.8Hz downfield and gradually moved upfield as the ratio of styrene increased, i.e. percent of styrene complexed decreased whilst the aromatic protons shifted 5.9 Hz downfield and gradually moved up as the ratio of styrene increased. It thus appears that the complex is of type I. If this is the case, other aromatic compounds should also form donor complexes with triethylaluminium.

Five n.m.r. tubes were prepared using the same apparatus shown in Fig. II.6, each tube containing 10% triethylaluminium in benzene, phenylcyclohexane, toluene, o-xylene, and mesitylene respectively. Phenylcyclohexane, being solid, was weighed into the tube before sealing on to the dispenser. All of the other solvents were added via a breakseal.

The internal chemical shift of the triethylaluminium (δ_{int}) was measured for all tubes at 302K. Table II.2 shows the values of δ_{int} obtained.

TABLE II.2.

Aromatic complexes

solvent	$-\delta_{int}$/Hz
cyclohexane	40.3
benzene	42.9
phenylcyclohexane	41.0
toluene	43.6
o-xylene	42.4
mesitylene	42.5

Thus aromatic compounds form complexes with triethylaluminium, and it appears that two effects influence the degree of complexing. Alkyl substituents increase the electron density of the benzene ring, and so increase the degree of complexing. Opposing this is the fact that alkyl substituents increase steric hindrance around the aromatic ring. A single alkyl group appears to be the optimum degree of substitution. A recent calorimetric study of triethylaluminium in mesitylene has confirmed the presence of a donor complex in this solvent.[31]

The postulated aromatic π complex with styrene is thus shown to be a reasonable assignment. This is supported by the fact that, in spite of many efforts, no appreciable concentrations of a vinyl π complex have ever been demonstrated (e.g. 2-methylhept-1-ene).

3.3.2. Kinetics of the addition reaction

Two hypotheses were tested: that the reaction proceeded predominately from the unassociated monomer, or predominately through the complex I. A reactive Al_2Et_6 dimer is neglected as also is the hypothesis of concurrent mechanisms. This latter rejection will be justified later. The stoichiometric relationships are

$$\begin{array}{lccccc}
 & \tfrac{1}{2}Al_2Et_6 & + \; C_8H_8 & \overset{K_S}{\rightleftarrows} & I & \xrightarrow{k_2} \; \text{products} \\
t = 0 & a & b & & c & 0 \\
t = t & a-x/2 & b-y-x & & c-y+x & y \\
 & K_d^2 \uparrow\downarrow & & & & \\
 & AlEt_3 & + \; C_8H_8 & \xrightarrow{k_1} & \text{products} & \\
t = 0 & m & b & & 0 & \\
t = t & m & b-y-x & & y &
\end{array}$$

At small extents of reaction, m may be assumed to be constant and the two alternative rate equations are thus:

$$-d[C_8H_8]/dt = dy/dt = k_1 m \; (b-y-x)$$

and

$$-d[C_8H_8]/dt = dy/dt = k_2 \; (c-y+x)$$

The relationship between y and x is obtained from the equilibrium

II.3.

$$K_S = \frac{(c-y+x)}{(a-x/2)^{\frac{1}{2}}(b-y-x)}$$

in a similar fashion to that already described for 2-methylhept-1-ene, to give

$$x = py^2+gy+r$$

The rate equations are thus

$$dy/dt = k_1m\ (b-r-py^2-(g+1)y) \qquad ....(14)$$

and

$$dy/dt = k_2\ (c+py^2+(g-1)y+r)$$

which are both standard integrals of the form

$$dy/(ay^2+by+c) = kdt$$

The computer program used to calculate the integrated values was very similar to Appendix II and a typical plot for the integrated form of equation (14) is shown in Fig. II.16. Calculated rate co-efficients between 373K and 408K for both mechanisms are given in Table II.3. and Arrhenius plots in Fig. II.17. Least squares regression yields the kinetic parameters

k_1 : $E = 66.7\pm0.6$(s.e.)kJ mol^{-1}
$A = 10^{4.5\pm0.1\text{(s.e.)}}$ dm^3 mol^{-1}s^{-1}

k_2 : $E = 109.3\pm4$(s.e.) kJ mol^{-1}
$A = 10^{9.5\pm0.7\text{(s.e.)}}$ s^{-1}

II.3.

TABLE II.3.

Styrene rate data

Temp/K	concentrations/mol dm^{-3}		k_1/dm^{3}mol^{-1}hr^{-1}	k_2/hr^{-1}
	styrene	Al_2Et_6		
373	8.085	0.275	.0735	.020
	7.532	0.507	.0305	.011
	6.485	0.947	.0640	.020
	4.335	1.850	.0591	.007
	1.412	3.078	.0317	.009
			$.05_{17}\pm.016$	$.013\pm.005$
383	5.959	1.168	.0870	.023
	5.449	1.382	.0851	.018
	5.765	1.250	.0857	.029
	3.902	2.032	.0798	.008
	5.715	1.294	.0905	.022
			$.08_{56}\pm.002$	$.020\pm.006$
393	7.067	0.707	.1354	.073
	7.451	0.542	.0472	.033
	6.963	0.747	.0916	.067
	5.917	1.186	.1686	.074
	6.082	0.466	.1507	.097
			$.13_{65}\pm.022$	$.06_7\pm.015$
398	1.481	0.362	.2332	.047
	2.592	0.362	.2117	.116
	2.963	0.362	.1466	.084
	4.886	0.362	.1189	.111
	5.926	0.362	.1104	.127
			$.1621\pm.04_6$	$.09_7\pm.025$
403	8.032	0.298	.1436	.177
	7.492	0.551	.2637	.263
	6.214	1.061	.2471	.202
	3.998	1.991	.1930	.051
	9.626	0.327	.1401	–
			$.19_{76}\pm.046$	$.17_3\pm.049$
408	4.370	1.620	.4446	
	4.370	1.370	.4320	
	4.370	0.990	.4734	
	4.370	0.920	.4092	
	4.370	0.690	.4404	
	4.370	0.460	.3630	
	4.370	0.280	.3258	
			$.41_{26}\pm.040$	

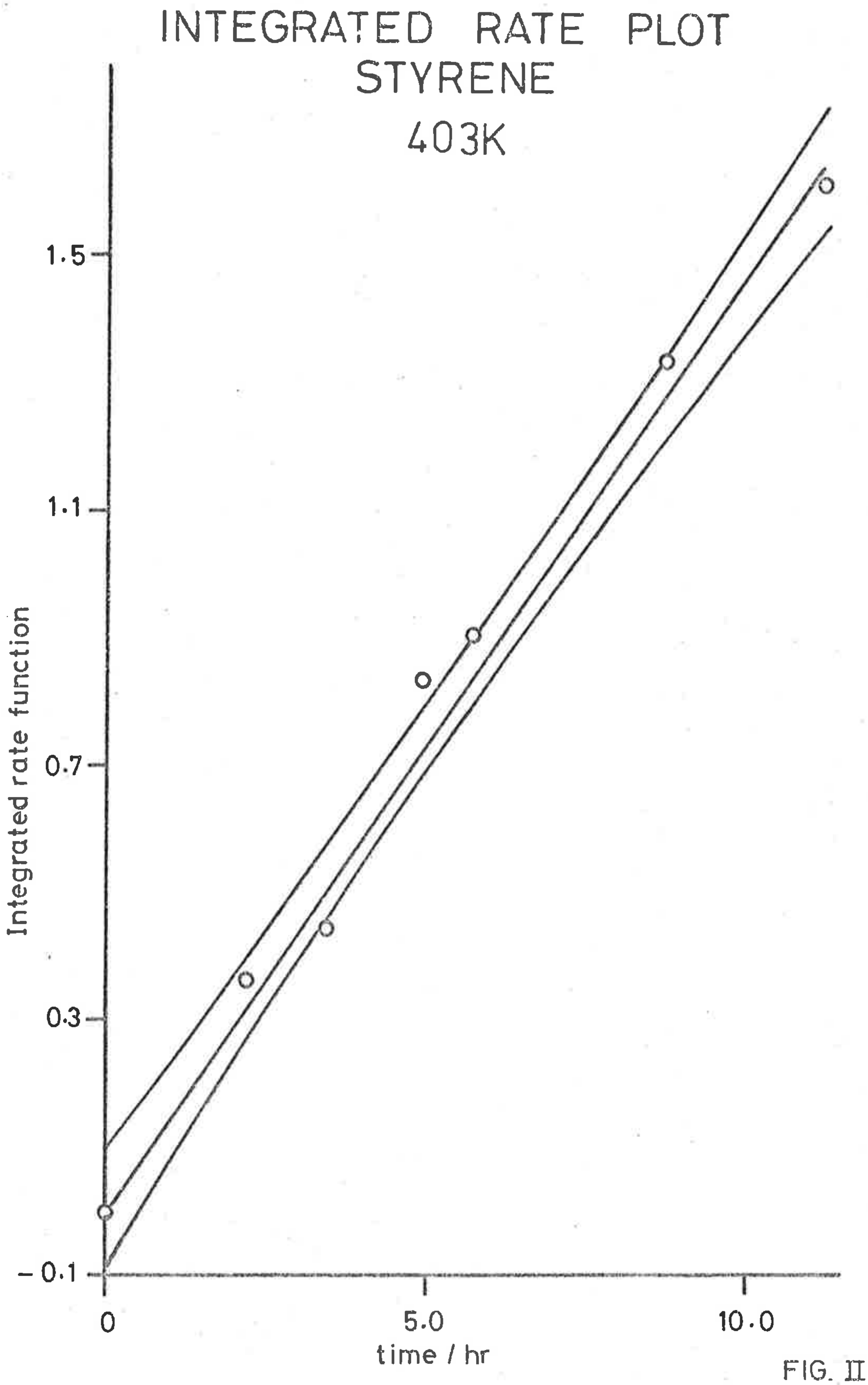

INTEGRATED RATE PLOT
STYRENE
403K
Integrated rate function
1.5
1.1
0.7
0.3
– 0.1
0
5.0
10.0
time / hr

FIG. II. 16

ARRHENIUS PLOT–STYRENE

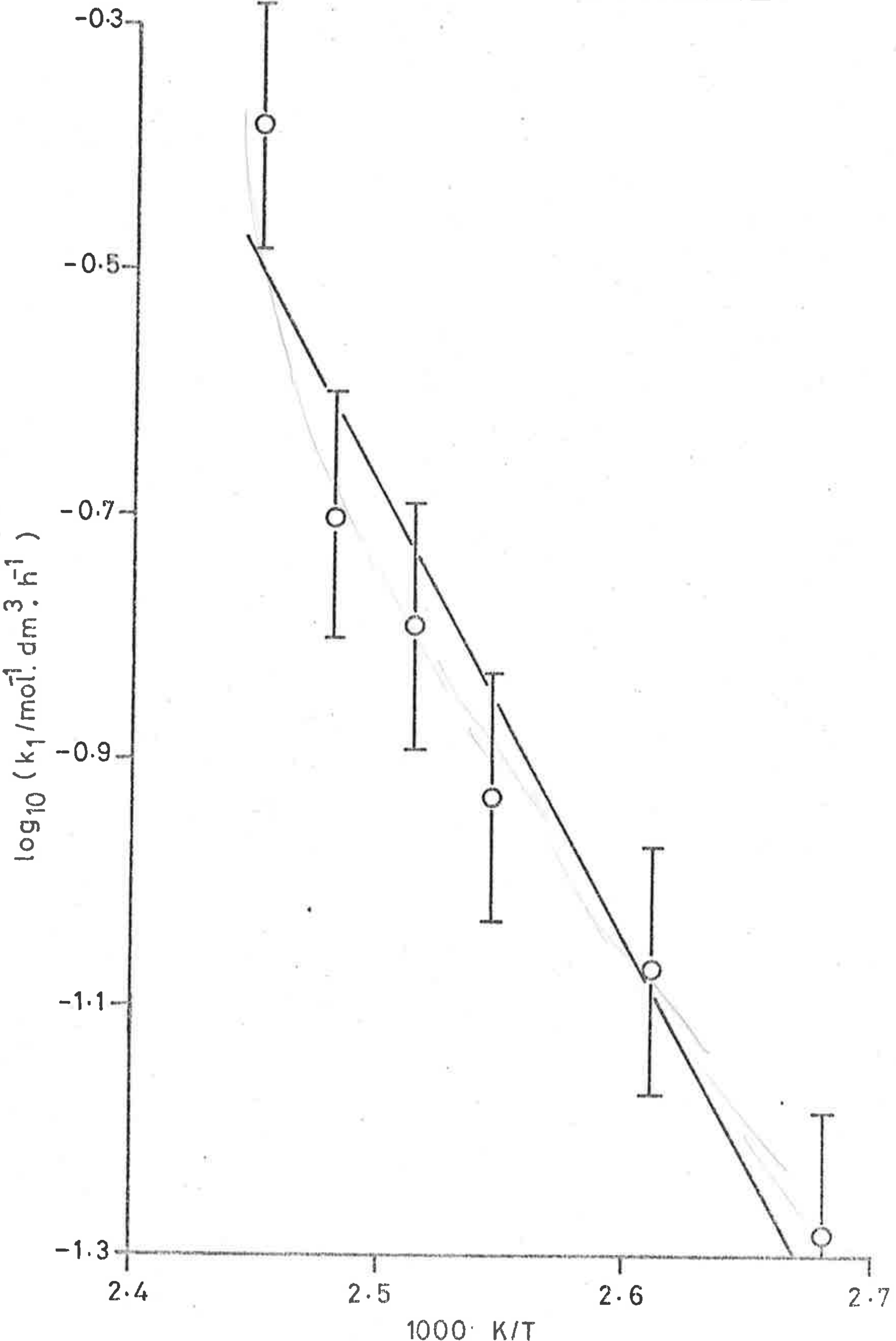


FIG. II. 17

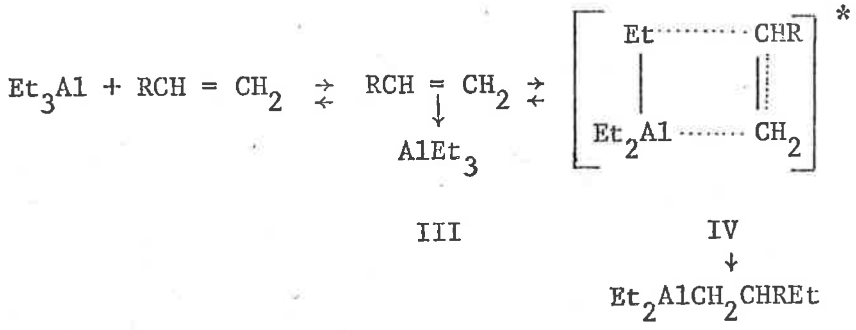
II.4.

4. DISCUSSION OF MECHANISM

The results presented in Section II.3. show that the addition of triethylaluminium to styrene leads to ethylation of the least substituted olefinic carbon atom. In this respect styrene differs from the other alkenes, but this is not surprising as styrene has an electron-withdrawing phenyl substituent while saturated alkyl groups are electron-donating. This behaviour is consistent with that of phenyl substituted ethylenes with most other reactive organometallic reagents.[32,33] Only in the case of dialkylaluminium hydrides have both modes of an addition been reported.[34] Although a reaction path involving the aromatic π complex (I) cannot be entirely excluded on kinetic grounds, it seems unlikely. As it is an aromatic π complex, a non-dissociative reaction path to any hypothetical transition state would involve very extensive rearrangement. The putative enthalpy of activation for the reaction of I directly by first order kinetics is very high (*ca*110 kJ mol^{-1}), and it is unlikely to be competitive with a dissociation mechanism proceeding via the triethylaluminium monomer. The possibility that the two mechanisms are concurrent can also be discounted from the observation that, although the two mechanisms must surely have quite large differences in their enthalpy and entropy of activation, the calculated parameters obey the Arrhenius equation. We are thus led to the conclusion that the kinetics of the reaction are best explained in terms of a mechanism involving $AlEt_3$ as the sole reagent and the aromatic π complex (I) is not an intermediate.

II.4.

As discussed previously (Section II.1.2) the kinetic parameters for triethylaluminium addition to alkenes are usually interpreted in terms of a reaction path proceeding through a vinyl π complex (III) to a four-centre transition state (IV)



$$\mathrm{Et_3Al + RCH=CH_2} \rightleftarrows \underset{\displaystyle \mathrm{AlEt_3}}{\mathrm{RCH \underset{\downarrow}{=} CH_2}} \rightleftarrows \left[\begin{array}{ccc} \mathrm{Et} & \cdots\cdots & \mathrm{CHR} \\ | & & \vdots\| \\ \mathrm{Et_2Al} & \cdots\cdots & \mathrm{CH_2} \end{array}\right]^{*} \xrightarrow{} \mathrm{Et_2AlCH_2CHREt}$$

III IV

The extant data for k_1 in liquid solution are given in Table II.4. If the alternative values of K_d are used (Allen and Byers[19] instead of Smith)[31] the values of $\log_{10}A$ are increased by ca. 1.1 and E by 10 kJ mol^{-1}.

When the data determined here are combined with the other values for the kinetic parameters for addition that are available in the literature, the trends in the Arrhenius parameters are apparent and the proposed mechanism can be subjected to critical examination. It is known from earlier data that both Arrhenius parameters increase with increasing size of the alkene. Examination of Table II.4 shows that the factor is steric: the Arrhenius parameters are highest for the 1,1 - disubstituted ethylenes and the alkene that is branched at C3. It is unusual for steric

II.4.

TABLE II.4.

Alkene Arrhenius Parameters

	$\log_{10}\left[\frac{A}{\mathrm{dm^3\ mol^{-1}\ s^{-1}}}\right]$	E/kJ mol^{-1}	ref.
propene	3.3	50.6	17[a]
but-1-ene	3.6	54.8	17[a]
pent-1-ene	4.6	63.1	17[a]
hex-1-ene	4.8	62.3	17[a]
3-methylpent-1-ene	4.5	66	18[a]
4-methylpent-1-ene	3.8	60	18[a]
3,3-dimethylbut-1-ene	7.4	94.7	18[a]
oct-1-ene	4.6	65.5	18[a]
	5.3	68.6	19,20
2-methylhept-1-ene	7.6	95.0	this work
styrene	4.5	66.7	this work
cyclohexene	2.6	63.3	18[a]

a; Recalculated from the data originally presented using K_d values appropriate to the liquid state.

Note: $\log_{10}A$ values increase by ca 1.1 if values from ref. (19) are used instead of ref. (31).

effects to lead to an increase in the Arrhenius *A* factor because it is generally assumed that they lower an already negative entropy of activation due to a decrease in the contributions of some group rotations in the transition state.[35] The high Arrhenius parameters observed with alkenes with either two substituents attached to the double bond or one bulky substituent can be accounted for if it is assumed there is a change in the rate controlling step of the reaction path. In the case of n-alk-1-enes and alk-1-enes branched on carbon atoms remote from the double bond, the slow step is the passage of the π complex (III) through a four-centre transition state (IV) (Fig. II.18a). The low *A* factors can be explained qualitatively by attributing them to the loss of translational and rotational degrees of freedom in the four-centre transition state. Attempts to make a semiquantitative assessment of the absolute magnitude of *A* using this model suggest that the values in Table II.4 are too low, and the higher values that would arise if Allen and Byers'[19] value of K_d was used in the calculations, are further into the predicted range. This is not, however, in itself a sufficient reason for influencing the choice of values for K_d, the reasons for which are given in Section I. Values of *A* factors predicted from considerations of models for the transition state cannot be reliable within less than an order of magnitude, and in the case of solution reactions, too little is known about changes in solvent structure in the environment of the reacting species for allowance to be made for their effects. Absolute values notwithstanding, the trend

$AlEt_3$-ALKENE REACTION PROFILES

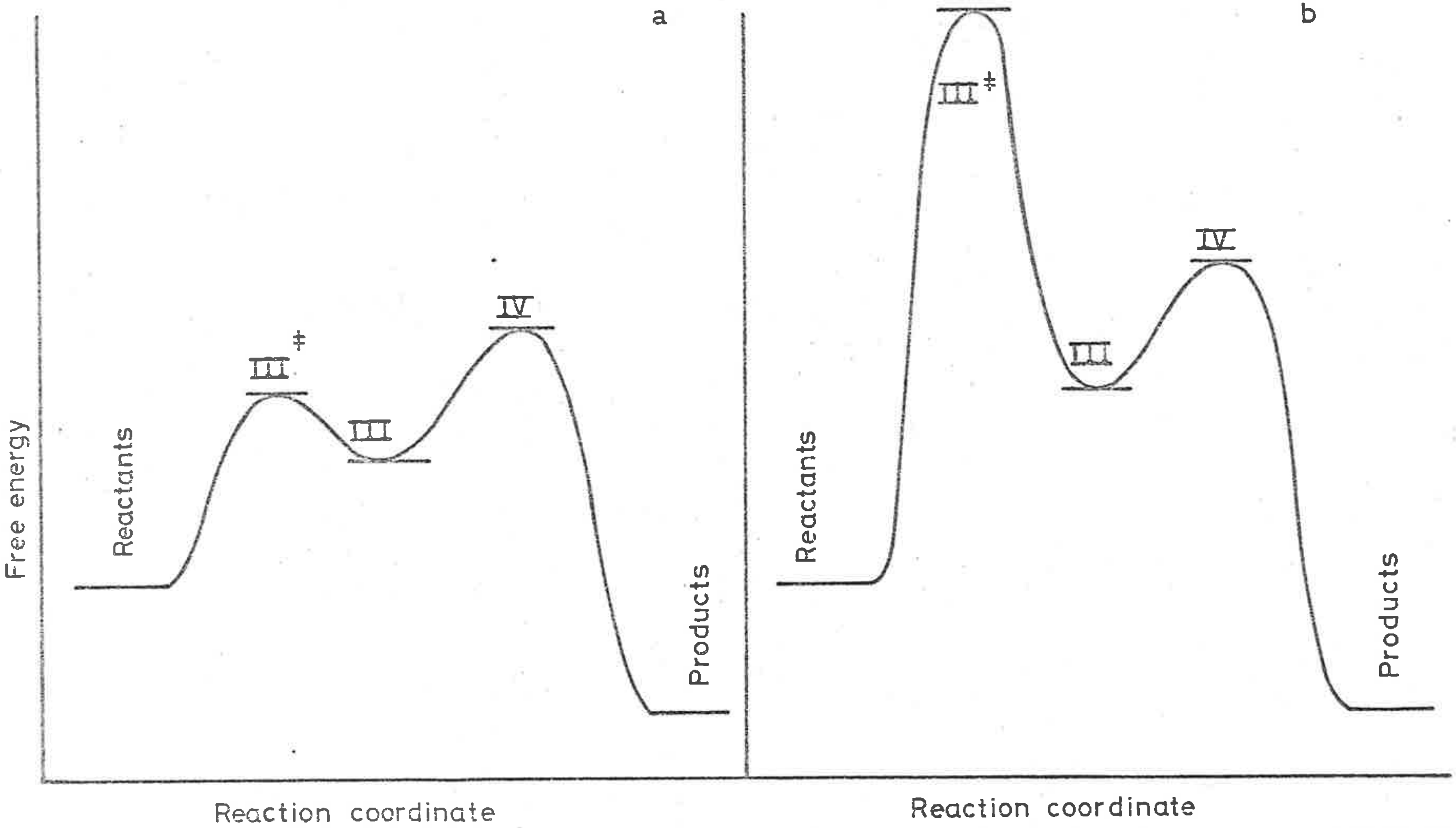


FIG.II 18

in Arrhenius parameters of the n-alk-1-enes and those alkenes branched remote from the double bond, although small, is real. This effect is also seen when alkene eliminations from alkylaluminiums in the gas phase are considered. (Table II.5.)

TABLE II.5.

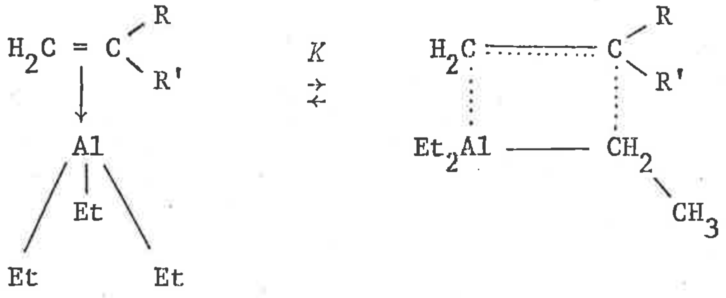
	$\log_{10}(A/s^{-1})$	E/kJ mol^{-1}	ref
Triisobutylaluminium	11.2	111.3	11
Dimethyl-n-butylaluminium	10.6	116.3	13
Triethylaluminium	10.5	125.9	21

For these eliminations a four-centre transition state analagous to that proposed for the addition of HI to isopropyl iodide has been postulated and indeed seems the only way to explain the relatively low unimolecular *A* factors.[36] The trend in the Arrhenius parameters for both the addition and the elimination can thus be rationalized on the basis of steric repulsions making the four-centre transition state somewhat "looser" in the case of alkenes with large substituents, thus increasing the *A* factor. These same steric repulsions would also require a higher thermal barrier to be overcome in forming the transition state, and therefore increasing the enthalpy of activation, but this will be partly offset by the greater electronic stabilization that larger alkyl groups provide.

For 2-methylhept-1-ene and 3,3-dimethylbut-1-ene the *A* factors are 10^3-10^4 higher than for the other alkenes. This suggests a change in mechanism and we propose that bulky substituents in the vicinity of the double bond increase the energy barrier for formation of the π complex(III)and that, in the two cases under consideration this is sufficient to make the formation of III rate determining, with a reaction profile similar to Fig. II.18(b). The transition state for the rate controlling step (III*) can be visualized as a structure similar to III but with looser interactions between the aluminium atom and alkene π system. The observed differences in the *A* factors can be explained in terms of group rotations permitted in III but blocked in (IV). These rotations contribute about 64 J mol^{-1} to the entropy difference between the two states.

4.1. Calculation of the Entropy difference IV -III*

For the calculation, a simple equilibrium can be assumed to exist between the two states.



III IV

II.4.

In terms of statistical thermodynamic parameters, the equilibrium constant K, is

$$K = \frac{\phi_{IV}}{\phi_{III}} \cdot e^{-E_o/RT}$$

where ϕ is the molecular partition function for each molecule and E_o is the difference in zero point energy between the two states. To a first approximation the zero point energy E_o can be identified with the standard enthalpy difference ΔH^o and thus:

$$e^{\Delta S^o/R} = \phi_{IV}/\phi_{III}$$

The molecular partition function can be factorized into several components:

$$\phi = \Pi^{n}_{i=1} f_i$$

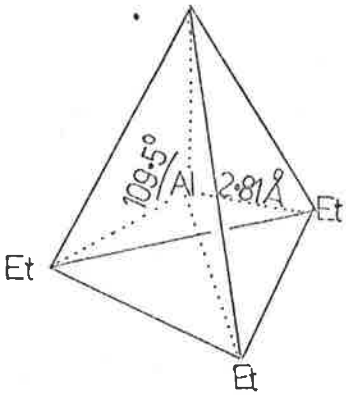
covering translation, vibration, rotation, electronic transitions and electronic and nuclear spin.

In the case under consideration, the only changes are in the internal rotations of the molecule and, to a very small extent, in the vibrational characteristics of the molecule. This latter can be discounted, as a four-centre structure has little scope for independent bond vibration, and so will contribute a negligible amount to the entropy difference, the whole of which can be attributed to changes in the internal rotations of the molecule.

$$\frac{\phi_{IV}}{\phi_{III}} = \frac{f_{int.rot(IV)}}{f_{int.rot(III)}} \, .$$

The single major group rotation lost on going III→IV is the rotation about the C3 axis of the AlEt$_3$ rotor. Its contribution to the entropy was determined as follows

The moment of inertia of the rotor was calculated using an Al–C bond of 2.0 Å and a C–C bond length of 1.54 Å. The ethyls were assumed to be a point mass residing along the projection of the Al–C bond at their centre of gravity.



II.4.

$$I_r = \sum_{i=1}^{n} m_i r_i^2 = 3(29 \;.\; 2.81^2 \;.\; \sin^2 70.5) = 610 \text{ amu Å}^2$$

The partition function is given by:

$$Q_f = \frac{\pi^{\frac{1}{2}}}{\sigma}\left[\frac{\pi^2 I_r kT}{h^2}\right]^{\frac{1}{2}}$$

where k = Boltzmann constant

T = absolute temperature

h = Plank's constant

σ = symmetry factor (in this case 3)

This reduces to

$$Q_f = \frac{3.6}{\sigma}\left[\frac{I_r T}{100}\right]^{\frac{1}{2}} \quad \text{for } I_r \text{ in amu Å}^2$$

For the $AlEt_3$ rotor at 300K; Q_f = 51.7 and this corresponds to an entropy change of 32.7 J mol^{-1}. On going from III to IV an ethyl rotation is lost, but this is partly compensated for by the gaining of a methyl rotation. Entropies for these rotors are tabulated (S.W. Benson, Thermochemical Kinetics, Wiley, 1968, Table A10) and the nett change is 10 J mol^{-1}. Other rotations lost or partly lost are some of the alkyl group rotations that become more hindered as the carbon hybridization changes from *sp*^{2} to *sp*^{3}, with the corresponding decrease in the angle between substituents from 120° down to 109.5°. From some analagous compounds listed by Benson,[35] an estimate of the contribution to the entropy difference from these hindered rotations is 21 J mol^{-1}. Another possible contribution to the entropy difference arises from the solvent medium, as even in a non-polar hydrocarbon medium, a change in polarity of the molecule on going from III-IV will change the solvent shell a little. The structures do appear to indicate that some polarity change does occur but, as mentioned previously, too little is known to ascribe a set value for the entropy change. In this case, it is suggested that the effect is small. The total estimated entropy change is thus:

$$32.7 + 10.0 + 21 = 64 \text{ J mol}^{-1}$$

As $\log_{10}A$ varies as $\Delta S/2.303R$, these entropy changes correspond to a change in $\log_{10}A$ of 3.3. This must be regarded as a lower limit due to the intangible solvent environment effect.

The difference in A factors between the lower alkene homologues and the hindered alkenes lies between 10^3 and 10^4, so the agreement is quite good. For the higher homologues (n-oct-1-ene for example) the difference is not so great as the four-centre transition state can be expected to be looser, as stated previously. Therefore not all of the calculated rotations will be lost.

II.4.

In conclusion, it is apparent that the high A factor for 3,3-dimethylbut-1-ene is neither unique nor anomalous as previously suggested.[18] When K_d values obtained in liquid solution are used, the high A values found with alkenes sterically encumbered in the vicinity of the double bond are quite consistent with a plausible reaction path (Fig. II.18(b).) The kinetic parameters for styrene are similar to those of n-alk-1-enes, and it can be assumed that a reaction path similar to Fig. II.18(a) is followed. If this is the case, the absence of any significant aromatic substituent effect is not surprising, as the electron withdrawing phenyl group will have less influence on the formation of the four-centre transition state IV than on the transition state that is similar to the vinyl π complex III. The only apparent anomaly in Table II.4 is cyclohexene, where the very low A factor has been attributed to increased ring strain in the six-membered ring when the four-centre transition state is formed.[18] This is not plausible as overcoming ring strain would increase the thermal barrier for four-centre formation considerably, but would be expected to have only a minor effect on the entropy of activation. The rate measurements were obtained in this case by product analysis using gas-liquid chromatography. This technique is not such an accurate kinetic method as those used for the other substrates - gas absorption, dilatometry and p.m.r. spectroscopy, and this could explain the apparent anomaly.

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SECTION III

REACTION OF TRIETHYLALUMINIUMS WITH ALKYNES

Synopsis

Introduction - Metallation was first observed in 1962. Before this only addition was thought to occur. Addition to alkynes is more facile than to alkenes. The first addition mechanism proposed was "alkyne insertion", but on the basis of further observations, a π complex intermediate was subsequently postulated.

$AlEt_3$-Phenylacetylene Complex - P.m.r. shifts show that the complex is an alkyne-Al π complex of 1:1 stoichiometry. Calculations on p.m.r. data give a K_{eq} for complex formation of 0.064 dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$.

Kinetics - Metallation was followed from the release of ethane, using an automatic recording manometer. Addition was followed using p.m.r. spectroscopy. Both kinetics were determined using the same reaction solution.

Results - The Al_2Et_6 dimer is the reactive aluminium species for metallation. Addition proceeds from a monomeric Al species. Rate constants were calculated for all possible reaction paths using a complicated best fit computer programme.

Discussion of Mechanism - Arrhenius parameters indicate that addition occurs via the π complex and a four-centre trapezoidal transition state. High *A* factors are accounted for by little change in the number of degrees of freedom between the two states.

III.1.

1. INTRODUCTION

As in alkenes, the pioneering work in studying the reactions of alkylaluminiums to alkynes was done by Ziegler,[1] who reacted triethylaluminium with acetylene at 423K. This work was followed closely by that of Wilke and Muller[2] in 1958-9, who established that the reaction was addition of triethylaluminium across the triple bond

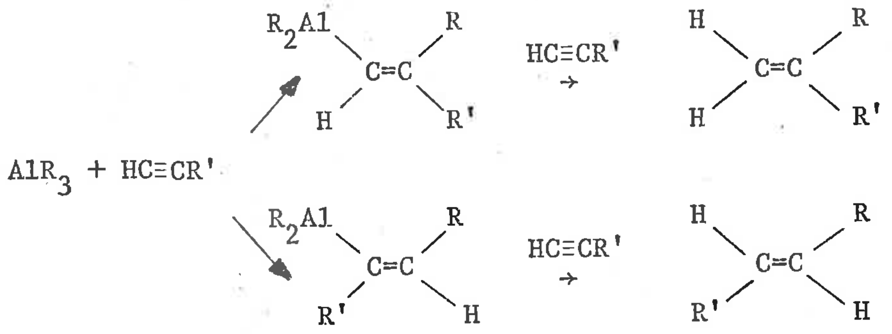
$$Et_2Al\text{-}C_2H_5 + HC{\equiv}CH \rightarrow Et_2Al\text{-}CH{=}CH\text{-}C_2H_5 \qquad ....(1)$$

thus discovering the first vinylaluminium compound. In this early work no report was made of the reaction of the acidic acetylenic proton with triethylaluminium, prompting Ziegler[1] in his 1960 summary, to say: "...as a rule, the acidic hydrogen atoms of acetylene itself and of the mono-substituted acetylenes do not react." This was shown to be an over-generalization by Mole and Surtees[3,4] and Eisch and Kaska[12,13] who reported the reaction:

$$C_6H_5\text{-}C{\equiv}CH + R_3Al \rightleftarrows C_6H_5\text{-}C{\equiv}C\text{-}AlR_2 + RH \qquad ....(2)$$

where R can be methyl, ethyl, propyl, isobutyl or phenyl. 1-napthylacetylene also undergoes the metallation reaction quite readily.[5] More recently, Rienacher and Schwengers[6] have shown that the metallation reaction is also predominant when the monoacetylene substituent is

C_4H_9, C_5H_{11}, C_6H_{13} and C_8H_{17}. They also observed that addition occurred to give both the Markownikoff and anti-Markownikoff addition product, and, as Mole had previously observed, the vinylaluminium compound formed exchanges with unreacted alkyne to give disubstituted alkene and an alkynylaluminium compound above 313K:



(a)

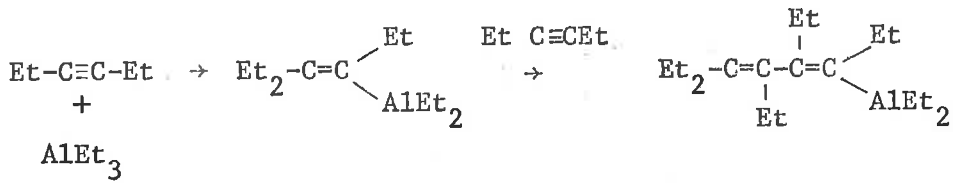
....(3)

(b)

The ratio of addition/metallation increased with increasing temperature (90/10 at 293K, 65/35 at 373K), thus indicating that the addition reaction has the higher energy of activation. It was also found that the ratio of Markownikoff/anti-Markownikoff did not alter with temperature.

The addition of trialkylaluminiums to alkynes is a much more facile addition than that to alkenes, as unlike alkenes, triethylaluminium adds to the unsaturated bond of 1,2 disubstituted alkynes quite rapidly above 373K. At this temperature a second molecule of alkyne may be added to the alkenylaluminium produced, and a dienylaluminium compound is formed.

III.1.

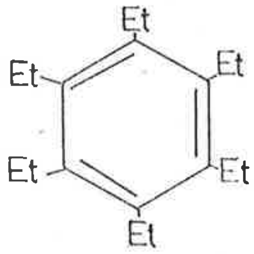


....(4)

I

II

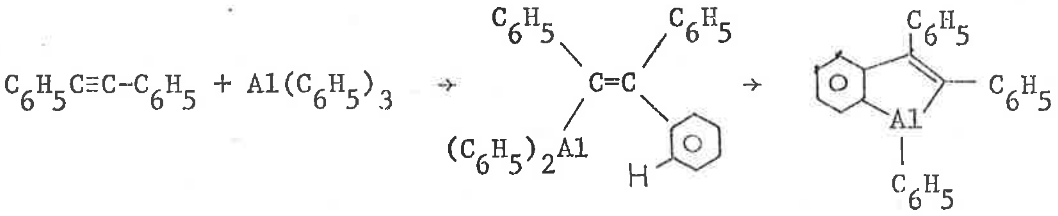
An additional step leading to cyclotrimerization is also possible, giving III



III

Wilke and Muller[2] suggested that II arises from I simply by the insertion of the alkyne into the vinylaluminium bond. In turn, a Diels-Alder addition of alkyne to II, with subsequent loss of $AlEt_2H$ was thought to result in III.

Triphenylaluminium adds to diphenylacetylene and the addition product is transformed at 473K with loss of benzene into triphenylbenzaluminole.[11]



III.1.

To try and gain insight into electronic factors governing addition, Eisch and Hordis investigated the addition of triphenylaluminium to various *p* substituted phenylacetylenes.[7] It was found that

a) almost exclusively cis addition to the C≡C linkage,

b) the ratio of geometric isomers (eqn. (3)) correlated strongly with the Hammett σ values of the para substituents (ρ=-0.713),

c) significant rate retardation in ethers,

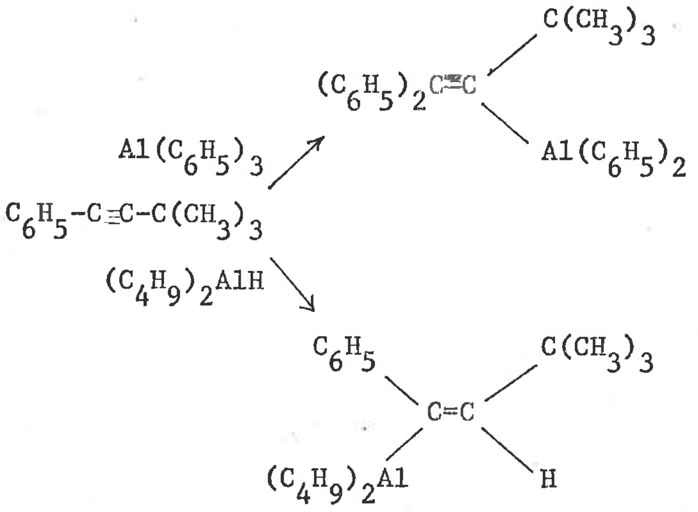
d) the reaction was first order in the alkyne and half order in $AlPh_3$, and

e) the rate decreased as the para substituent changed from methyl to hydrogen to chlorine. It was inferred from these results that the reaction involved a dimer dissociation of triphenylaluminium, followed by an electrophilic attack of the triphenylaluminium on the alkyne.

Eisch, Amtmann and Foxton[8] demonstrated the importance of steric factors in addition when, on studying the addition of diisobutylaluminiumhydride and triphenylaluminium to t-butyl(phenyl)acetylene, they found that in the former case the aluminium finished up geminal to the phenyl group (5(b)), whilst in the latter case it ended geminal to the t-butyl group (5(a)).

Thus:

III.1.

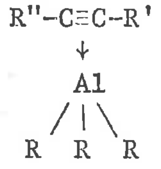


(a)

....(5)

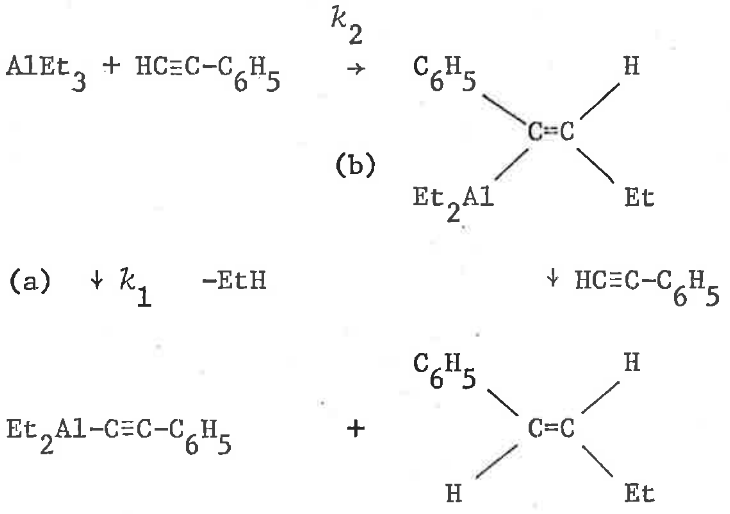
(b)

In attempting to rationalize their results, Eisch *et al* rejected the "alkyne insertion" put forward by Wilke and Muller, and instead postulated a π complex similar to that already proposed for alkenes



Thus the greater reactivity towards addition of alkynes over alkenes can be explained by the greater π donor nature of the former. The selectivity in the direction of C-Al bond additions to alkynes can also be explained as being due to the electronic and steric factors that influence the disruption of the π complex. If this complex exists, and plays a significant role in the mechanisms of addition and elimination, the kinetic parameters for each reaction should show such, and so we decided to investigate the reaction of triethylaluminium with an alk-1-yne that undergoes metallation and addition fairly readily at accessible temperatures.

Such an alk-1-yne is phenylacetylene. With this compound, the metallation reaction is enhanced due to the electron withdrawing phenyl group accentuating the acidic nature of the acetylenic proton. An added advantage is that the products of the reaction between triethylaluminium and phenylacetylene have been completely characterized by IR and p.m.r. spectroscopy. Only addition (3b) occurs thus:



....(6)

The alkene was shown to be trans β-ethylstyrene by the presence of a peak at 960cm^{-1} in the IR and a sharp olefinic proton resonance in the p.m.r. similar to trans β-methylstyrene. An interesting point is that, due to the increased electron density of the alkyne bond, the π complex should be more stable than the corresponding alkene complex. It was initially decided, therefore, to try to find evidence for the existence of an alkyne π complex.

III.2.

2. TRIETHYLALUMINIUM-PHENYLACETYLENE COMPLEX

2.1. Nature of Complex

The method used to detect the triethylaluminium-phenylacetylene complex was the same as that used in the attempt to find a vinyl-triethylaluminium π complex: i.e. a p.m.r. method.

Purification of materials

a) *Triethylaluminium*

Breakseals of this compound were prepared as described earlier.

b) *Phenylacetylene* (A.R. grade, Pfaltz and Baur, N.Y., U.S.A.)

After being dried over calcium hydride for forty eight hours, the alkyne was vacuum distilled into large breakseals. These were subsequently broken down into smaller breakseals using an apparatus similar to Fig. II.3. Phenylacetylene undergoes an auto-oxidation reaction at room temperature, and so the breakseals were stored at 253K.

Preparation of n.m.r. tubes

Due to the fact that, even at 302K, the metallation reaction occurs to a limited extent, it was not considered safe to prepare n.m.r. tubes exactly as before, as the gas evolved would increase the pressure in the limited vapour space above the liquid to a dangerous level. Consequently, the n.m.r. tubes were modified by having them attached to 100 ml. cylindrical flasks. The cylindrical nature was necessary as

PREPARATION OF NMR TUBES

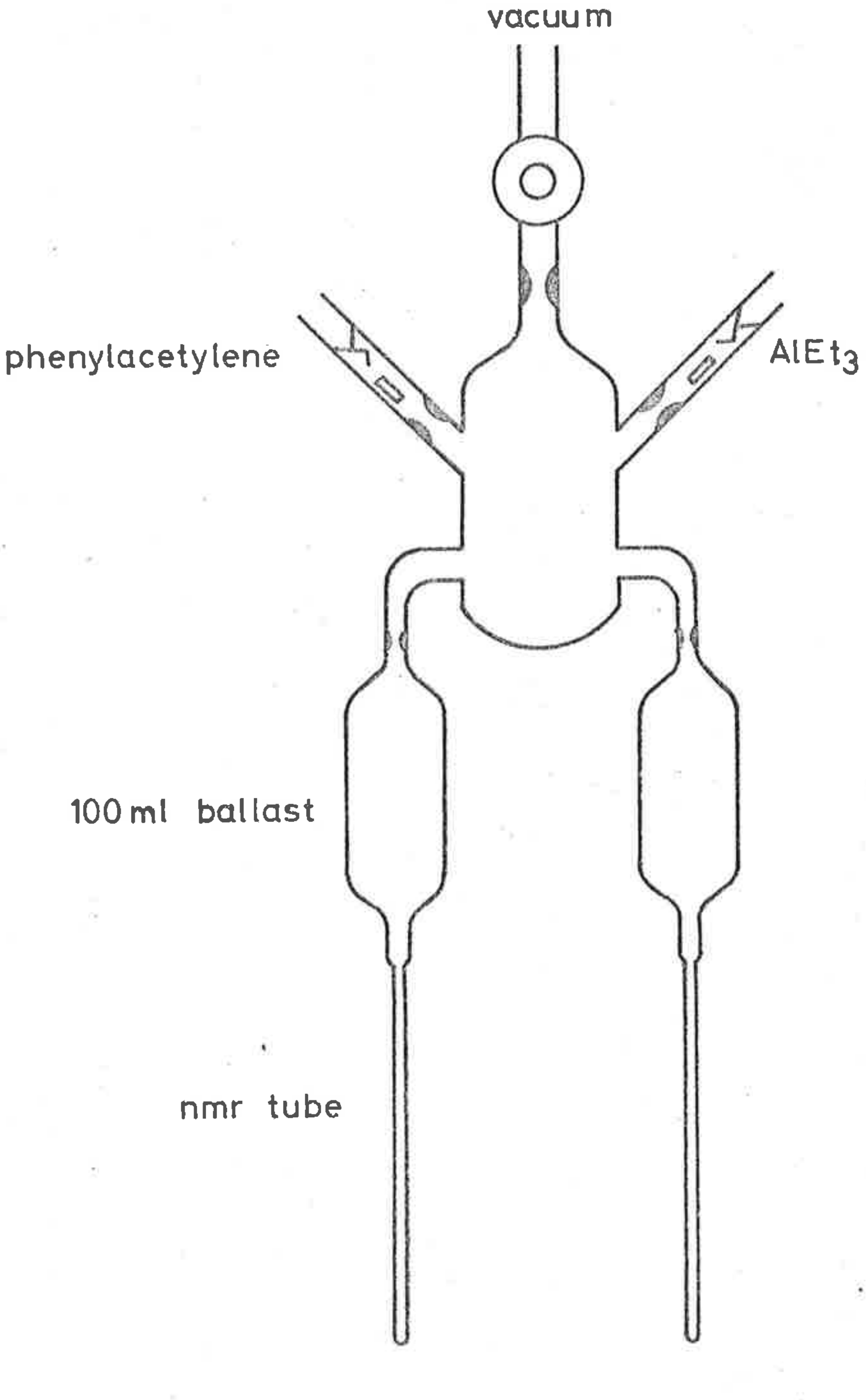


FIG. III 1

the gap between the magnet poles in the n.m.r. probe is only 1½ inches. The n.m.r. tubes were filled in a similar fashion to that described previously (Section II.2), using the apparatus shown in Fig. III.1. The prepared tubes were stored at 253K until measured, to suppress any reaction.

P.m.r. spectra

Any slight asymmetry of the n.m.r. tube/flask would create a large moment if spun in the n.m.r. probe, which would probably result in fracture, and so the p.m.r. spectra were recorded without the sample spinning. This has the effect of reducing the resolution of the spectrum, which was mostly offset by carefully tuning the instrument before each determination.

The aromatic phenylacetylene protons, offset 419.0Hz, provided a convenient lock for the determination of the internal chemical shift between the methyl and methylene groups of triethylaluminium δ_{int} (see Fig. II.5). A preliminary experiment showed that for one sample of $[C_8H_6]/[Al]=.9/1$, the value of δ_{int} was -42.0Hz, compared with -40.0Hz for pure triethylaluminium. A further eleven tube/flasks were prepared having ratios ranging from 0.17/1 to 13/1 (C_8H_6/Al) and δ_{int} was recorded for each tube at 300K, using the cyclohexane resonance, offset 105.0 Hz, as the internal lock. Fig. III.2 shows the plot of δ_{int} against molar ratio C_8H_6/Al, and it can be seen that a complex of 1:1 stoichiometry is

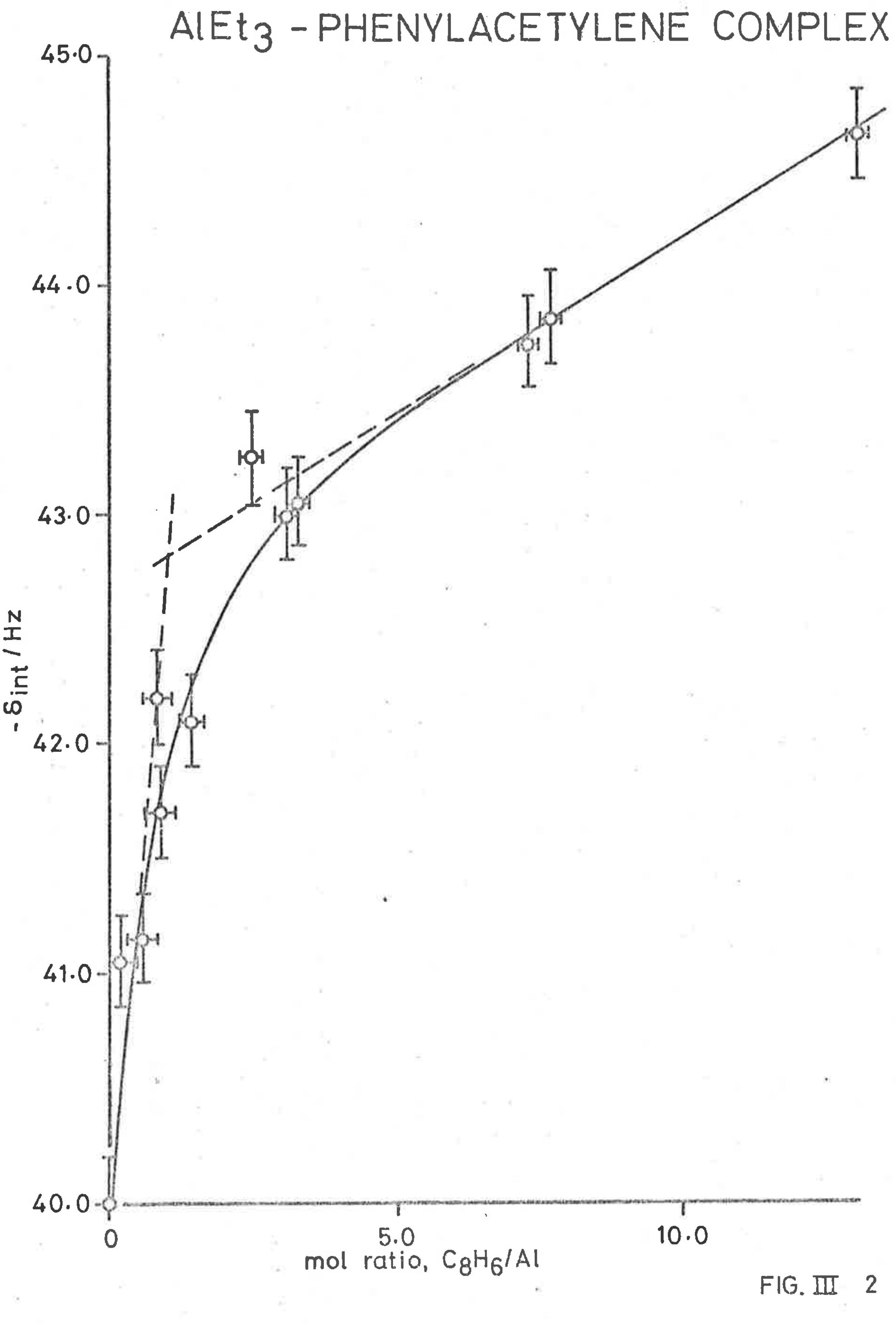
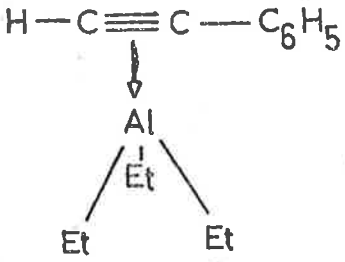
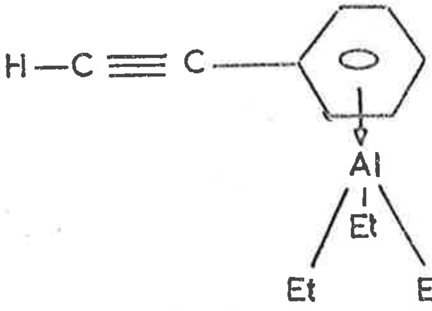

AlEt3 - PHENYLACETYLENE COMPLEX
45·0
44·0
43·0
42·0
41·0
40·0
- δint /Hz
0
5.0
10·0
mol ratio, C8H6/Al

FIG. III 2

formed. Two possible complexes could result from interaction between the phenylacetylene and the triethylaluminium; an alkyne π complex (I) or an aromatic π complex (II), analagous to the two possible situations arising when styrene was considered.



I



II

The composite spectrum for the phenylacetylene/triethylaluminium system with a cyclohexane marker, is shown in Fig. III.3. As with the alkenes, this was obtained by recording two spectra: one with an aromatic lock, and the other with a cyclohexane lock, followed by superimposition to remove the lock signals. At a reagent ratio of C_8H_6/Al =1, the aromatic resonances were 0.023 p.p.m. upfield of those of pure phenylacetylene at the same concentration in cyclohexane, and did not shift to any measurable extent between 243K and 313K, while the acetylenic resonances were 0.127 p.p.m. downfield of those of the pure substance at concentration, and moved 0.027 p.p.m. downfield as the temperature decreased from 313K down to 243K. In the case of acetylenic proton shifts, it is of primary importance to obtain the same concentrations for comparison, as, of all the proton resonances, the acetylenic are probably

P.M.R. SPECTRUM OF
$AlEt_3$–PHENYLACETYLENE
in cyclohexane

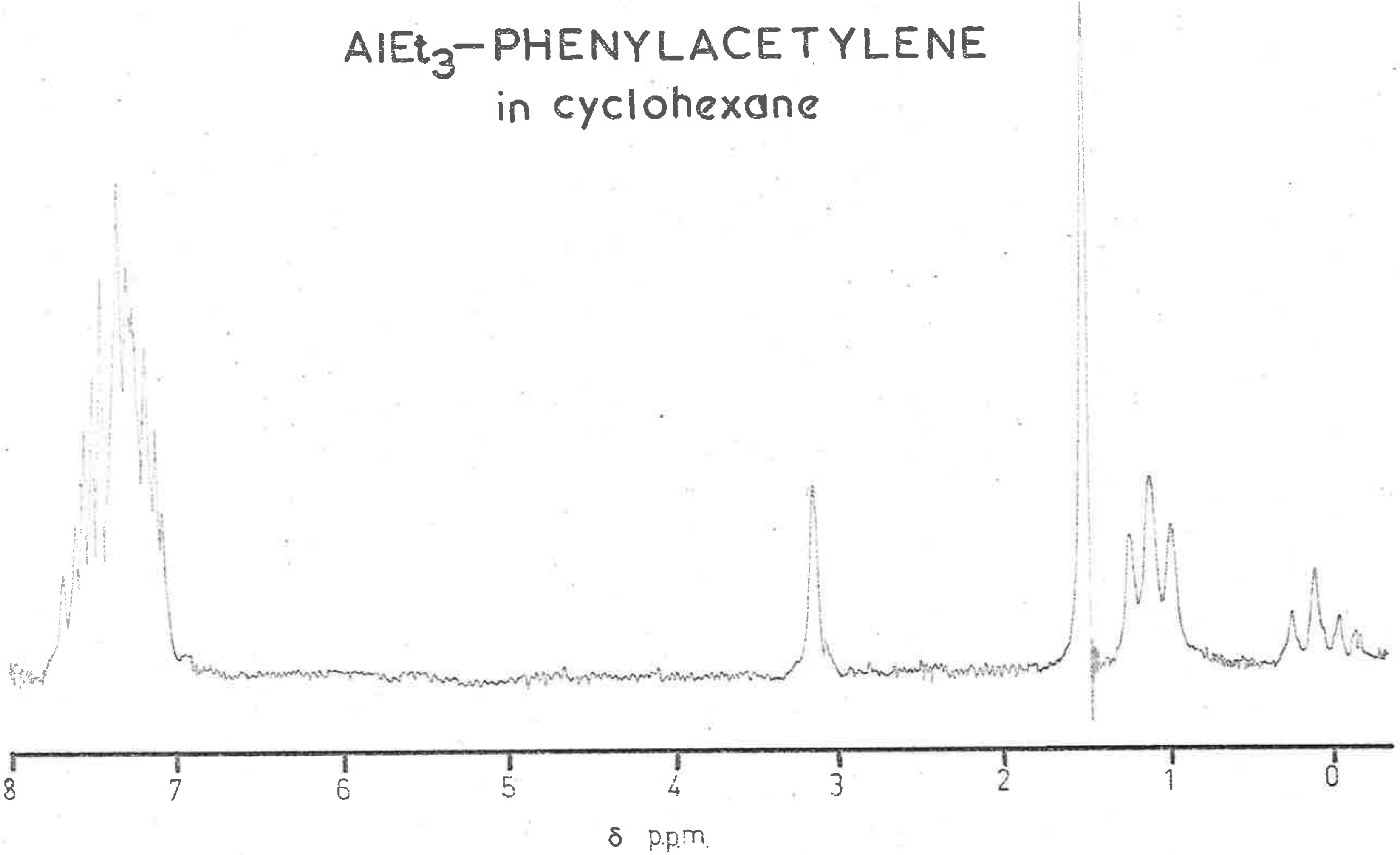


Fig III.3

the most prone to "solvent shift". In acetylenes, this is due to weak self association by formation of hydrogen bonds involving the acidic hydrogen atom and the alkyne system.[9] Dilution of phenylacetylene with cyclohexane will disrupt the self association and thus alter the observed chemical shift of the acetylenic proton. Consequently, any measure of the complexing to aluminium must be measured against a background of complexing that is already present. Hence identical concentrations are necessary.

The relative magnitudes of the shifts of the aromatic and acetylenic proton resonances on formation of the complex indicate that it is an alkyne complex (I) and not aromatic (II). Some support for this is offered by the fact that propagyl chloride ($HC\equiv C-CH_2Cl$) associates through alkyne π bonds, even in benzene solution.[10] The evidence for this is that the shift for $-CH_2$ and the acetylenic proton are identical when the solvent is changed from carbon tetrachloride to benzene.

The existence of an alkyne aluminium interaction was proved by studying the p.m.r. spectra of the system hex-3-yne/triethylaluminium in cyclohexane. In this system any change in δ_{int} can only arise from alkynylaluminium interactions. Eight n.m.r. tubes containing hex-3-yne/aluminium concentration ratios varying from 0/1 to 7/1 were prepared by the method already described for the alkenes (Section II.2), and their p.m.r. spectra measured, using cyclohexane offset downfield 105Hz as the lock.

III.2.

Unfortunately the alkyl proton resonances of hex-3-yne overlap the triethylaluminium triplet resonances, making a direct measurement of δ_{int} impossible. However, the trend in δ_{int} was obtained by observing the shift of the methylene resonances. This is not as accurate as measuring δ_{int} directly as the methylene resonances move only approximately half of the change in δ_{int} that occurs when the molar ratio is altered.

The absolute chemical shift of the methylene quartet as a function of molar ratio at 302K is shown in Fig. III.4 and it can be seen that a complex between hex-3-yne and triethylaluminium exists, and that it has a 1:1 stoichiometry, as expected.

Once the existence and nature of the phenylacetylene/triethylaluminium complex has been established, it follows that a three stage equilibrium is present in solution prior to addition or metallation.

$$\begin{tikzcd} \frac{1}{2}Al_2Et_6 + HC\equiv C-C_6H_5 \arrow[rr, shift left, "K_c"] \arrow[dr, shift left] & & Et_3Al.HC\equiv C-C_6H_5 \arrow[ll, shift left] \arrow[dl, shift left] \\ & AlEt_3 + HC\equiv C-C_6H_5 \arrow[ul, shift left, "K_d^{\frac{1}{2}}"] \arrow[ur, shift left] & \end{tikzcd} \qquad ....(7)$$

In order to understand the kinetic parameters relating to addition and metallation, it is first necessary to characterize this equilibrium. K_d is already known and so a value for K_c will complete the characterization.

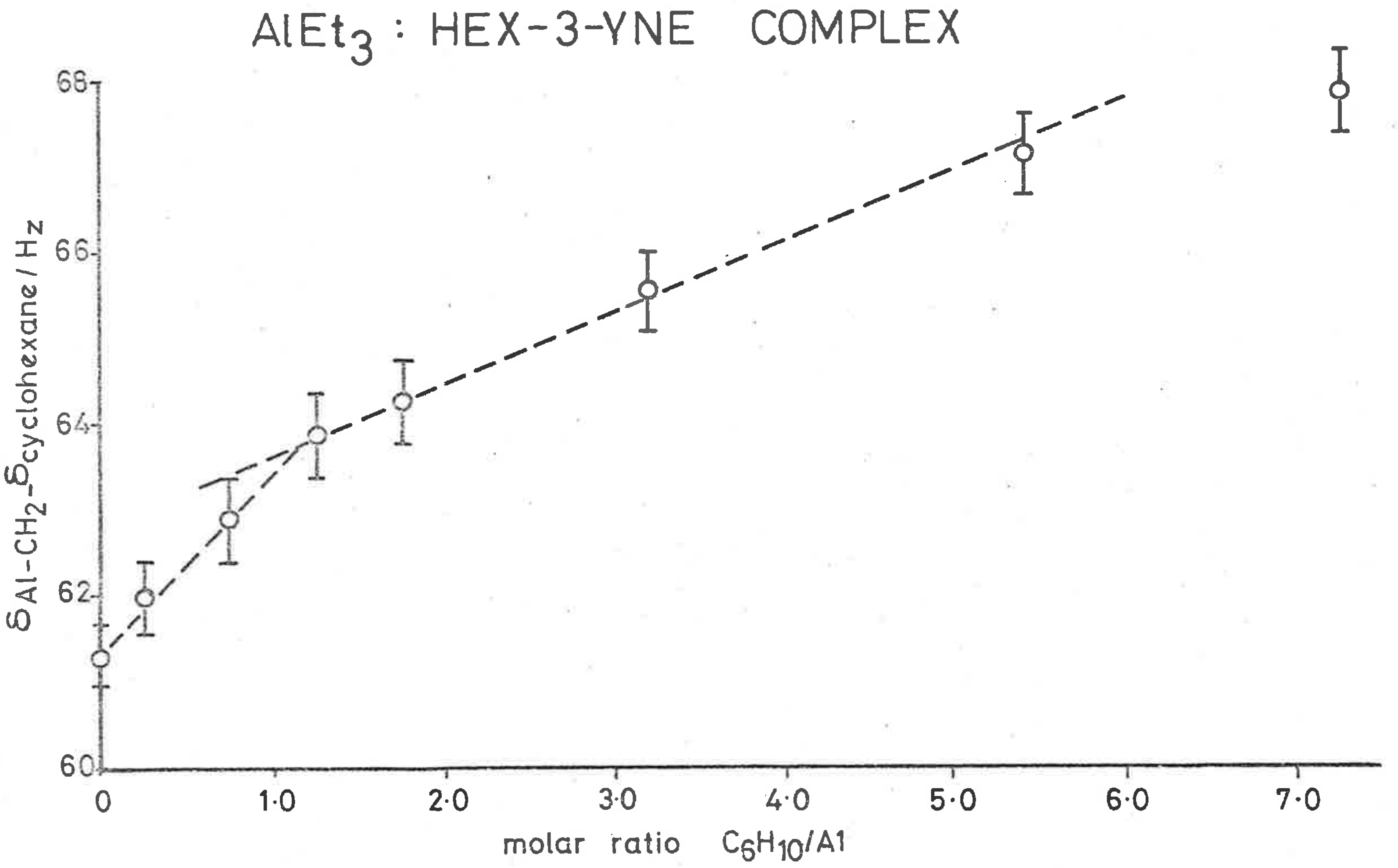

AlEt$_3$: HEX-3-YNE COMPLEX
$\delta_{Al-CH_2}-\delta_{cyclohexane}$ / Hz
68
66
64
62
60
0
1·0
2·0
3·0
4·0
5·0
6·0
7·0
molar ratio C$_6$H$_{10}$/A1

FIG. III. 4

III.2.

2.2. Estimation of K_c

Several methods are available to measure the equilibrium parameters of a donor-acceptor equilibrium such as the C_8H_6:$AlEt_3$ complex. Ebulliometry is to be avoided if possible, as apparent molecular weight determinations by this method suffer many experimental errors (see Section IV.5.1). A method based on the heat of solution is possible but requires a complicated and expensive apparatus which was not available to this laboratory. As the technique for looking at the system by p.m.r. spectroscopy has already been established, and a spectroscopic parameter (δ_{int}) to characterize the equilibrium is available, it was decided to use this method to obtain the equilibrium parameters.

The eleven tube/flasks used in determining the stoichiometry were again used to evaluate the equilibrium constant. δ_{int} was recorded for each at three other temperatures (268K, 280K, 290K) in addition to the determination at 300K. Table III.1. shows the δ_{int} values for each sample.

TABLE III.1.

δ_{int} for $AlEt_3:C_8H_6$ complex

Molar ratio C_8H_6/Al	268K	280K	290K	300K
	$-\delta_{int}/Hz$			
0.169	41.35	41.40	41.00	41.05
0.561	41.15	41.50	41.50	41.15
0.865	41.35	41.70	41.45	42.20
0.901	41.90	42.10	41.90	41.70
1.370	42.20	42.30	42.25	42.10
2.486	42.10	42.35	42.80	43.25
3.097	43.00	42.85	42.85	43.00
3.236	42.75	42.80	42.95	43.05
7.300	43.50	43.60	43.75	43.75
7.695	43.75	43.75	43.70	43.85
13.015	44.20	44.20	44.70	44.65

The concentration of triethylaluminium monomer is very small compared to the other species in solution and so the stoichiometry for complex formation is:

$$Al_2Et_6 + 2HC\equiv C\text{-}C_6H_5 \overset{K_c^2}{\rightleftarrows} 2Et_3Al.HC\equiv C\text{-}C_6H_5$$

	A	B	C
initially	a	b	0
equilibrium	$a-x$	$b-2x$	$2x$

$$\text{and } K_c^2 = 4x^2/(a-x)(b-2x)^2 \qquad \text{....(8)}$$

III.2.

The absolute value of the observed internal chemical shift is a weighted average of the shift of those protons in free triethylaluminium and those in the complex. Thus:

$$\delta_{obs} = \frac{n_a}{n_a+n_c} \cdot \delta_o + \frac{n_c}{n_a+n_c} \cdot \delta_c$$

where δ_{obs} = observed internal chemical shift

n_a, n_c = no of protons in the sample present in Al_2Et_6 and complex

δ_o = internal chemical shift for pure Al_2Et_6 (40.0 Hz)

δ_c = internal chemical shift for the pure complex

This latter value was assumed to be 49.7 Hz, the internal shift observed when $C_8H_6/Al \approx 200/1$ at 268K. At this ratio, the limits of detectability of the instrument were reached.

The mole fractions of each type of proton can be identified with the concentration of each species:

$$\delta_{obs} = \frac{6(a-x)}{6(a-x) + 3(2x)} \cdot \delta_o + \frac{3(2x)}{6(a-x) + 3(2x)} \cdot \delta_c$$

therefore

III.2.

$$\delta_{obs} = \frac{2(a-x)\ .\ \delta_o + 2x\ .\ \delta_c}{2(a-x) + 2x}$$

rearranging

$$2(a-x)/(\delta_{obs} - \delta_o) = 2x(\delta_c - \delta_{obs})$$

Define

$$\Delta = \frac{(\delta_{obs} - \delta_o)}{(\delta_c - \delta_{obs})} = \frac{2x}{2(a-x)}$$

$$x = \Delta a/(1+\Delta)$$

Define

$$r = b/2a$$

and substituting

$$K_c{}^2 = x^2/(a-x)\ (ar-x)^2$$

substituting for x:

$$K_c{}^2 = \frac{\Delta^2 a^2}{(1+\Delta)^2} \Bigg/ \left[1 - \frac{\Delta a}{1+\Delta}\right]\left[ar - \frac{\Delta a}{1+\Delta}\right]^2$$

$$= \frac{\Delta^2(\Delta+1)}{a[r+(r-1)\Delta]^2} \qquad \ldots.(9)$$

When the components Δ are examined, it can be seen that when δ_{obs} is very close to either δ_o or δ_c any error is quite exaggerated. Consequently, the low C_8H_6/Al concentration ratios (0.17, 0.56) were omitted in the calculation of K_c. Values obtained for K_c from the remaining nine samples by substituting the corresponding values in equation (9) are shown in Table III.2: the standard deviations are high due to the fact that the resolution of the spectrometer amounted to about 10% of the observed change in δ_{int}.

TABLE III.2.

Equilibrium constant for Et_3Al: C_8H_6

	268K	280K	290K	300K
$1/T.10^3$	3.73	3.57	3.45	3.33
$K/dm^{\frac{3}{2}}\ mol^{-\frac{1}{2}}$	$.05_{54}$	$.05_{65}$	$.06_{04}$	$.06_{42}$
s.d.	.044	.044	.046	.049
$\log_{10} K_c$	-1.256	-1.248	-1.219	-1.192

The Van't Hoff plot of the data is shown in Fig. III.5 and gives a value

$$\Delta H^o = 3.1 \pm \text{(s.e.) } 0.8 \text{ kJ mol}^{-1}$$

Because of the errors involved and the narrow temperature range, no reliance can be placed on the extrapolation to obtain ΔS^o. The ΔH^o value determined includes the heat of dissociation of the dimer and shows that the formation of the Al_2Et_6 dimer is thermally favoured. Reported $\Delta H^o_{d(1)}$ for dimer dissociation vary (Section I), but the better value shows that the bond strength between Al and phenylacetylene is 32 kJ mol^{-1}.

VAN'T HOFF PLOT FOR $AlEt_3/C_8H_6$ COMPLEX

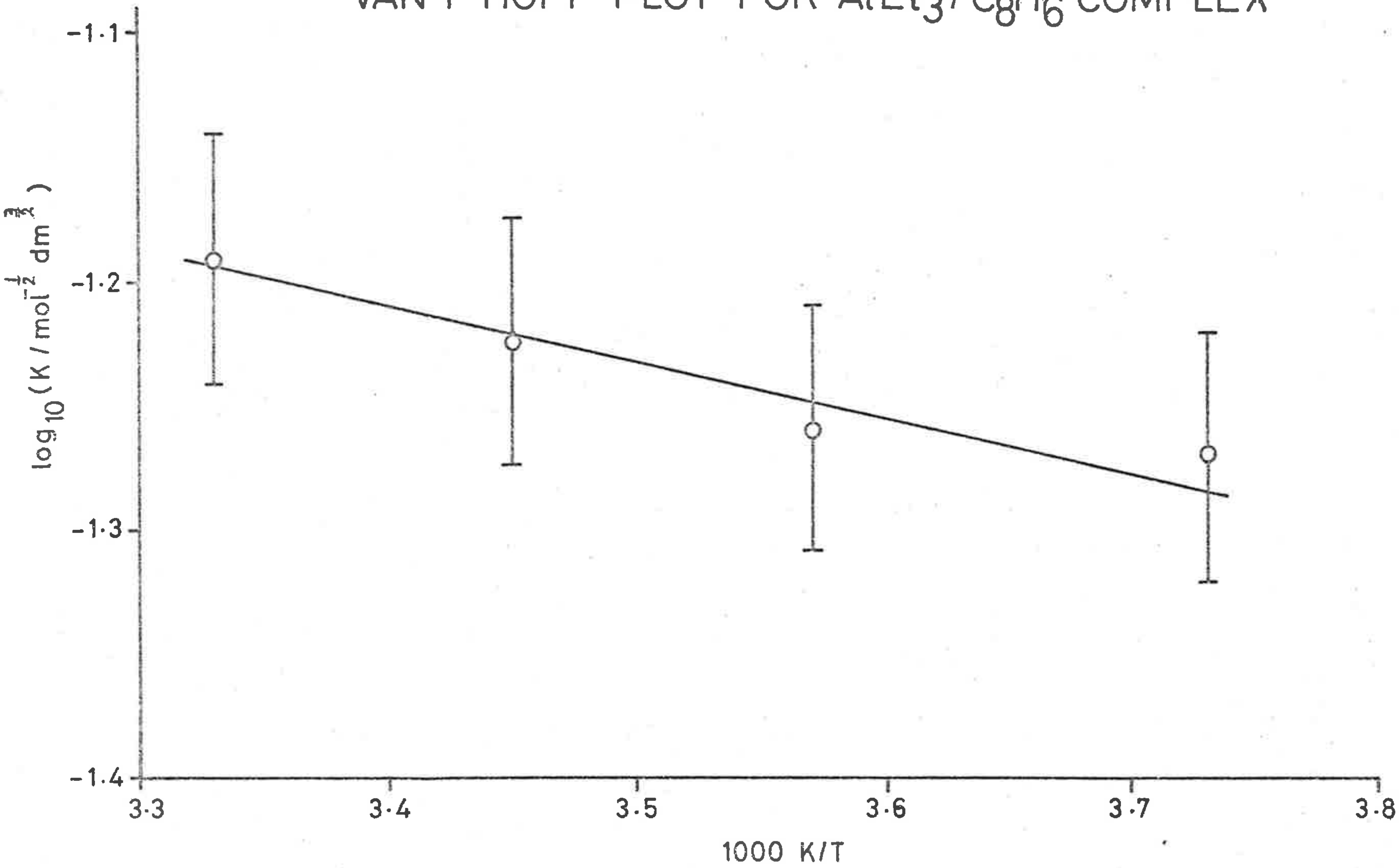


FIG. III 5

III.3.

3. DETERMINATION OF TRIETHYLALUMINIUM/PHENYLACETYLENE REACTION RATES

3.1. Preliminary

Breakseals of triethylaluminium and phenylacetylene were prepared as previously outlined. Cyclohexane breakseals were dispensed under vacuum into burettes which had their normal greased taps replaced with a 4mm. Springham "Viton A" greaseless tap. (Fig. III.6.) These were slightly displaced from the line of the burette in order to assist the flow of the liquid through the tap when the burette is upright.

Reaction (6a) involves the release of ethane gas, so the most convenient way of measuring the rate of this reaction is to manometrically follow the release of ethane. To do this it is necessary to establish that, under the conditions used, no elimination of ethylene or release of any other gaseous product from side reactions takes place. This was accomplished using the apparatus in Fig. III.7 and mass spectrometry.

After evacuation for one hour ($<10^{-1}Nm^{-2}$) the greaseless tap (A) was closed and the breakseals of triethylaluminium (1 ml.) and phenylacetylene (1.76 ml.) were broken. Using the 4mm. greaseless tap (B), 5.24 ml. of cyclohexane were admitted to the reaction apparatus. The 150 ml. reaction flask was cooled with liquid nitrogen and the rest of the apparatus heated with a hairdryer in order to get all components into the reaction flask. A small, cool flame was used to distill the last few drops of triethylaluminium into the flask. The apparatus was then sealed at constriction (1) and the reactant solution thawed. Tap D on the mass spectrometer gas filler was then opened at the same time

FILLING OF VACUUM BURETTES

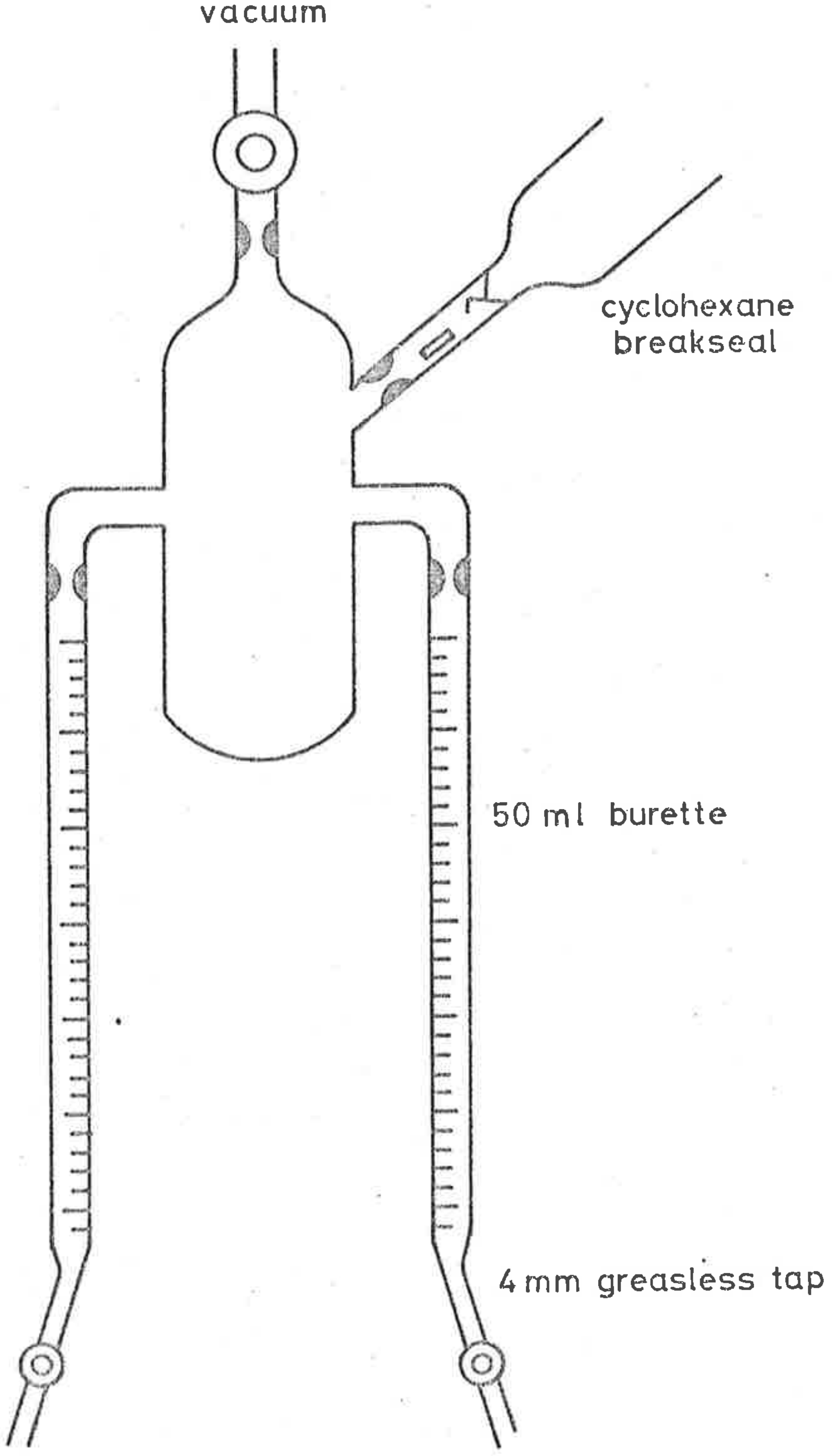


FIG. III. 6

MANOMETRY APPARATUS

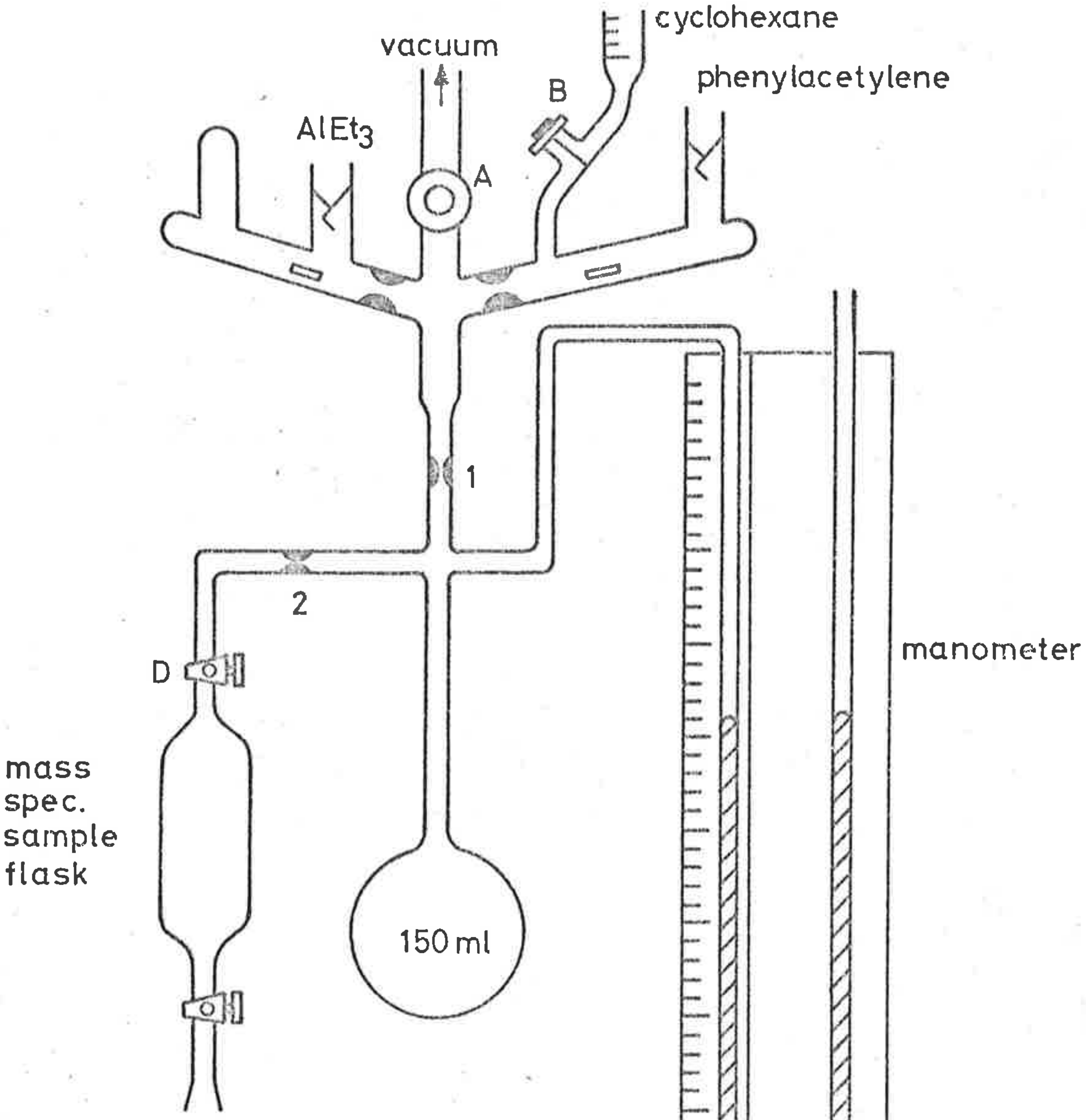


FIG. III 7

as the reaction flask was heated to 50°C in an oil bath. After approximately three hours, all reaction appeared to have ceased with the manometer indicating about 25 cm. Hg pressure in the apparatus. The constriction (2) was sealed with Tap D closed, and the mass spectrometry gas filler removed to be run on the mass spectrometer. The mass spectrum obtained with the evolved gas was consistent with its being solely ethane (Fig. III.8).

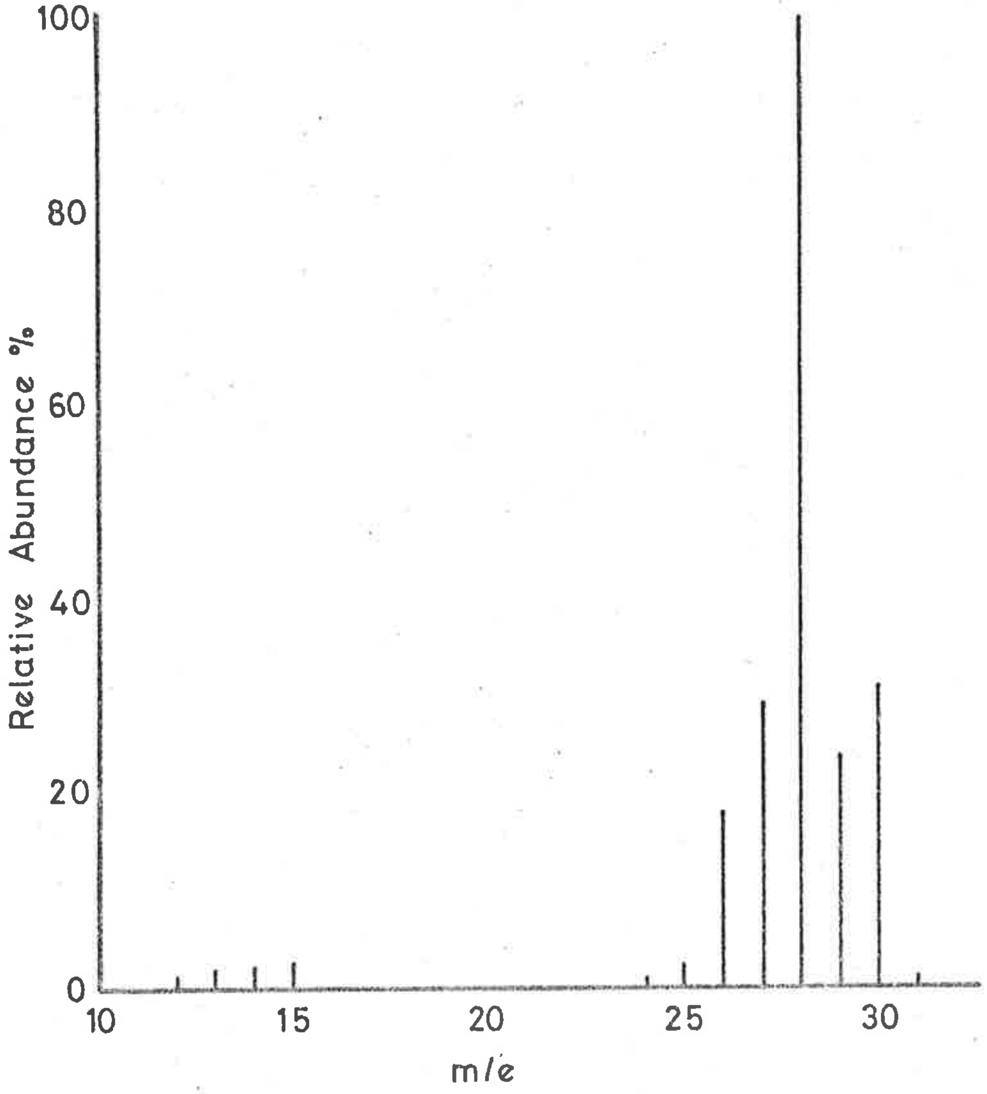
This preliminary run, therefore, established that the only gas evolved was ethane, and that 1.0 mls. of triethylaluminium, in excess phenylacetylene, provided a satisfactory amount of ethane for kinetic evaluation.

3.2. Manometry

It seemed to us that, for a consistent rate determination for both (6a) and (6b), the kinetics of each reaction at the same reactant concentrations should be obtained from the same reaction mixture. This is quite easily accomplished using the modified form of the manometry apparatus shown in Fig. III.9.

After evacuation for one hour ($<10^{-1}Nm^{-2}$), the Tap A was closed, the triethylaluminium and phenylacetylene breakseals broken, and a set amount of cyclohexane released into the apparatus through Tap B. The components were collected in the small (50 ml.) flask using liquid nitrogen, a hair dryer and a small, cool flame as before. The apparatus was then sealed from the main line at constriction (1) and the reaction mixture thawed. A small amount of the reaction mixture was then dis-

MASS SPECTRUM OF EVOLVED GAS



Note : identical to ethane [17]

FIG.III.8

MODIFIED MANOMETRY APPARATUS

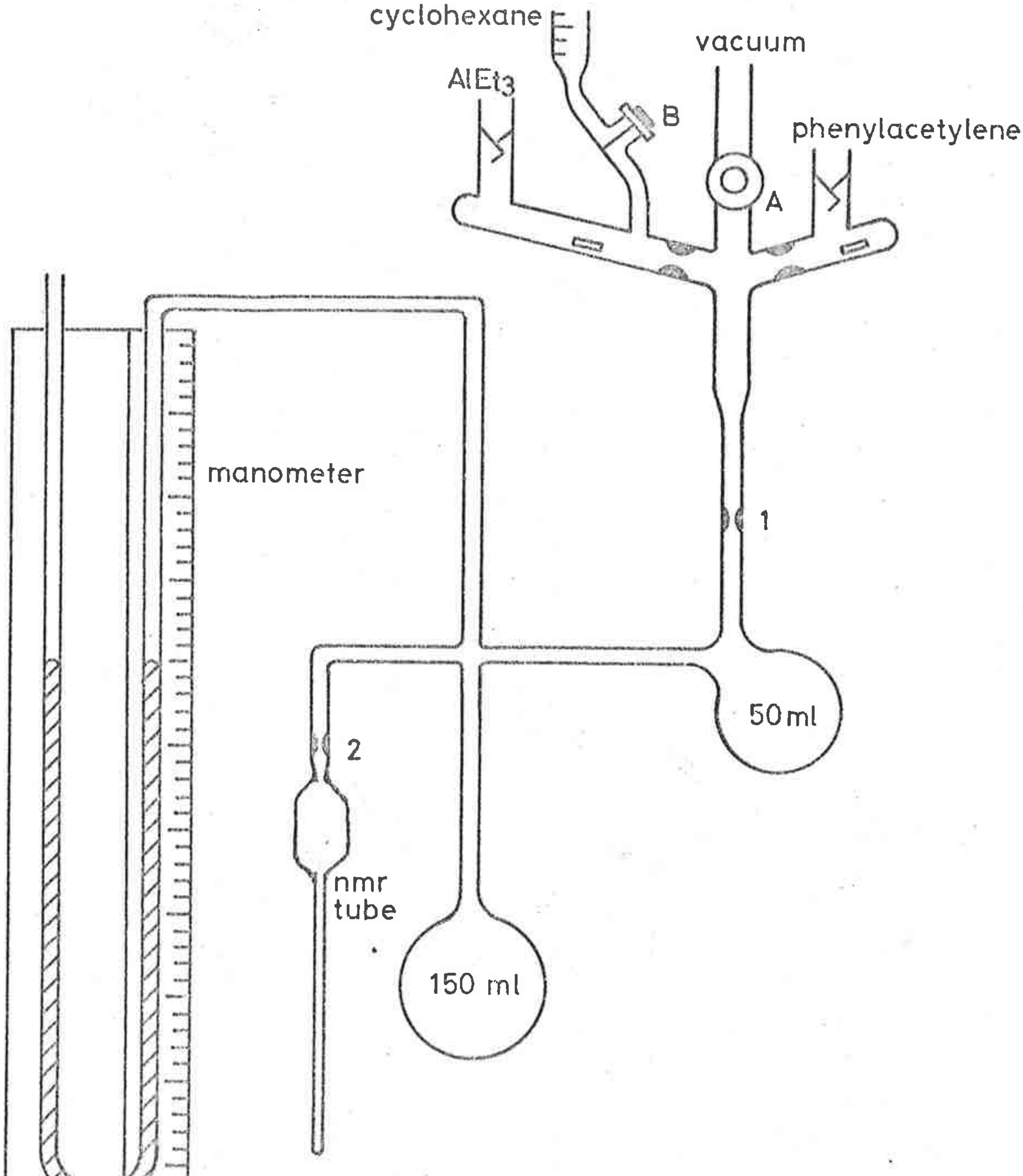


FIG. III 9

pensed into the n.m.r. tube by carefully tilting and tipping, followed by sealing at constriction (2). The n.m.r. tube was then stored at 253K until measured, to prevent any reaction occurring. After removal of the n.m.r. tube, the two interconnected reaction flasks were placed in an oil bath at desired temperature and the evolution of gas was followed. The attached manometer had a heavy based wooden stand to which it was securely fixed, making the whole apparatus free standing, so no special fitting was necessary to hold the flask in the oil bath. When preparing the reaction apparatus, it was necessary to make the tubing connecting the manometer with the reaction flasks long enough to ensure that the top crossover to the manometer was high enough, and therefore cool enough, to prevent distillation of the cyclohexane into the manometer.

Gas evolution was followed by monitoring the height of the mercury in the manometer. This was performed automatically, using a nichrome resistance probe (Fig. III.10) consisting of a .125" stainless steel rod, 90 cms. long, with each end brazed to assist electrical connection, and on to which p.v.c. tubing had been sweated, and the upper end was joined to a junction box. Alongside the stainless steel rod ran a 9 mil nichrome wire, held away about 2 mm. from the p.v.c. coated rod by nichrome wire loops, spaced 5 cms. apart along the length of the rod. Electrical connection between the steel and the nichrome was made at the lower end. The output leads from the junction box at the upper end were held rigid in a brass holder to ensure that no small changes in the

NICHROME RESISTANCE PROBE

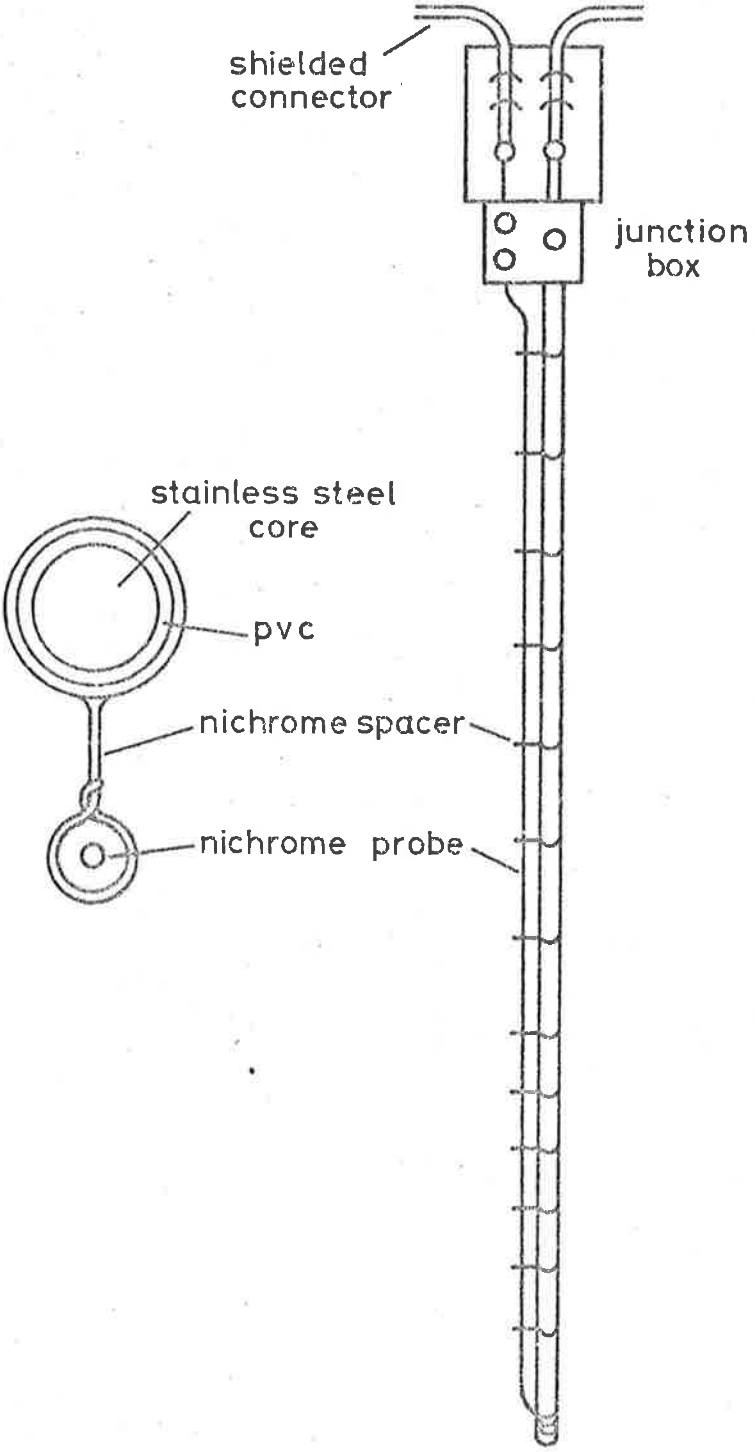


FIG. III 10

probe resistance resulted from a connection movement.

The probe formed part of the constant current circuit shown in Fig. III.11. Voltage output to the recorder from this circuit is thus directly proportional to the resistance of the probe setup. This resistance will decrease when the mercury level in the open arm of the manometer rises, progressively shorting out more of the nichrome wire. Voltage from the circuit was measured using a Heathkit Recorder modified to give a 10 mV full scale deflection.

A 60 cm. steel rule was glued to the supporting stand, at the back of each manometer on the evacuated side, and used to determine the total pressure change throughout the reaction, thus calibrating the recorder output. The only major assumption in this method of determining the pressure is that the diameter of the manometer, on both sides, is invariant and identical. This is difficult with the lengths and diameter (11mm OD) of the glass tubing used, as the commercial product varies considerably. It was thus necessary, for each of the three manometers made, to examine many lengths of tubing to obtain two lengths of the same diameter.

Commercial nichrome wire does not make a reliable electrical connection with mercury, due to a thin film of grease on the surface, necessitating cleaning the nichrome before use. After many attempts, we found the most efficient cleaning fluid to be Unibraze Stainless Steel Cleaner: a nitric acid based gel which removes the smooth surface of the nichrome, leaving a clean, rough finish, ideal for an electrical connection.

RESISTANCE MEASURING CIRCUIT

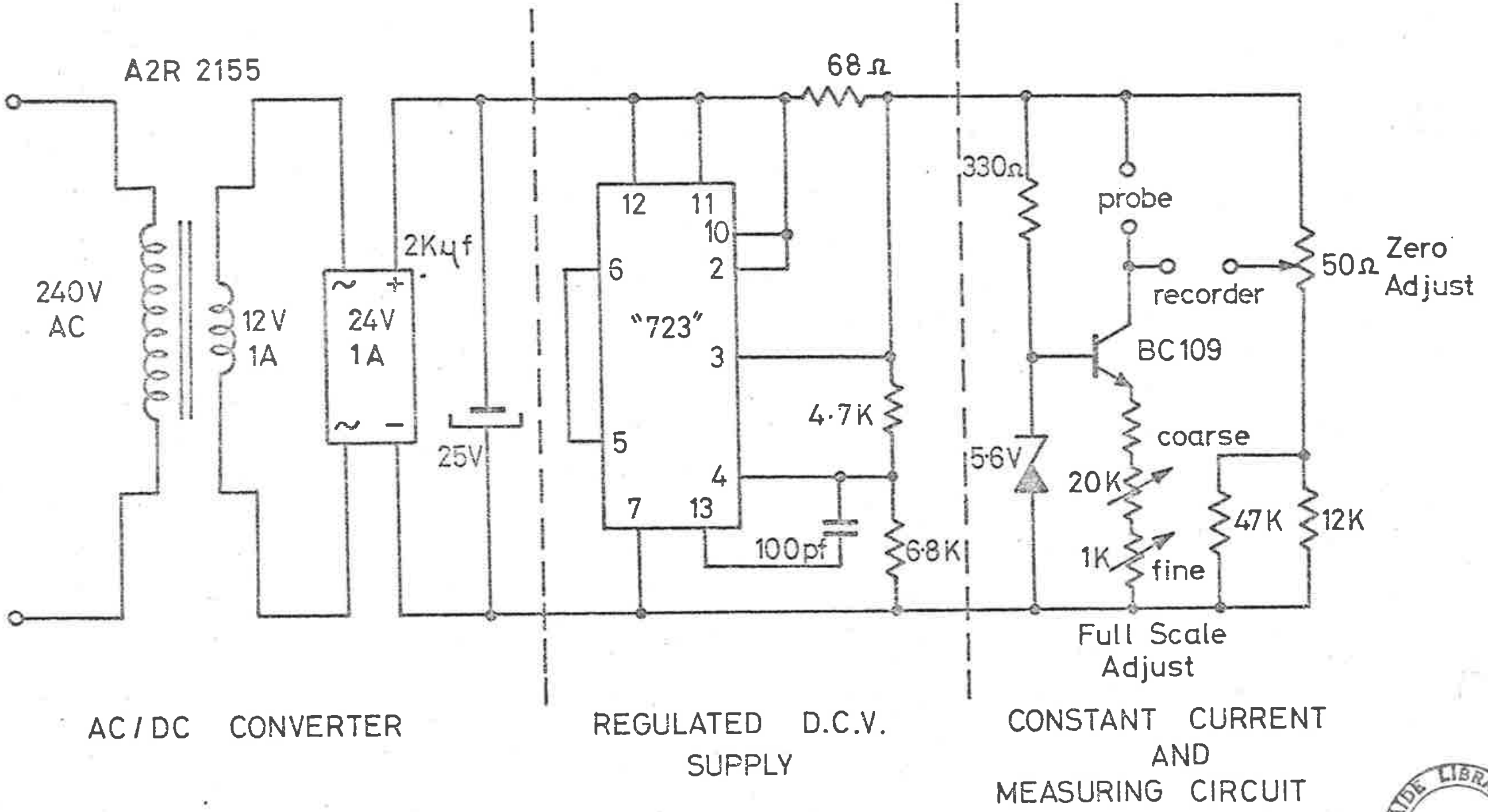


FIG. III.11

Contact with mercury or the atmosphere for any length of time destroyed the electrical surface, and so each nichrome wire was prepared immediately prior to use, and replaced after every five runs. A facsimile of a typical recorder output is shown in Fig. III.12. Calibration figures were necessary for each run because the diameter of each manometer varied and, as the cleaner removes some of the nichrome, the resistance/unit length depended on the length of time the cleaning gel was in contact with the nichrome.

The kinetic curve, as displayed, is actually a recording of ethane pressure against time. In order to become a true kinetic curve the pressure values have to be converted to mols of ethane released per litre of solution. This is simply done by assuming ethane is ideal and applying Boyle's Law.

$$PV = nRT$$

where p = pressure of ethane

V = Volume that gas occupies

R = gas constant

T = absolute temperature

n = number of mols.

The gas volume is subject to a correction to account for that part of the apparatus that is outside the oil bath, and hence is at a room temperature. Again, Boyle's Law was applied to obtain this correction.

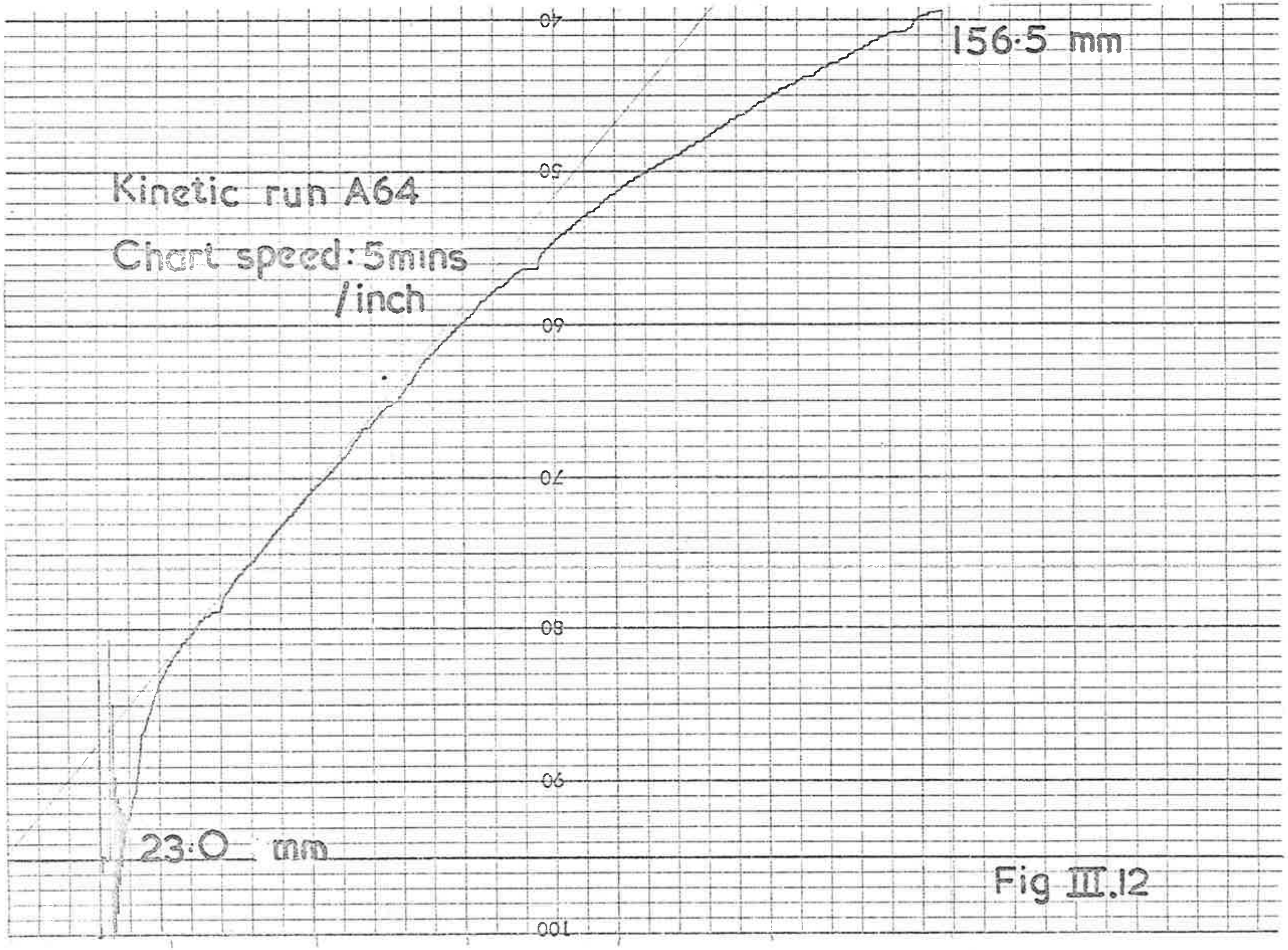

156·5 mm
Kinetic run A64
Chart speed: 5mins /inch
23·0 mm
40
50
60
70
80
90
100

Fig III.12

III.3.

3.3. P.m.r. Spectroscopy

The same limitations which applied to the recording of the spectra to determine the $AlEt_3:C_8H_6$ complex, also applied to the kinetic runs. Before any reaction has taken place, the p.m.r. spectrum of the reaction mixture was recorded (Fig. III.3) to check for impurities. Following the addition reaction can be achieved in two ways: monitoring the decrease in the peak area of the alkynyl proton or monitoring the increase in the peak area of the product vinyl protons. It was decided to use the latter, as, for a given conversion, the change in peak area will be double, due to the fact that there are two vinyl protons but only one alkynyl. Consequently, for the kinetic runs, the cyclohexane lock was offset 150 Hz upfield and a 250 Hz scan recorded. The integral of the aromatic protons served as the reference while the integral of the appearing vinyl proton resonances was recorded. A typical gradation of the spectrum with time is shown in Fig. III.13. Concentrations of each component at the beginning of the reaction were calculated from the set volumes used to make up the reaction mixture, so no preliminary integral scan to obtain initial concentrations was necessary. At any time during the reaction

$$[\text{vinyl product}]_t = [C_8H_6]_o \cdot \frac{\text{vinyl integral}}{\text{aromatic integral}} \cdot \frac{5}{2}$$

A typical kinetic curve obtained from p.m.r. spectra is shown in Fig. III.14.

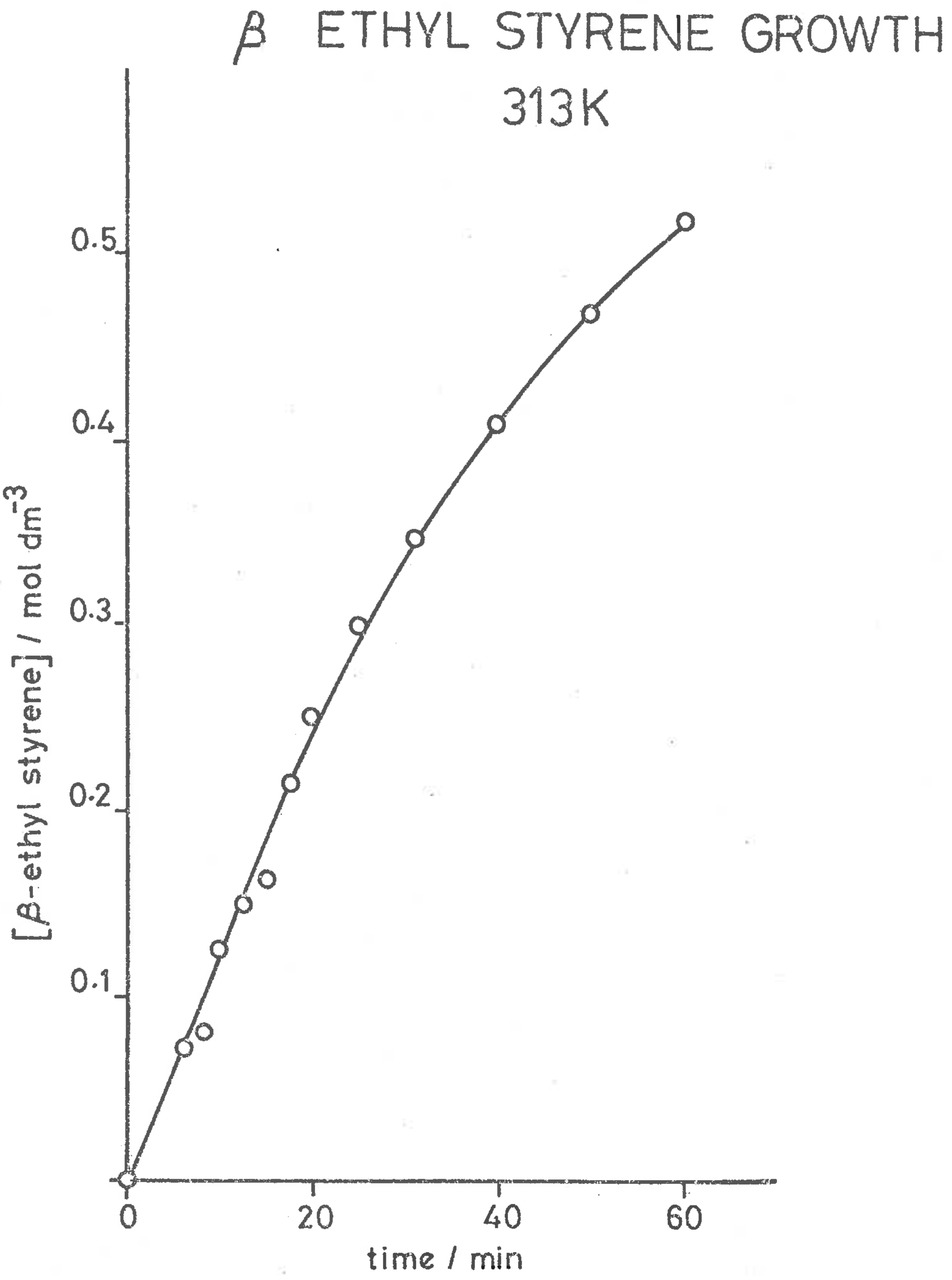

β ETHYL STYRENE GROWTH
313K
[β-ethyl styrene] / mol dm-3
0.5
0.4
0.3
0.2
0.1
0
20
40
60
time / min

FIG. III.14

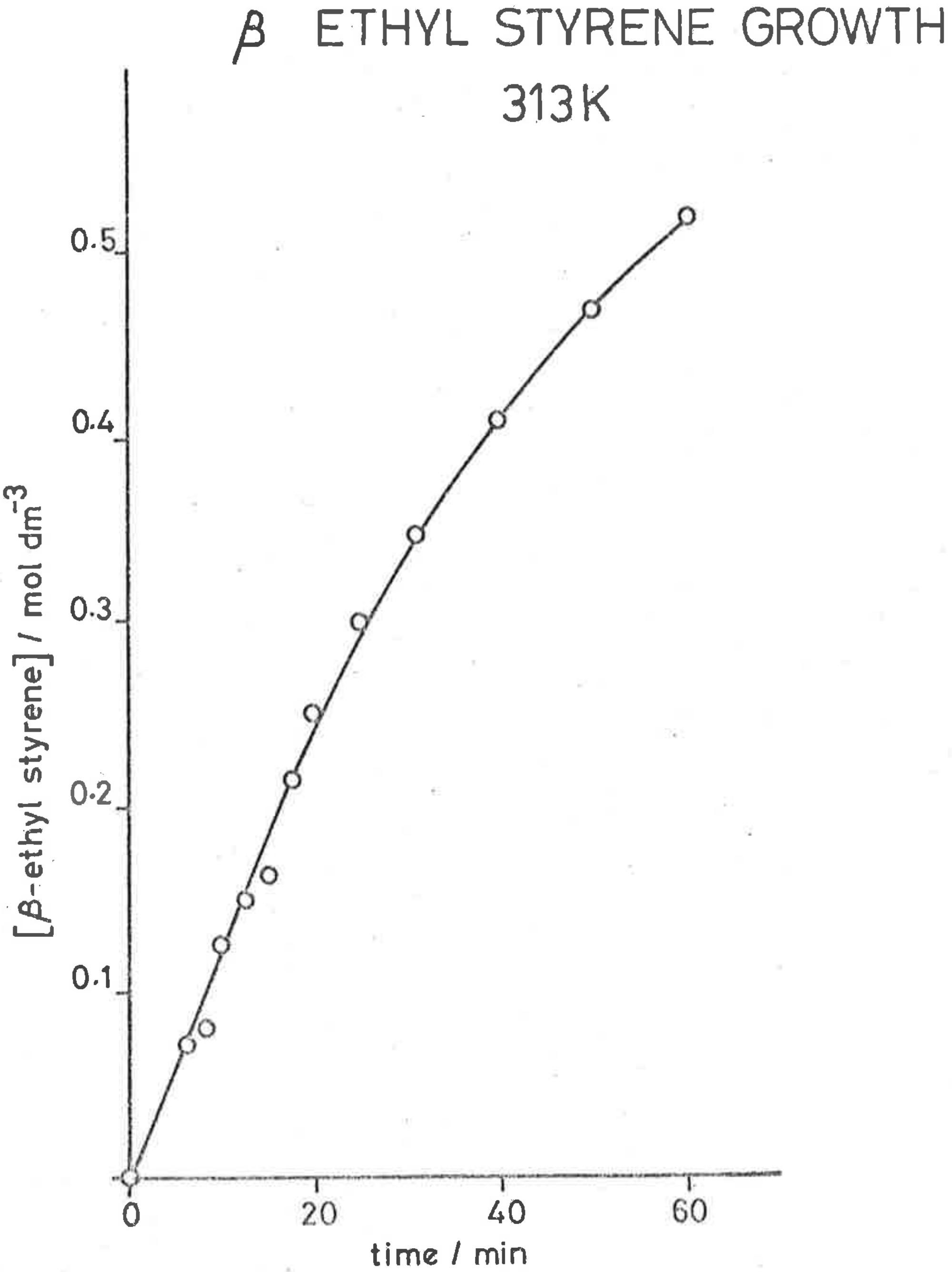

β ETHYL STYRENE GROWTH
313K
[β-ethyl styrene] / mol dm^{-3}
0·5
0·4
0·3
0·2
0·1
0
20
40
60
time / min

FIG. III. 14

III.4.

4. KINETIC RESULTS

4.1. External Orders of Reaction

Six kinetic determinations were performed, with triethylaluminium concentrations, ranging from 1.224M down to 0.229M, whilst the phenylacetylene concentration remained constant at 2.005M. The kinetic runs were determined at 313K.

Using the automatic recording manometer, the initial rates for the reaction, as determined by the release of ethane, were easily and accurately determined. With the p.m.r. kinetic runs, the inherent accuracy was not as great, but a very reasonable estimate of the initial rate was determined by increasing the number of data points at low conversion. External reaction orders with respect to total triethylaluminium species ($[Et_6Al_2] + \frac{1}{2}[AlEt_3{:}C_8H_6] + \frac{1}{2}[AlEt_3] = a$) at 313K obtained were

Metallation;

$$\log_{10} v^{o}_{EtH}/[C_8H_6]_o = 1.23 \pm (\text{s.e.})\ 0.09 \log_{10} a + C$$

Addition;

$$\log_{10} v^{o}_{vinyl}/[C_8H_6]_o = 0.75 \pm (\text{s.e.})\ 0.06 \log_{10} a + D$$

Log-log plots that gave these reaction orders are shown on Fig. III.15.

These non-integral orders of reaction, with respect to a indicate that only some of the molecular forms of the reagent are responsible for each reaction. Initial concentrations of each component of a were

ORDER WITH RESPECT TO TOTAL ALUMINIUM AT 313K

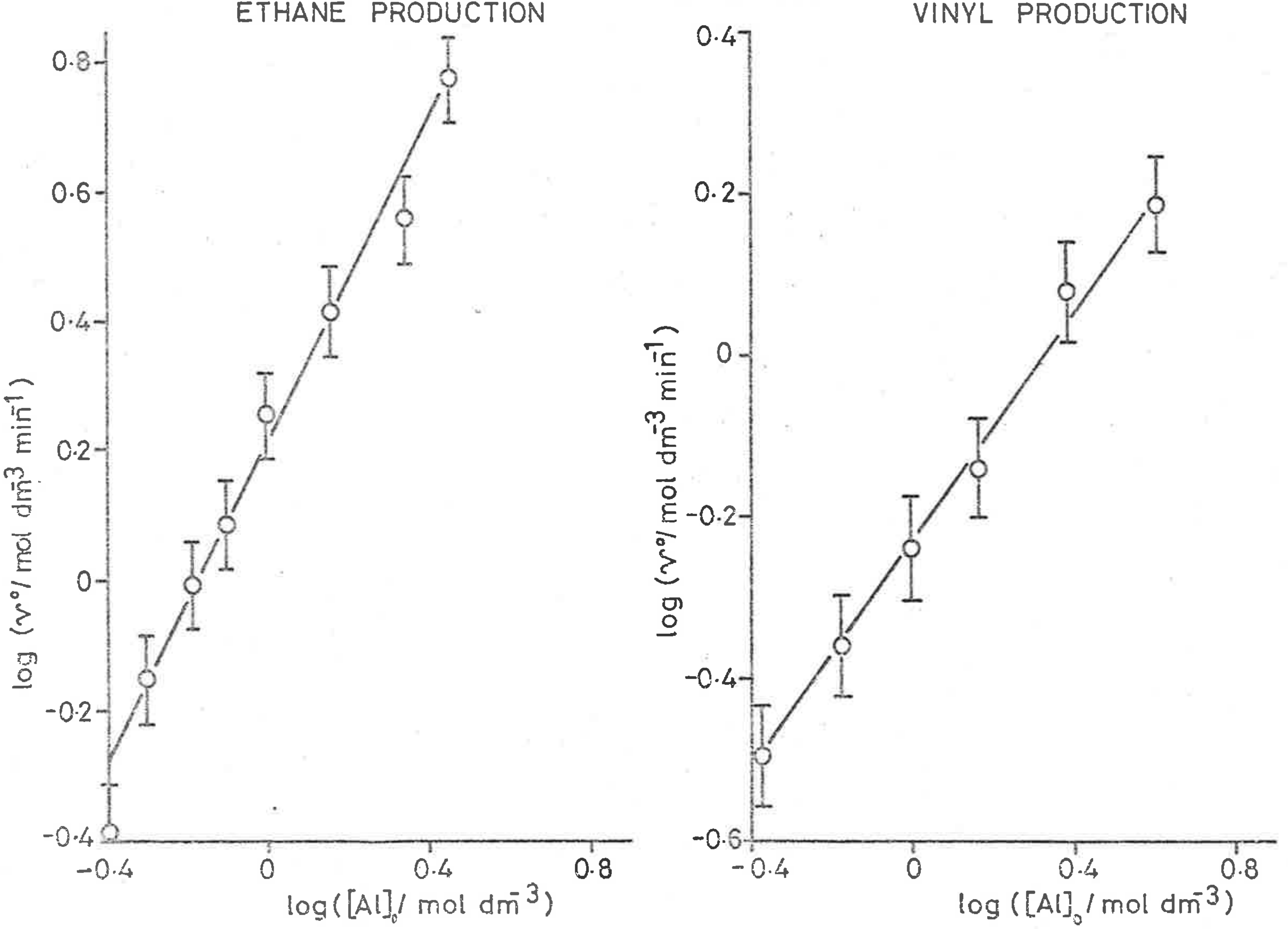


FIG. III. 15

III.4.

calculated using the Van't Hoff plot determined for the dimer-complex equilibrium (K_c), and the parameters of the triethylaluminium monomer-dimer equilibrium (K_d). These calculations show that at 313K all of the triethylaluminium can be regarded as existing either as dimer or complex; the monomer concentration being so small as to be insignificant.

The overall order with respect to a from ethane release suggests that the Al_2Et_6 dimer and phenylacetylene are reacting. A plot of $\log_{10} v^o_{EtH}/[C_8H_6]_o - [I]_o$ against $\log_{10} [Al_2Et_6]_o$ confirms this, as the plot has a slope of 1.1±0.2. This order is substantiated by the fact that a plot of $v^o_{EtH}/[C_8H_6]_o - [I]_o$ against $\log_{10} [Al_2Et_6]$ is a straight line passing through the origin with 90% confidence. Fig. III.16 shows both plots. Error bars indicate $\log (s.d.(v^o_{EtH}))$ and the hyperlola shows the 90% confidence limits of the least squares regression line of the data points (see Section II.2.3). They are not symmetrical about the straight line as the latter is weighted to pass through the origin. For the addition reaction, it seemed to us that an external order with respect to a of 0.75 indicates that a monomeric triethylaluminium species is reacting. This can of course mean either a reactive complex (I) or monomer. A plot of $\log v^o_{vinyl}/[C_8H_6]_o - [I]_o$ against $\log [Al_2Et_6]_o$ has a slope of 0.70±0.05 while a plot of $\log_{10} v^o_{vinyl}$ against $\log [I]_o$ has a slope of 0.9±0.1. A direct plot of the latter passed through the origin with 90% confidence (Fig. III.17).

ORDER WITH RESPECT TO Al_2Et_6 – ETHANE

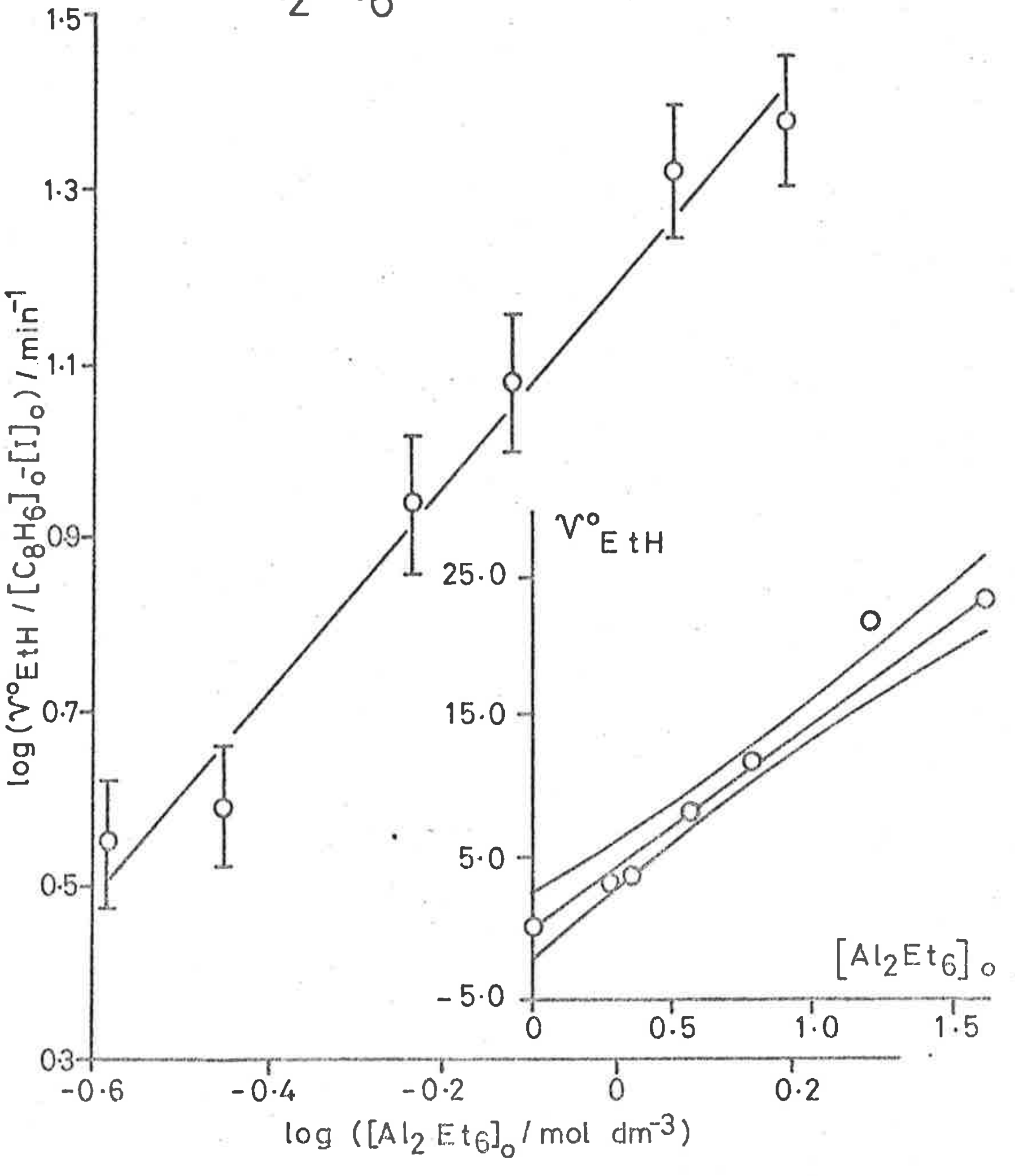


FIG. III.16

ORDER WITH RESPECT TO COMPLEX - VINYL

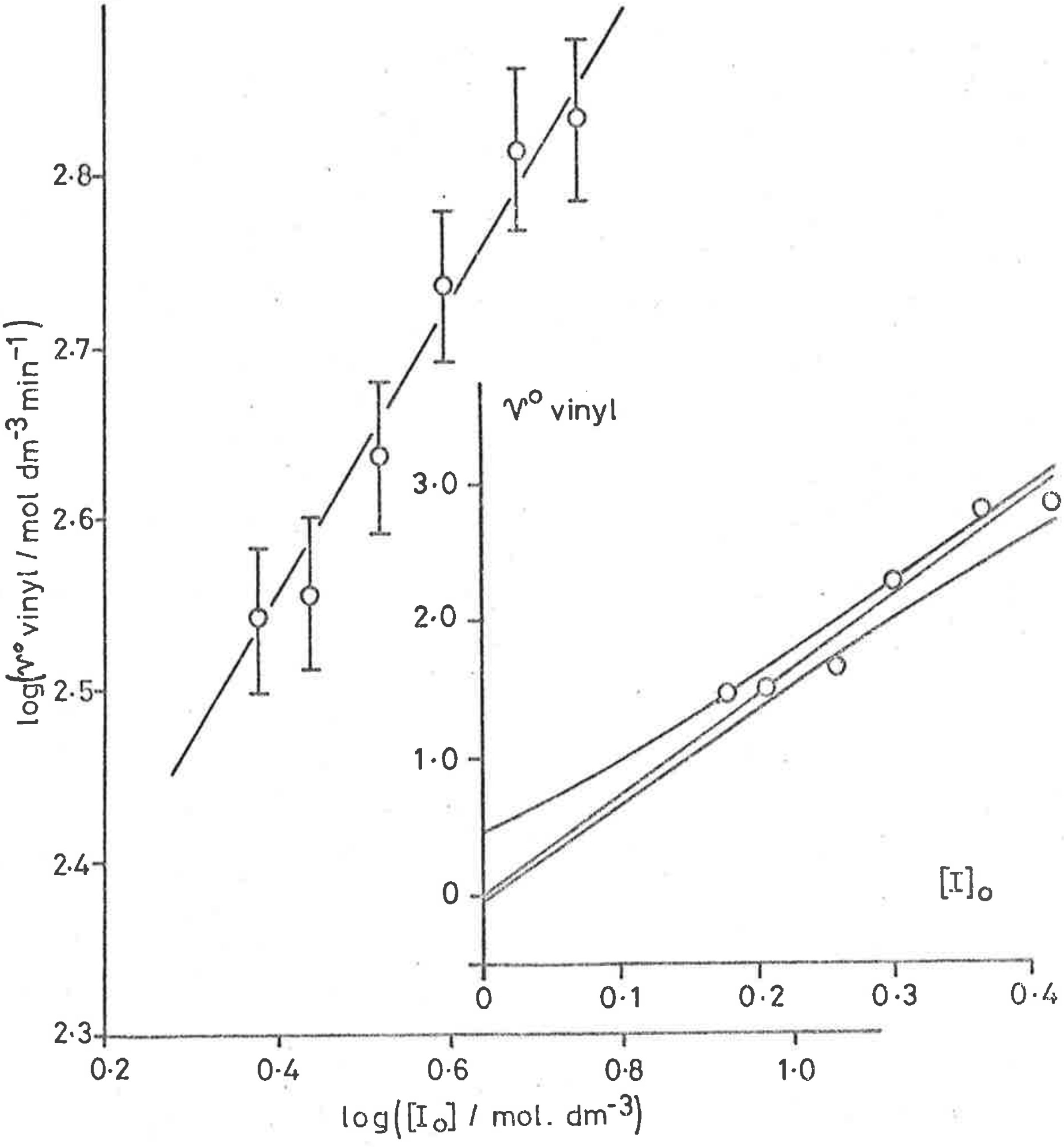


FIG. III. 17

III.4.

From this preliminary look at the kinetics using external reaction orders, it seems clear that the metallation occurs at the dimer and the addition reaction by way of complex [I], although addition involving free triethylaluminium monomer and phenylacetylene has not been ruled out. An assumption made throughout all of the above work was that the order with respect to excess phenylacetylene is unity, because, if the reaction consists of simple steps, it is difficult to imagine it being different. However, it was felt that in order to be conclusive, the unity order with respect to phenylacetylene should be demonstrated.

It was impossible to obtain an order with respect to excess phenylacetylene by varying its concentration, while keeping that of triethylaluminium constant, using the breakseals of reaction compounds available at the time of the determination, and so the following procedure was adopted. Initial rates from ethane release and vinyl appearance were determined with varying total triethylaluminium (a) and varying concentrations of excess phenylacetylene. It was found that plots of $\log_{10} v^{o}/[C_8H_6]_o$ against $\log_{10} a$ at 313K and 333K had identical slopes (within the standard error) to those determined previously. Unit order with respect to phenylacetylene is thus confirmed.

4.2. Kinetic Parameters

The postulated mechanism, stoichiometric and rate relationships are;

III.4.

$$\begin{array}{llclcccc}
 & \tfrac{1}{2}\mathrm{Al_2Et_6} & + & \mathrm{HC{\equiv}C{-}C_6H_5} & \xrightarrow{k_2} & \mathrm{Et_2Al{-}C{\equiv}C{-}C_6H_5} & + & \mathrm{EtH} \\
t=0 & a-c & & b-c & & 0 & & 0 \\
t=t & a-(c+z+x)/2 & & b-c-z-x-y & & x+y & & x \\
 & \uparrow\downarrow K_c & & & & & &
\end{array}$$

$$\begin{array}{llcl}
 & \mathrm{(I)} & \xrightarrow{k_1} & \mathrm{Et_2Al{-}C{=}CHEt} \\
t=0 & c & & \\
 & & & \downarrow \mathrm{HC{\equiv}C{-}C_6H_5} \\
t=t & c+z-y & &
\end{array}$$

$$\begin{array}{lccc}
 & \mathrm{Et_2Al{-}C{\equiv}C{-}C_6H_5} & + & \mathrm{C_6H_5CH{=}CHEt} \\
t=0 & 0 & & 0 \\
t=t & y+x & & y
\end{array}$$

$$K_c = \frac{(c+z-y)}{(a-\tfrac{1}{2}c-\tfrac{1}{2}z-\tfrac{1}{2}x)^{\frac{1}{2}}\ (b-c-z-y-x)} \qquad \ldots.(9)$$

$$v_{\mathrm{EtH}} = \frac{dx}{dt} = k_2(a-\tfrac{1}{2}c-\tfrac{1}{2}z-\tfrac{1}{2}x)\ (b-c-z-x-y) \qquad \ldots.(10)$$

$$v_{\mathrm{vinyl}} = \frac{dy}{dt} = k_1(c+z-y) \qquad \ldots.(11)$$

As with the alkenes, equation (9) has no closed form solution of the form $z = f(x,y)$ but as both x and y are functions of t, z must be.

III.4.

The equilibrium equation was solved for z for every x, y experimental determination, and the z values so determined were fitted to a sixth degree polynomial in t, to give $z=f'(t)$. A sixth degree polynomial was found to be the simplest capable of describing the experimental variation of z with time accurately. The rate equation (11), now in the form

$$dy/dt = k_1\ (c+f'(t)-y) \qquad \ldots.(12)$$

was programmed into a non-linear least squares package which had incorporated in it a Runge-Kutta numerical integration programme.[14] The non-linear least squares package fitted a line to the experimental y data, using k_1 as the only adjustable parameter (Appendix III).

A similar procedure was followed in determining values of k_2, but here an added complication is the presence of another independent variable, y. This was fitted to a sixth degree polynomial in t to give $y=f''(t)$, and the rate equation thus becomes

$$dx/dt = k_2[a-c/2-f'(t)/2-x/2]\ [b-c-f''(t)-x-f'(t)] \qquad \ldots.(13)$$

Numerical integration and non-linear least squares fitting then followed.

From the above procedure it can be appreciated that the errors involved in determining rate co-efficients by this method must be greater than those derived by the normal method of exact integrals.

III.4.

An alternative procedure to obtain the rate co-efficients is to fit the first derivatives of the kinetic curve dy/dt, dx/dt to the actual rate equations. However, dy/dt and dx/dt vary over a much smaller range than y or x and consequently would be subject to much larger fitting errors.

Identical concentrations to those used in the external order determination were used in the kinetic runs to find the rate co-efficients at five temperatures between 313K and 333K. The calculated rate co-efficients k_1, k_2 are displayed in Table III.3.

TABLE III.3.

Rate Co-Efficients for $Et_3Al + C_8H_6$

		$k/M^{-1}\ min^{-1}$(a) or min^{-1}(b)$\times 10^3$				
	Temp/K	313	318	323	328	333
Total Al_2	1.224	6.173	18.40	27.59	26.27	44.13
/M	.918	6.766	13.87	19.92	22.59	25.18
	.612	5.610	14.14	14.62	19.77	24.38
a) k_2	.459	5.301	7.07	9.08	16.96	23.23
	.306	4.100	8.80	15.89	25.97	
	.229	5.917	10.99			21.50
Ave.		5.7_6	12.2_1	17.4_2	21.0_3	27.8_8
	1.224	3.791	11.93		49.72	23.7
	.918	4.232	10.41	12.08	43.05	24.4
	.612	3.937	7.94	13.95	39.84	30.5
b) k_1	.459	3.265	8.65	11.45	43.23	30.4
	.306	3.524	7.42	13.92	29.23	
	.229	4.213	11.51	9.19	25.76	28.3
Ave.		3.8_3	9.6_3	12.1_2	$38._5$	$28._5$

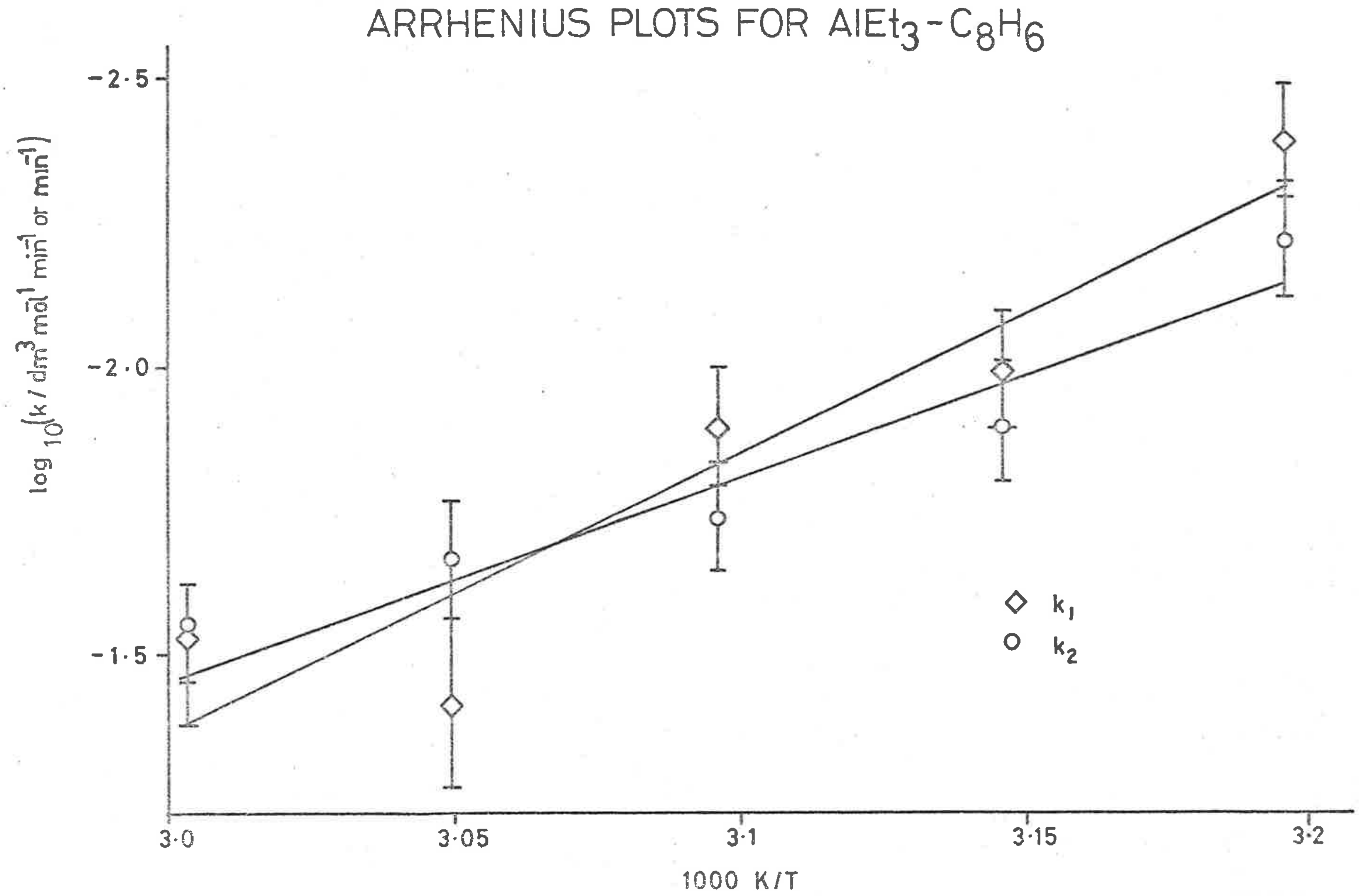

ARRHENIUS PLOTS FOR $AlEt_3-C_8H_6$
$\log_{10}(k / dm^3 mol^{-1} min^{-1}$ or $min^{-1})$
-2·5
-2·0
-1·5
3·0
3·05
3·1
3·15
3·2
1000 K/T
◇ k_1
○ k_2

FIG. III. 18

III.4.

Arrhenius plots for both k_1 and k_2 are shown in Fig. III.18. Error bars indicate log (s.d. (k)). Calculated parameters are

$$\begin{array}{lll}
\text{Metallation } (k_2) & E = 64\pm2.9 \text{ kJ mol}^{-1} \\
 & A = 10^{6.8\pm1.5(\text{s.e.})}\text{dm}^3 \text{ mol}^{-1}\text{s}^{-1} \\
 & \\
\text{Addition } (k_1) & E = 94\pm2.5 \text{ kJ mol}^{-1} \\
 & A = 10^{11.6\pm0.9(\text{s.e.})}\text{s}^{-1}
\end{array}$$

The errors in the kinetic data arise from the multiple fitting procedures used. However, they are probably exceeded by the uncertainties in the equilibrium parameters which are of instrumental origin.

From the external order of reaction with respect to total triethylaluminium as determined by vinyl appearance, it is possible that the addition reaction proceeds through the AlEt$_3$ monomer.

$$\begin{array}{lccccc}
 & \tfrac{1}{2}\text{Al}_2\text{Et}_6 & + & \text{HC}\equiv\text{C-C}_6\text{H}_5 & \overset{K_c}{\rightleftarrows} & \text{I} \\
t = 0 & a-c/2 & & b-c & & c \\
t = t & a-c/2-z/2-x/2-y/2 & & b-c-z-x-2y & & c+z \\
 & \uparrow\downarrow K_d^{\frac{1}{2}} & & & & \\
 & \text{AlEt}_3 & + & \text{HC}\equiv\text{C-C}_6\text{H}_5 & \xrightarrow{k_1} & \text{vinyl products} \\
t = 0 & m & & b-c & & 0 \\
t = t & m & & b-c-z-x-2y & & y
\end{array}$$

where x is again the amount lost to metallation.

III.4.

The equilibrium concentration of triethylaluminium monomer, m is so small that it may be assumed to remain constant throughout the reaction. As before, the equilibrium relationship links x, y and z.

$$K_c = \frac{(c+z)}{(a-\frac{1}{2}c-\frac{1}{2}z-\frac{1}{2}x-\frac{1}{2}y)^{\frac{1}{2}}\ (b-c-z-x-2y)} \qquad ....(14)$$

and

$$v_{\text{vinyl}} = \frac{dy}{dt} = k_1'm\ (b-c-z-x-2y) \qquad ....(15)$$

Using the predetermined polynomial $z=f(t)$ and fitting x to a sixth degree polynomial in t, $x=f'''(t)$ yields the rate equation

$$\frac{dy}{dt} = k_1'm\ [b-c-f(t)-f'''(t)-2y] \qquad ....(16)$$

Since $K_d = m^2/(a-c/2)$, the rate equation now becomes

$$\frac{dy}{dt} = k_1'\ K_d^{\frac{1}{2}}\ [a-c/2]^{\frac{1}{2}}\ \ [b-c-f(t)-f'''(t)-2y] \qquad ....(17)$$

This was then programmed to obtain k_1', using numerical integration and non-linear least squares regression as outlined above. Table III.4 shows the resulting rate co-efficients calculated using Smith's[15] value of K_d.

III.4.

TABLE III.4.

Rate Co-efficients for $AlEt_3 + C_8H_6$ Addition via Monomer

		$k_1'/M^{-1}s^{-1}$				
	Temp/K	313	318	323	328	333
Total Al_2 /M	1.224	.083	.154		.654	.233
	.918	.092	.135	.175	.558	.249
	.612	.086	.103	.206	.510	.317
	.459	.072	.113	.165	.558	.358
	.306	.078	.098	.135	.363	
	.229		.156		.316	
	Ave.	.082	.126	.177	.489	.289

Values of k_1' extracted obviously depend on the value of K_d taken. When the preferred values of Smith are used, the Arrhenius parameters for k_1' are

$$A_1' = 10^{9.5\pm2}\ \mathrm{dm^3\ mol^{-1}s^{-1}}$$

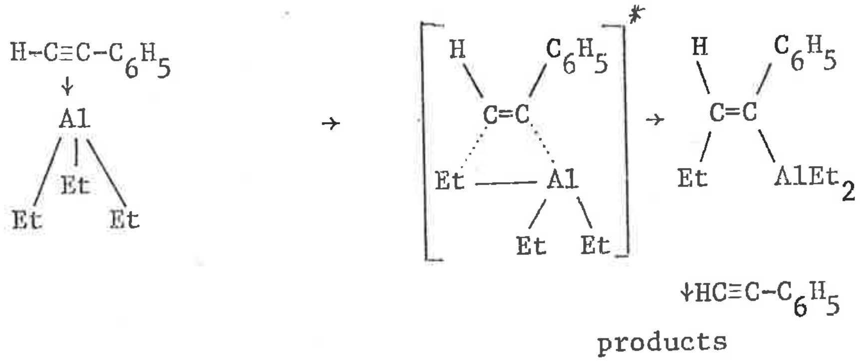
$$E_1' = 80\pm3\ \mathrm{kJ\ mol^{-1}}$$

If other values are used,[16] the *A* factor decreases by an order of magnitude and the enthalpy of activation decreases by approximately 10 kJ mol^{-1}.

5. DISCUSSION OF MECHANISM

Metallation is a second order reaction between dimeric triethylaluminium and phenylacetylene. The *A* factor lies within the range to be expected for a simple bimolecular liquid phase reaction. Observed orders of reaction exclude the possibility of a significant contribution from the complexed monomer (I) while the equilibrium concentration of uncomplexed monomer ($AlEt_3$) is too small for any contribution to be detected.

The addition reaction probably proceeds by way of the intermediate complex (I) with the rate controlling step being the unimolecular rearrangement of I. By analogy with alkenes, it is suggested that a four-centre trapezoidal transition state is involved.



....(18)

This is the obvious conclusion from both the structure of the complex and the dependence of the rate on its concentration. Apart from the external orders indicating that the addition reaction does not proceed from a bimolecular reaction between monomeric $AlEt_3$ and phenylacetylenes, the *A* factor calculated for this mechanism appears to be too high to account for the loss of transitional and rotational degrees of freedom in forming the four-centre transition state directly from monomer and alkyne.

The *A* factor calculated for the rate determining steps of equation (18) is consistent with the postulated mechanism. The entropy of activation is -23 J mol^{-1}. This is accounted for on the same basis as the alkenes, namely the loss bond rotational entropies on going through the rate determining step. In this case, however, the π complex is much stronger than for alkenes, and is presumably tighter. Models show that, as it is in the same plane as the π bond, the phenyl group hinders the rotation of the Al-Et bond and the Al-alkyne bond, and so that on going to the transition state, only some of the rotation terms are lost. This is partially compensated by the freeing of the hindered $\equiv C-C_6H_5$ entity as the hybridization changes from *sp* to *sp*^{2}. Thus the main contributions to ΔS arise from partial interruptions to minor complex rotational and vibrational modes.

In order to compare the alkene and the alkyne π complexes absolutely, it is necessary to assume that the entropies of the four-centre transition states in both the alkene and alkyne additions are identical. This is certainly not the case. Nevertheless they should be similar, and in this light it is difficult to see how the entropy difference between the alkyne and alkene π complexes can contribute as much as 10^4 to the *A* factor. As previously mentioned, the effect of solvent on transition states is little known and thus any detailed explanation must wait until all the solvent factors are understood.

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SECTION IV

REACTION OF TRIETHYLALUMINIUM AMINE COMPLEXES WITH ALKYNES

Synopsis

Trialkylaluminium-donor complexes - These complexes have important effects on rate and stereospecificity of Ziegler-Natta catalysts. Many complexes have been studied. The stability of each complex depends on electronic and steric effects. These are discussed.

Reaction of Triethylaluminium complexes with Unsaturated Hydrocarbons - Rate retardation of the addition reaction is due to donor molecule occupying the acceptor site on the aluminium. Reactions studied to date show that the donor complex is unreactive. Metallation of alkynes is the only reaction where donor complexes are known to be the reactive species.

Reaction of Triethylaluminium-trialkylamine complexes with Phenylacetylene - Preliminary results show that not only the $AlEt_3.NR_3$ species is present. P.m.r. studies on $AlEt_3.NR_3$ dimers and $AlEt_3NR_3C_8H_6$ complexes are inconclusive, but indicate the latter to be possible. Ebulliometric results show that no $AlEt_3NR_3$ dimeric species are predominant. The kinetics of the metallation reaction are determined using manometry, and the rate parameters calculated by assuming two simultaneous reactions - one involving a $AlEt_3NR_3$ bimolecular reaction and one involving a ternary complex. Arrhenius parameters are also calculated and different mechanisms are proposed to account for the large difference in *A* factors observed between the triethylamine and tri-n-butylamine complex with triethylaluminium.

IV.1.

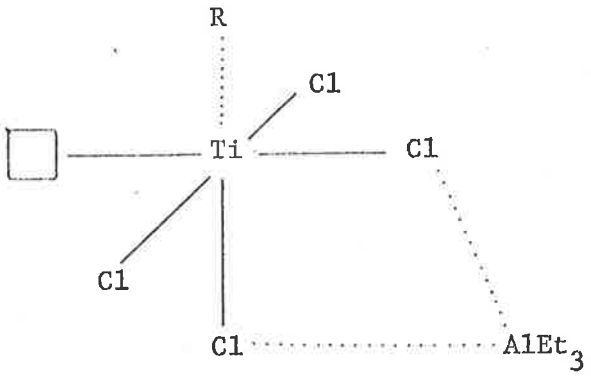
1. TRIALKYLALUMINIUM DONOR COMPLEXES

An important property of all the trialkyl derivatives of the elements of Groups I, II and III is their ability to form donor complexes. Of the elements of Group IIIb, the trialkylaluminiums show the greatest tendency to complex formation, mainly forming four co-ordinate complexes where the aluminium has a stable octet of electrons. Five co-ordinate complexes of trialkylaluminiums are also known,[1] but the only six co-ordinate aluminium compounds are ones with very electronegative ligands: e.g. AlF_6^{3-}, $Al(H_2O)_6$. Trialkylaluminiums are known to form stable, distillable complexes with ethers,[2-6] thioethers[2,7,8] amines,[2,6] phosphines,[2,6,7,9] phosphine oxides,[10,11] nitriles[12,13] and sulphoxides,[14] amine oxides,[11] phosphites[9] and trifluorosilanes.[15] It has also been shown in this treatise that less stable complexes are formed between trialkylaluminiums and aromatic and alkynyl compounds.

To understand the underlying principles of complex formation and stability to reactive substrates is especially important in the case of trialkylaluminiums, as they (the complexes) are often used to form Ziegler and Ziegler-Natta catalysts for industrial polymerization. Even if a co-ordinating complex is not part of the reaction mixture, often the trialkylaluminium appears to end up in a complexed state. For example, in a typical Ziegler-Natta catalysts, triethylaluminium and a titanium chloride are combined. The most generally accepted mechanism, that of Cossee,[16] proposes that polymerization takes place at a vacant site on the titanium atom. The aluminium compound, while not taking any

IV.1.

direct part in the polymerization, must assist it by either complexing, or acting as a reducing agent, as the polymerization rate is very much faster in a Ziegler-Natta catalyst than with titanium chloride alone.



The exact nature of this complexing and its role in the polymerization is, at present, conjectural.

Most other postulated mechanisms[17] for Ziegler-Natta catalysis involve complexed aluminium in one form or another, and this premise is substantiated partly by the observation that strongly solvating solvents such as tetrahydrofuran and trimethylamines have quite marked effects on rate and form of polymerization in several systems.[18-21] Any interpretation of increased rate in donor solvents must be based on an increase in the number of active sites on the catalyst, because neither the Al-C bond nor the Ti-C bond is polar enough for donor solvents to aid the formation of ion pairs to any degree.

IV.1.

An explanation in terms of the Cossee mechanism is that complexing facilitates the regeneration of triethylaluminium after site formation:

$$\text{site-Cl} + AlEt_3 \rightarrow \text{site-Et} + Et_2AlCl$$
$$Et_2AlCl \rightleftarrows \tfrac{1}{3}AlCl_3 + \tfrac{2}{3}AlEt_3$$

Donor complexes of $AlCl_3$ are stronger than those of Et_2AlCl, thus driving the second reaction to the right. Therefore more $AlEt_3$ is regenerated, with the consequent increase in the number of new sites that can be formed because $AlEt_3$ is a better alkylating agent than Et_2AlCl towards titanium chloride, and hence the observed reaction rate is faster. The change in stereospecificity that is observed when donor solvents are added to certain polymerization catalysts cannot, however, be rationalized in these simple terms. Many other assumptions concerning the role of the donor solvent in forming the active site need to be made in order to account for the observed changes.

The aluminiumtriethyl-diethylether complex was first recognized in 1923[22] but its reactions were not studied until 1953.[4] In 1955, the first quantitative work was reported when stoichiometry and heats of formation of several $Et_3Al \leftarrow$ Donor complexes were determined by a calorimetric technique:[23] most complexes were found to be of a 1:1 stoichiometry. Brownstein *et al*[24] first studied the p.m.r. of the $Et_3Al \leftarrow OEt_2$ complex, correctly interpreting their data in terms of the reduced electronegativity of the aluminium. This work was followed up by Hatada and Tuki[25] and Takashi[26] who looked at p.m.r. spectra of triethylaluminium with a variety of donors. On the basis of their work, the latter established a "basicity constant" for each donor which appeared to reflect the proton basicity, but which, in fact, contains contributions from other effects as well (see later).

Al^{27} n.m.r. of $Et_3Al \leftarrow$Donor complexes has been reported[28,31] and these studies show the existence of the other main spectroscopic parameter that indicates complexation, the nuclear quadrupole coupling constant. An excellent review is available covering all Al^{27} n.m.r. work on trialkylaluminiums and their complexes.[27]

Lehmkuhl and Kobs[29] have studied the disproportionation of several complexes by conductometric techniques and recently Smith[30] has completed a characterization of the equilibrium of the system $AlEt_3$/mesitylene (see Section II.2). This is the first quantitative work reported for a complex involving a trialkylaluminium and an aromatic π system. P.m.r. spectra of the phosphine complexes of trialkylaluminiums have also been studied.[32]

All of the above work reported on the structure of $AlEt_3 \leftarrow$Donor complexes is consistent with a stoichiometry of one acceptor atom per donor atom, and the existence of a definite donor-acceptor bond. During the last few years, this has been shown to be indeed the case by x-ray and electron diffraction studies. Thus Whitt reported that the crystal structure of the trimethylaluminium-quinuclidine complex has a stoichiometry and an Al-N bond length of 2.06 Å.[33] The structure of the

$Me_3Al \leftarrow$dioxan complex has been shown to be 2:1, and has an Al-O bond length of 2.02 Å.[34] In both of these, and other reported cases of tetraco-ordinate triethylaluminium, such as the normal dimer, the bond angles of the atoms attached to aluminium have been found to be a slightly distorted tetrahedron.

The stability of each donor complex with trialkylaluminiums depends on both donor and Al alkyl group. Most, if not all of the factors which determine this stability can be divided into electronic and steric effects.

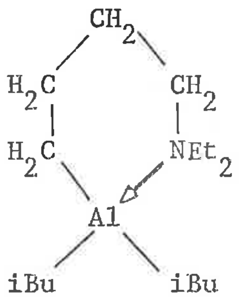
As is to be expected, the single most important property deciding the stability of the complex is the availability of the electron pair from the donor atom, as exemplified in the proton basicity. This is shown by the fact that, even though $Me_3Al \leftarrow NMe_3$ and $Me_3Al \leftarrow PMe_3$ are not dissociated to any great extent in the vapour phase, the equilibrium

$$Me_3Al \leftarrow PMe_3 + Me_3N \rightleftarrows Me_3Al \leftarrow NMe_3 + PMe_3$$

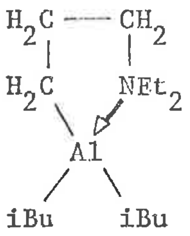
lies wholly on the right.[35, 8] This dissociation equilibrium has been studied with several donors. The stability of trimethylaluminium complexes declines in the sequence $NMe_3 > PMe_3 > OMe_2 > SMe_2 > SeMe_2 > TeMe_2$.

Steric effects are also very important. Tetrahydrofuran is a better complexing agent than diethylether[23] and, as the inductive effects are about the same, the difference is usually explained in terms of the greater steric hindrance of diethylether. Brown distinguished two types of hindrances that occur during co-ordination, which he called *B* and *F* strains.[36] *B* strain is the strain arising from a branching substituent close to the donor atom, while *F* strain is hindrance by interaction of two solvent molecules on the same acceptor atom. In a 1:1 complex, the usual case with trialkylaluminiums, only the former applies. An example of this *B* strain is shown by the fact that the heat of formation of the trimethylaluminium complex of trimethylamine is about 12.5 kJ mol^{-1} less(more negative) than that of the trimethylaluminium-triethylamine complex.[6] In general, however, steric strain is not nearly as marked as in trialkylboron adducts[37] owing to the larger co-valent radius of aluminium, and seems to be more marked for the triarylaluminiums than for the trialkylaluminiums.[38]

A second steric factor influencing complex stability, apparent in multidentate ligands, is that the formation of five and six membered rings tend to enhance stability. For example, the chelates I and II are stable up to 513K[39]



I



II

while regular iBu$_3$Al←NR$_3$ complexes breakdown well below this temperature.

IV.1.

Other than proton basicity, the major electronic effect influencing stability is the inductive effect of substituents adjacent to the donor and acceptor atoms. The feeble donor properties of diphenylether can be attributed to the interaction of the shared electron pair of the oxygen with the π electrons of the phenyl group. Conversely, aryl ligands on the metal should facilitate stronger complexes with donor solvents than aliphatic ones, although this is not always the case.

Considering solely inductive effects, the replacement of hydrogen by methyl adjacent to the donor atom should aid complexing. However, the heats of formation of $Me_3Al{\leftarrow}OMe_2$ and $Me_3Al{\leftarrow}OEt_2$ are-79.5 and-46 kJ mol^{-1} respectively.[40] The discrepancy is due to the steric effects being dominant over inductive effects. This is further confirmed by the fact that dimethoxyethane is preferred as a complexing solvent to diethoxyethane.

Another electronic factor that needs to be mentioned is the reorganizational energy. On complexing, the shape of the AlR_3 molecule changes from planar to basically tetrahedral. In the planar form the aluminium atom may be regarded as sp^2 hybridized with the unbonded p orbital contributing some π nature to the three Al-R bonds. Complexation removes this, and thus the reactivity of the Al-R bond is enhanced, but the effect is slight. This change may also occur in the donor atom, but is unusual since it is not likely that the donor molecule will undergo a major conformational change on complexation, although some restriction may be made on bulky groups.

IV.2.

2. REACTION OF TRIETHYLALUMINIUM COMPLEXES WITH UNSATURATED HYDROCARBONS

Apart from the observation that co-ordinating solvents alter the rate of polymerization of several Ziegler-Natta catalyst systems, little has been reported in the field of reactions of donor complexes of triethylaluminium. In 1963, Allison[41] studied the system triethylaluminium/tetrahydrofuran (THF)/hex-1-ene by product analysis using gas chromatography. He observed addition, but at a reduced rate compared to similar concentrations of reactants in the absence of THF. Allison admits, however, that the results may be in error due to the difficulty he had in obtaining a 1:1 mol ratio of $AlEt_3$/THF, and the inherent inaccuracies incorporated in using gas chromatography as a kinetic tool, especially at low conversions. Byers looked at the system triethylaluminium/p-dioxan/oct-1-ene by p.m.r. spectroscopy but could find no evidence to indicate reaction.[42] If Allison's results are correct, this is unexpected because THF co-ordinates more strongly to triethylaluminium than p-dioxan.[23]

The suppression or retardation of addition in co-ordinating solvents can be explained as being due to the donor molecule occupying the acceptor site on the aluminium atom and thus this site is not available to form a π complex with either an alkene or an alkyne. We recently found that, even with a weak co-ordinand such as diphenylether, the complex is completely unreactive towards oct-1-ene and that in the triethylaluminium/diphenylether/oct-1-ene system, reaction proceeds from the small concentration of uncomplexed monomeric $AlEt_3$ in equilibrium with the complexed species. This was conclusively shown from integrated rate plots and the fact that the specific rate constants for addition were the same in both ether and hydrocarbon solutions.[43]

In the case of alk-1-ynes, a similar situation towards addition probably exists. For metallation, however, differences are apparent. Triethylaluminium etherates do not react with alk-1-ynes to metallate the alkyne and release ethane to any measurable extent, even at 423K.[44] However, triethylaluminium-trialkylamine complexes react quantitatively with alk-1-ynes at 373K-393K to release ethane and give the diethylalkynylaluminium-trialkylamine complex.[44] This latter is the only reaction where a triethylaluminium donor complex is known to be reacting, because the equilibrium constant for the formation of the complex is very high, and therefore any contribution from uncomplexed triethylaluminium monomer must be minimal.

In trying to evaluate how complexing affects the mode of reaction of Ziegler-Natta catalysts, it seemed to us that the kinetic parameters of the only reaction where a donor complex of triethylaluminium is known to react could help. Such a study should reveal something about the nature of the aluminium-donor bond which may be used in the interpretation of polymerization data.

As mentioned in IV.1, two of the major factors affecting the nature of the donor-aluminium bond are the proton basicity of the donor atom (in this case nitrogen) and the steric hindrance of the substituents of the donor atom. It is difficult to evaluate the former while keeping the latter constant, as those substituents which affect the basicity of nitrogen also have a profound steric effect (e.g. phenyl). Chlorine or oxygen substituted phenyls cannot be used as the substituent is liable to react with triethylaluminium.

Gauging the effect of steric hindrance on the metallation reaction is a much easier task as the homologous series of trialkylamines have essentially the same proton basicity. It was thus decided to concentrate on trying to evaluate the kinetic parameters of the reaction between phenylacetylene and two triethylaluminium-trialkylamine complexes. Triethylamine and tri-n-butylamine have identical pK_a values[45] and are easy compounds to obtain and handle; consequently they were the amines used.

3. EXPERIMENTAL

3.1. Purification of materials

(a) *Triethylaluminium and phenylacetylene.*

These reagents were purified and dispensed as previously described.

(b) *Triethylamine, tri-n-butylamine.* (A.R. grade, Pfaltz and Baur, Flushing, N.Y., U.S.A.)

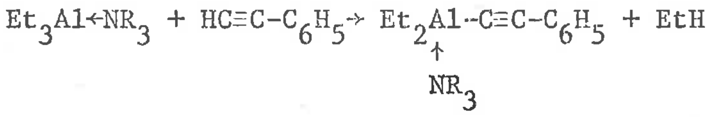
These compounds were dried over calcium hydride for 24 hours, degassed and then vacuum distilled into 50 ml. breakseals. The large breakseals were broken down into smaller, calibrated ones, or vacuum burettes as previously described.

(c) *Decalin.* (A.R. grade, Unilab., N.S.W. Aust.).

This solvent was purified by the same process as the amines except for a minor alteration. Substantial frothing occurred when vacuum distillation of the solvent off calcium hydride was attempted, due to the suspension of solid particles in the fairly viscous liquid. Therefore, the solvent was decanted off calcium hydride before degassing and subsequent vacuum distillation.

3.2. Kinetic measurements

The reaction to be followed is



$$Et_3Al\leftarrow NR_3 + HC\equiv C-C_6H_5 \rightarrow Et_2\underset{\substack{\uparrow\\ NR_3}}{Al}-C\equiv C-C_6H_5 + EtH$$

Since this is analogous to the metallation in the absence of amine the kinetics of the system were followed in a similar manner.

The manometric apparatus used to follow the release of ethane is that shown in Fig. III.7, without the mass spectrometry gas filler. Reactants were introduced into this apparatus in a similar fashion to that already described (Section III.3), the main differences being the presence of an extra breakseal containing the amine and the substitution of decalin for cyclohexane. This substitution was necessary since it was found that metallation by the $Et_3Al \leftarrow$amine complexes was much slower than metallation by Al_2Et_6 alone, and therefore kinetic runs had to be made at higher temperatures than previously. At increased temperature it was found that cyclohexane tended to distill over into the manometer , necessitating the change to a higher boiling solvent. It was also found necessary to allow for the fact that at these increased temperatures the vapour pressure of phenylacetylene becomes appreciable.

In order to provide correlation between the metallation reaction arising from both triethylaluminium and its amine complex, it is necessary to change to a solvent with essentially the same associative and solvating properties as cyclohexane. These properties are reflected in the solubility parameter of the solvent. This is a thermodynamic quantity defined as the square root the "internal pressure" or cohesive energy density of the solvent, which is, in turn, defined as the energy of vapourization/ml.

$$S = (\Delta E/V)^{\frac{1}{2}}$$

ΔE is easily calculable from the Clausius-Clapeyron equation and the first law of thermodynamics.

It seemed likely that a similar, but larger molecule than cyclohexane would be suitable. Such a compound is decalin, (decahydronaphthalene). From the latent heat of vapourization, molecular weight and density, the solubility parameter of decalin was calculated to be 8.78 cals/ml. This compares favourably with the value for cyclohexane (8.8); consequently decalin (b.p. 467.6K) was the solvent chosen.

The evolution of the product ethane was again followed using the automatic pressure recorded described in Section III.3. By varying the concentration of the triethylamine complex while keeping the phenylacetylene concentration constant at 2.005M, the external reaction order with respect to complex was established. Log/log plots of v^{o} against complex concentration for $Et_3Al{\leftarrow}NBu_3$ and $Et_3Al{\leftarrow}NEt_3$ at 343K are shown in Fig. IV.1. The least squares regression slopes of the lines are 1.51 and 1.52 respectively. Similar experiments were performed to determine the order with respect to phenylacetylene and excess trialkylamine. The order with respect to phenylacetylene was found to be unity at 343K and 373K and the order with respect to excess trialkylamine was found to be zero at the same temperatures. An average of nine kinetic runs was performed at each of five temperatures within the range 333K-378K, using

ORDER WITH RESPECT TO TOTAL ALUMINIUM

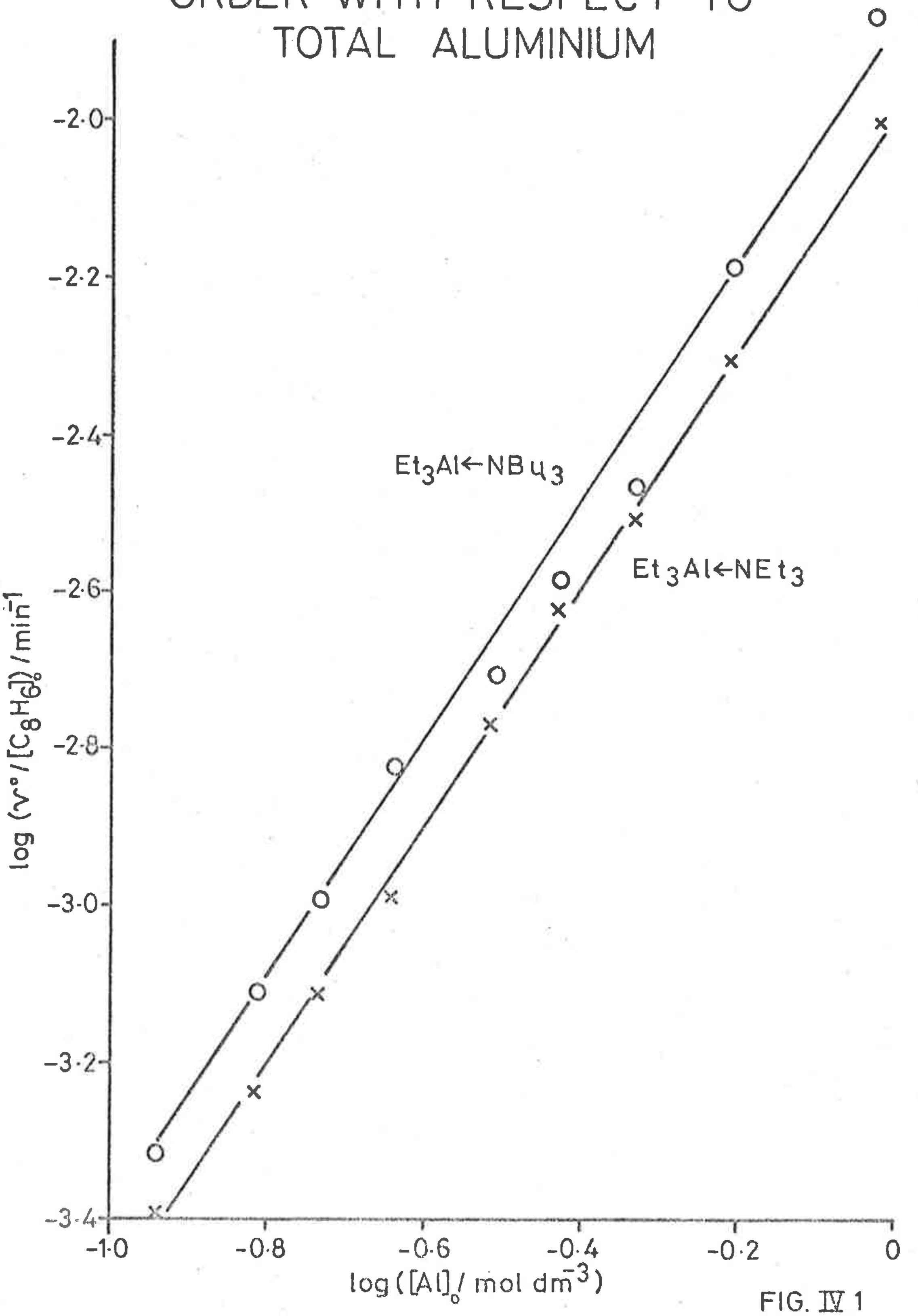
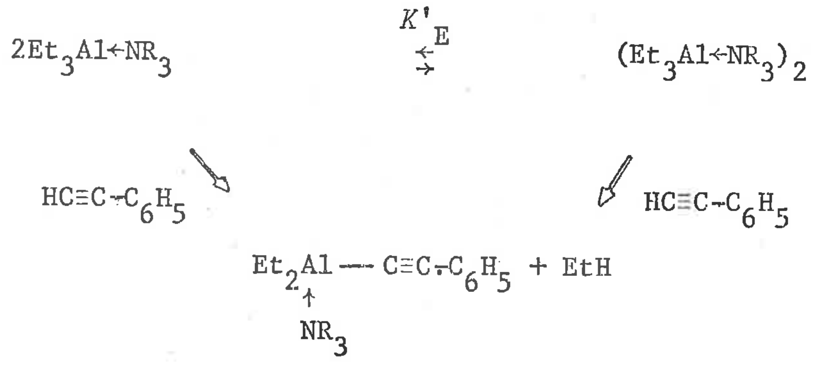


FIG. IV 1

triethylamine and tri-n-butylamine as the complexing reagent. Six kinetic runs, at 353K using N,N-diethylaniline as the complexing reagent were also performed. Two kinetic determinations at 353K using pyridine and THF as donors were also attempted, but no reaction could be observed in either case.

4. POSSIBLE MECHANISMS

The non integral external order of reaction with respect to $AlEt_3$:amine suggests that more than one triethylaluminium species is present in the reaction medium. Of the available possibilities there are two likely candidates: firstly, that the $AlEt_3$:amine associates and both the monomeric and dimeric species react. Thus

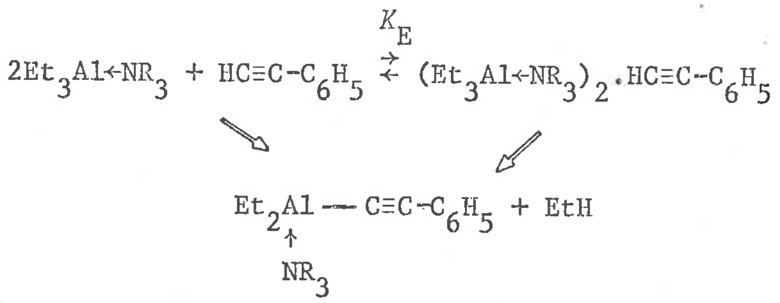


$$\begin{tikzcd} 2Et_3Al{\leftarrow}NR_3 \arrow[rr, shift left, leftarrow, "K'_E"] \arrow[rr, shift right] \arrow[dr, "HC\equiv C-C_6H_5"'] & & (Et_3Al{\leftarrow}NR_3)_2 \arrow[dl, "HC\equiv C-C_6H_5"] \\ & \begin{array}{l} Et_2Al - C\equiv C-C_6H_5 + EtH \\ \;\;\uparrow \\ \;NR_3 \end{array} & \end{tikzcd}$$

....(1)

....(2)

To obtain an order of between 1 and 2, K'_E, would have to be about 1. Secondly, it is possible that phenylacetylene complexes with two molecules of $Et_3Al{\leftarrow}NR_3$ and the reaction can then go either solely through the complex or be two simultaneous steps, thus



$$\begin{tikzcd} 2Et_3Al{\leftarrow}NR_3 + HC\equiv C-C_6H_5 \arrow[rr, shift left, "K_E"] \arrow[rr, shift right, leftarrow] \arrow[dr] & & (Et_3Al{\leftarrow}NR_3)_2 \cdot HC\equiv C-C_6H_5 \arrow[dl] \\ & \begin{array}{l} Et_2Al - C\equiv C-C_6H_5 + EtH \\ \;\;\uparrow \\ \;NR_3 \end{array} & \end{tikzcd}$$

....(3)

....(4)

Both dimeric species involve penta co-ordinate aluminium, but this is not unknown.

IV.4.

The first step in distinguishing between these mechanisms is the identification of the various complexes.

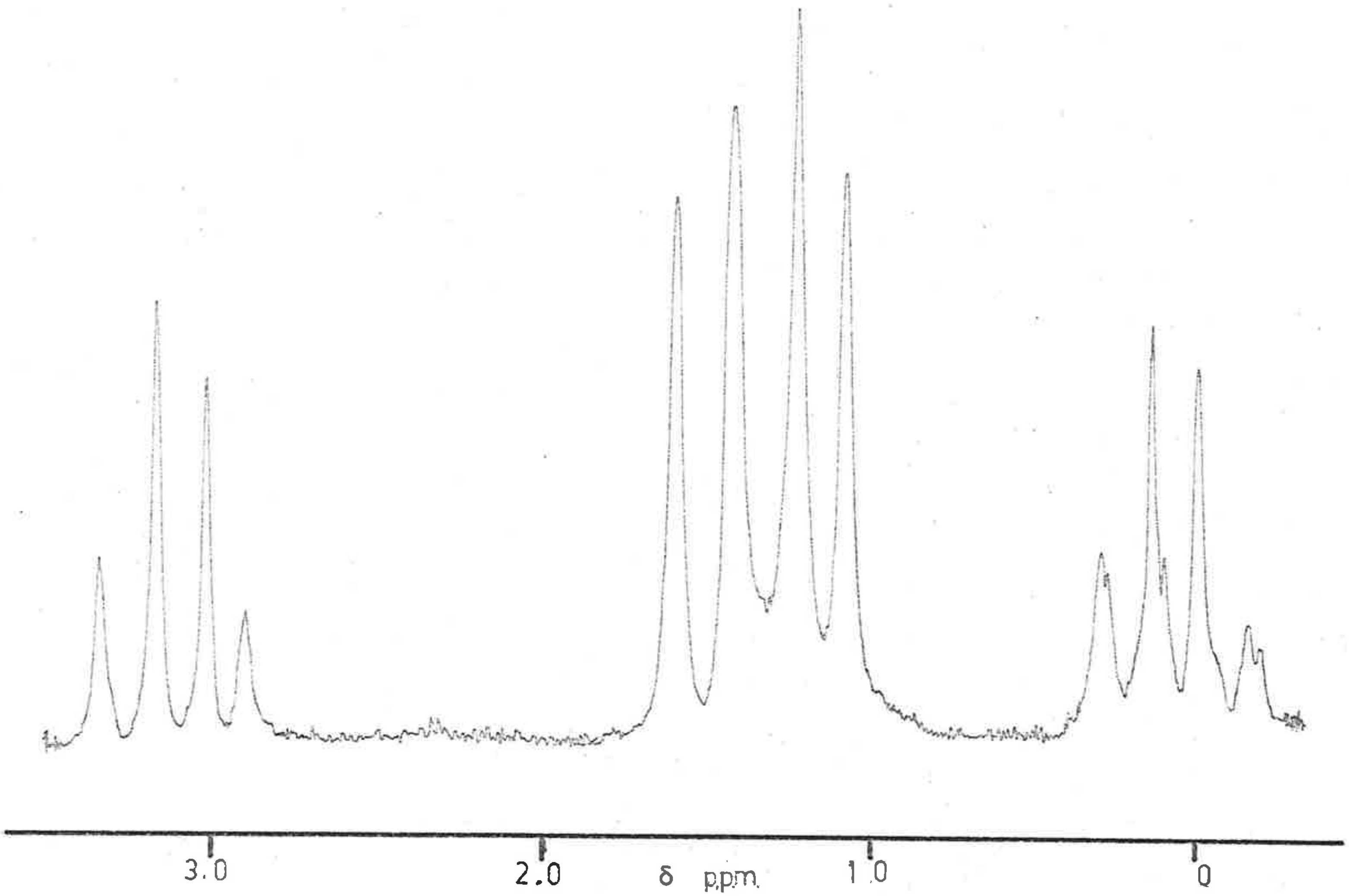
5. ASSOCIATION COMPLEXES

5.1. Triethylaluminium-amine Dimer

5.1.1. P.m.r. Studies

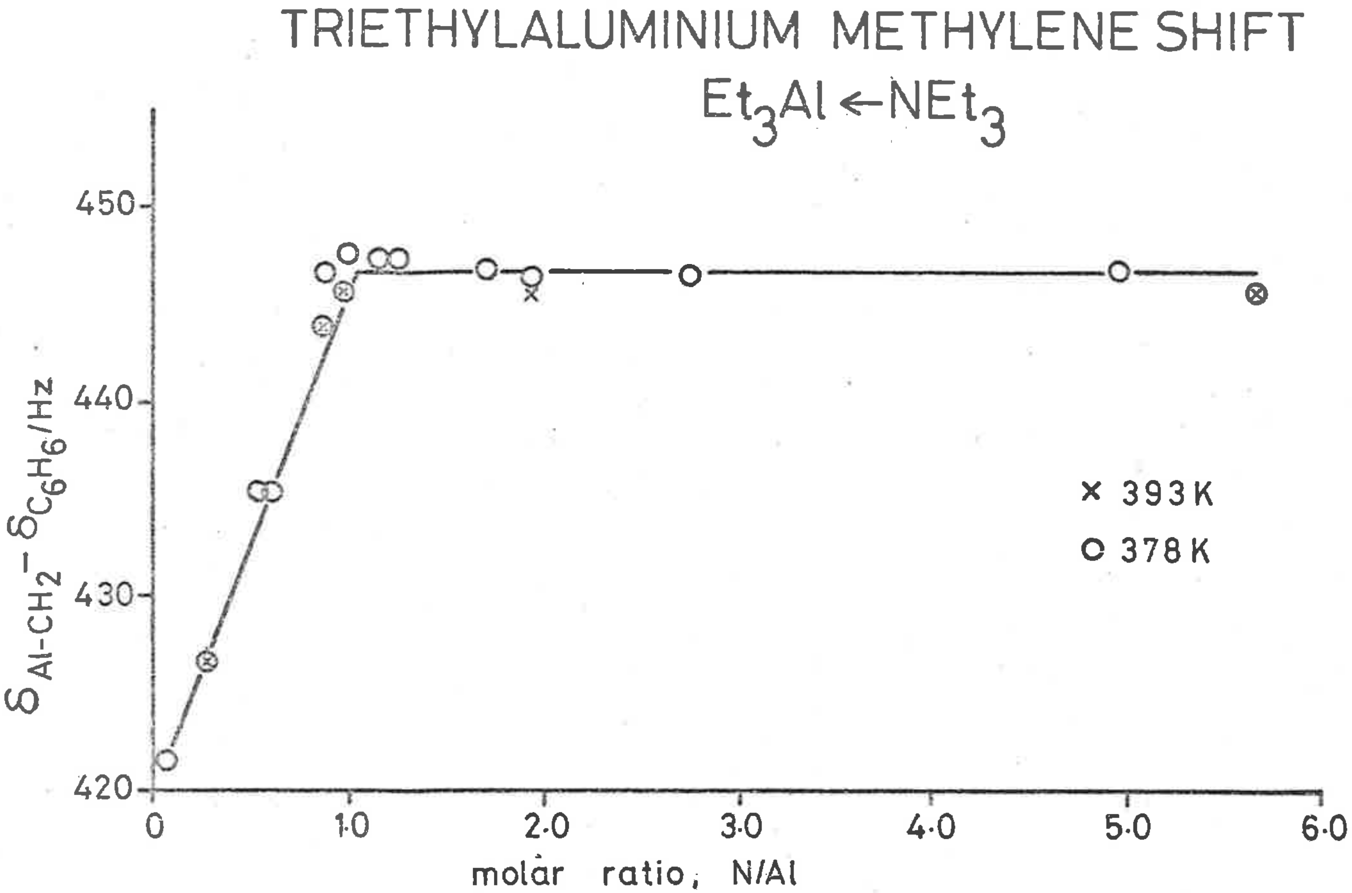
Although the trialkylamine complexes of triethylaluminium are reasonably well documented as stable, and their p.m.r. spectra recorded, we felt that, in the light of the kinetic studies, the 1:1 stoichiometry and stability of the complex should be verified. In addition, it may be possible to detect a change in some spectroscopic parameter with concentration. If this parameter can be shown to be normally concentration independent, this would indicate the existence of the dimer.

Fifteen n.m.r. tubes were prepared containing $NEt_3/AlEt_3$ molar ratios varying from 0.09 to 6 and a small constant amount of naphthalene, using the method and apparatus outlined in Section II.2.2. P.m.r. spectra for each tube were recorded at 303K and 378K, using the naphthalene resonances offset 500 Hz as the internal lock. As can be seen from the spectrum (Fig. IV.2), the alkyl resonances of the amine and the triethylaluminium methyl overlap, making a direct determination of the internal methylene-methyl shift of triethylaluminium (δ_{int}), the spectroscopic parameter indicating complexing, impossible. The method used to obtain an indication of δ_{int} was that used in determining the triethylaluminium-hex-3-yne complex; i.e. the chemical shift of the methylene quartet relative to the lock. A plot of δ_{CH_2} against mole ratio for the triethylamine complex is shown in Fig. IV.3. A similar plot was obtained for the tri-n-butylamine complex.



P.M.R. SPECTRUM OF $Et_3Al \leftarrow NEt_3$

Fig IV.2


TRIETHYLALUMINIUM METHYLENE SHIFT

$Et_3Al \leftarrow NEt_3$

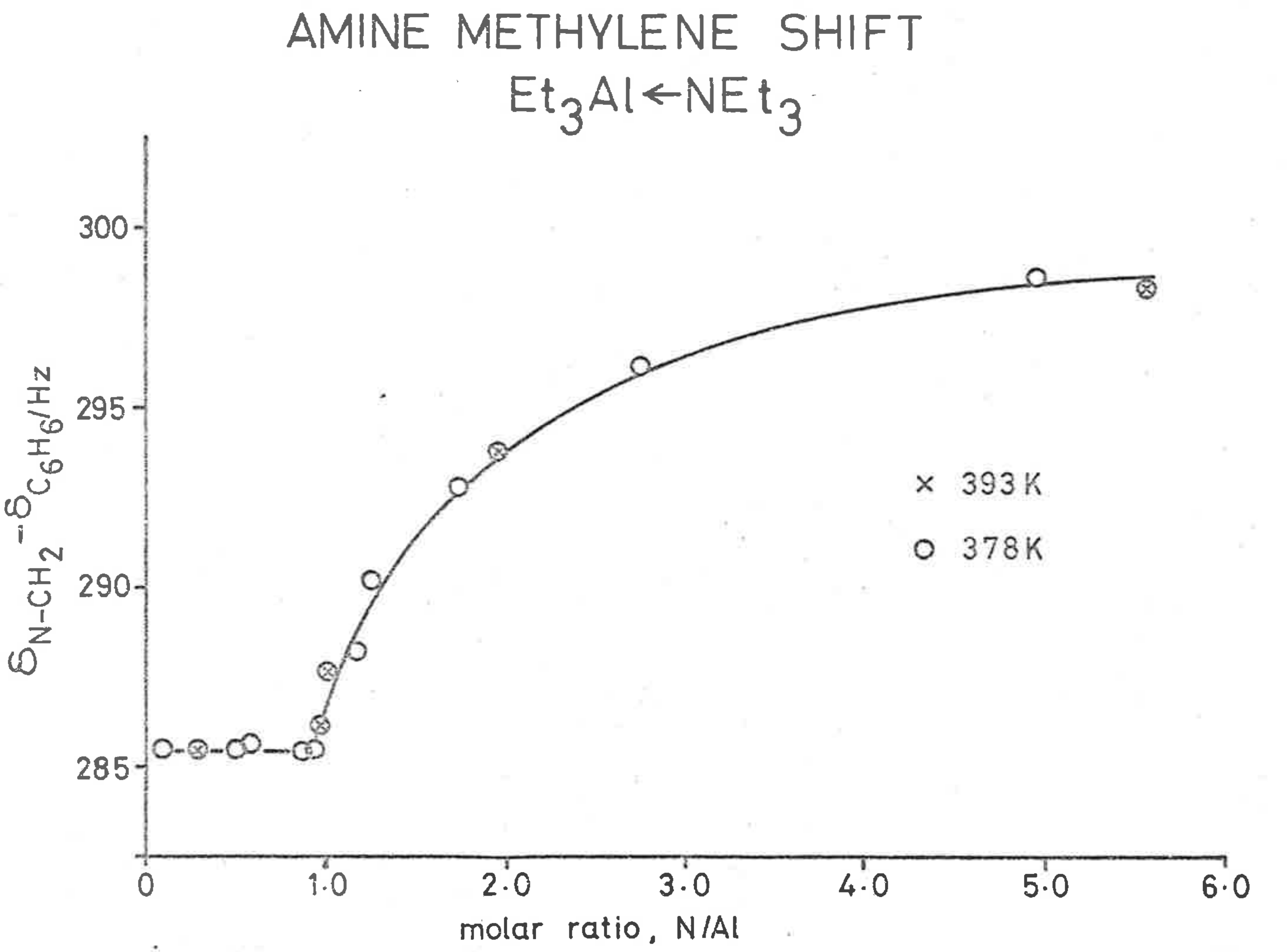
FIG. IV 3

IV.5.

In the $Et_3Al{\leftarrow}NEt_3$ system, a second parameter to indicate the extent of complexing is available and easily measured: the chemical shift of the amine methylene resonance. It appears that this methylene group is affected by the change in electronegativity of the nitrogen, and a plot of this parameter against mol ratio is shown in Fig. IV.4. Unfortunately, the alkyl proton resonances were not so easily distinguished in the $Et_3Al{\leftarrow}NBu_3$ complex.

Five n.m.r. tubes were prepared containing the same mol ratios as five of the above tubes. (N/Al = 0.1, 0.2, 0.5, 1.0, 2.0) but at 10% of the previous concentration. No difference in the spectroscopic parameters could be detected. This is not conclusive of the absence of the $Et_3Al{\leftarrow}NR_3$ dimer, however, as the parameters of both species may be very similar and their differences cannot be detected.

At a mol ratio of N/Al = 2/1, at 302K, the amine methylene of the $Et_3Al{\leftarrow}NEt_3$ resonances coalesce to form a broad peak. This has been attributed to the fact that, at this temperature and concentration, the rate of exchange of amine groups on triethylaluminium is similar to the resonance lifetime.[26] On cooling, two quartets appear, corresponding to complexed and free triethylamine, while on heating, the broad peak obtains the fine structure of a single quartet, as expected. At maximum instrument power, this high temperature (343K) spectrum was scanned approximately 100 Hz downfield from the $N\text{-}CH_2$ quartet. (Fig. IV.5.) As can be seen, two small quartets are apparent, centred approximately 36 Hz and 66 Hz downfield from the main quartet. They seemed to



AMINE METHYLENE SHIFT

$Et_3Al \leftarrow NEt_3$

FIG. IV 4

N–CH_2 RESONANCES

$Et_3Al \leftarrow NEt_3$

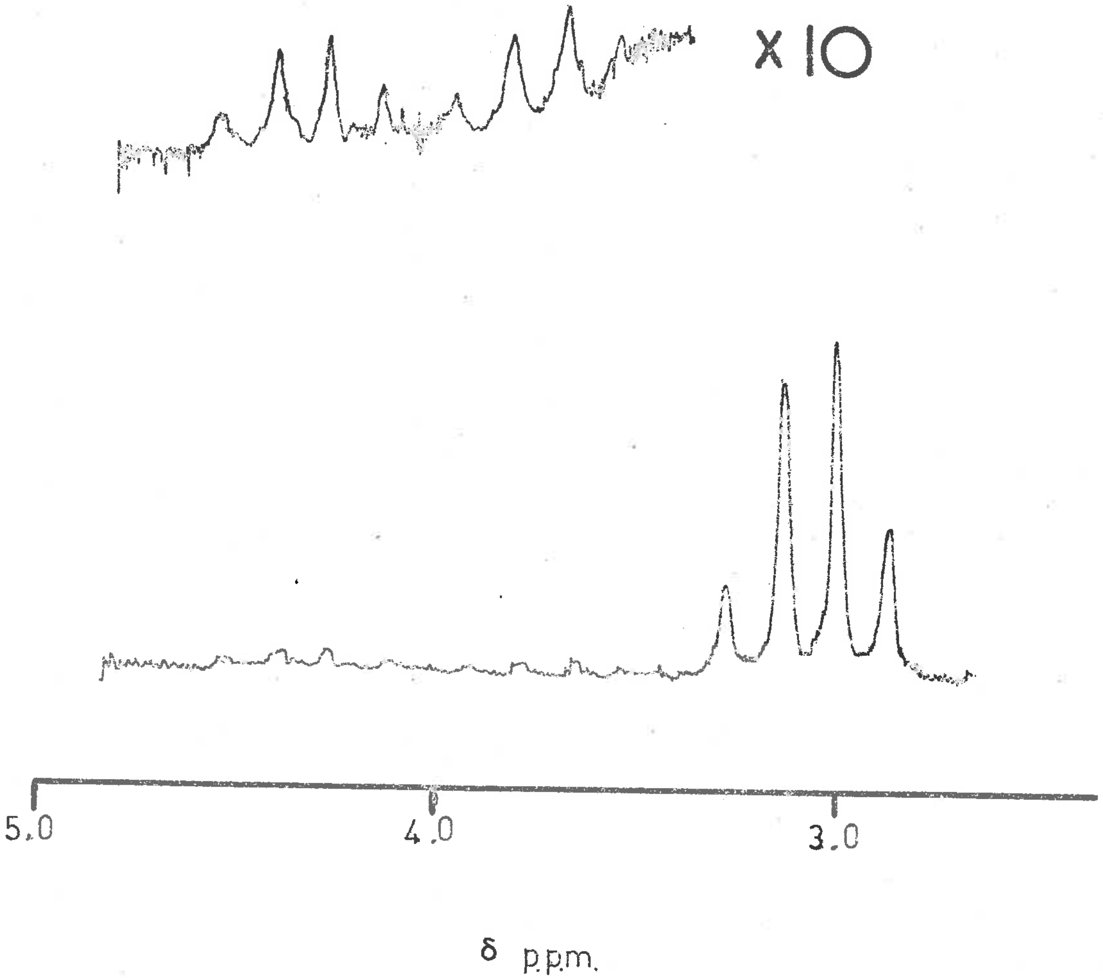
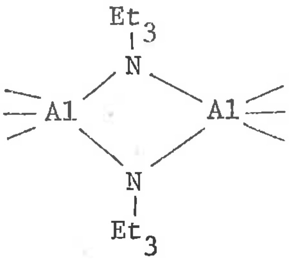
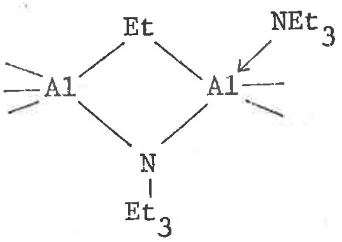


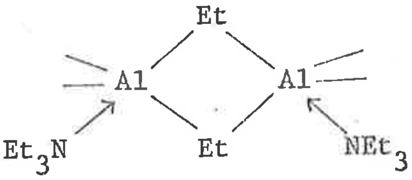
Fig IV. 5

disappear on cooling, but the instrument would probably not have detected them if they coalesced to a very small, broad peak.

These small quartets (<1% of total N-CH_2 peak area) are due to the amine being in two different magnetic environments from the major complexed or free amine. It appears reasonable to us that these resonances arise from amines that form a bridge across a dimer or are terminal. The possibilities are







It is possible that one of these is in equilibrium with the monomer, exchanging rapidly, while the other two are in very small concentration but do not exchange rapidly.

These p.m.r. studies, therefore, indicate but do not prove the absence of any significant concentration of a dimeric species in a solution of triethylaluminium-trialkylamine complex. We felt it necessary to try and prove this absence by determining the apparent molecular weight of the amine complex in hydrocarbon solution.

IV.5.

5.1.2. Ebulliometry

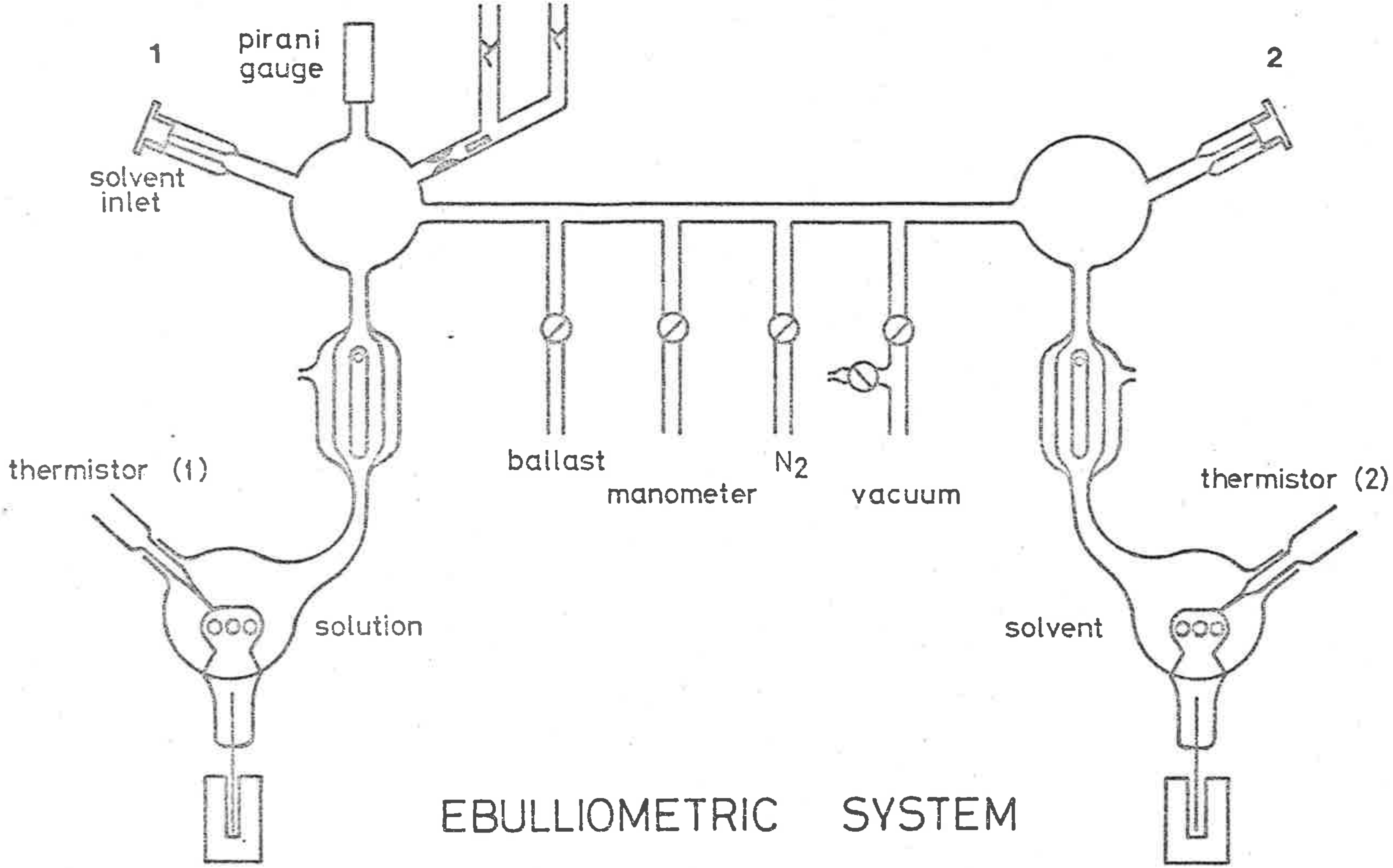
Of the two major apparent molecular weight determination methods, cryoscopy and ebulliometry, the latter is preferred in this case, because the molecular weight can be determined at a temperature close to that of the kinetic runs. Furthermore, cryoscopic measurements can be difficult to perform with compounds that may tend to phase separation.

Quite a large amount of data, dating from 1946, are available on ebullioscopic measurements of trialkylaluminiums,[46,47] and the methods of ebulliometry applied in these cases can be applied to the triethylaluminium-donor complex. The main departure from classical ebulliometry is the necessity for a closed system, due to the reactivity of triethylaluminium and related compounds with air and moisture.

As a result of having to work with a closed system, it was decided to adapt the apparatus to operate at variable pressures, thus determining apparent molecular weights at different temperatures without having to resort to changing the solvent. This is especially desirable in trialkylaluminium systems as it has been shown that particular solvents (e.g. aromatics) affect association.

The ebulliometer used in this determination is based on a commercial ebulliometric system marketed by Gallenkamp,[48] which is in turn based on a system developed by Heitler in 1958.[49,50] It consists of two borosilicate glass ebulliometer vessels, interconnected with various takeoffs, and a resistance measuring bridge incorporating a null detector. Each ebulliometer vessel consists of a modified Cottrell pump with a tungsten wire fused into the base to conduct heat to the solution. Heat is supplied to this wire by placing it in a heating block located in a heating stand. Efficient boiling produces rapid circulation of an intimate foam of solution and vapour, providing conditions under which the boiling point is precisely measured. Boiling temperature is sensed by a thermistor probe in the foam. A double surface condenser with both inlet and outlet at the top was attached to each vessel. As the vapour condenses, the condensate returns steadily to the solution, and in this way a state of dynamic equilibrium is evolved. The stand comprised a base with heating element and control, and included a plastic shield to protect the ebulliometer vessel from draughts. A schematic of the ebulliometric system is shown in Fig. IV.6. Atop each double surface condenser was a flask used to introduce liquids into each ebulliometer vessel. The triethylaluminium complex was introduced via a breakseal, while solvents were injected into the apparatus through a Viton 'A' septum inlet. In normal ebulliometric determinations, changes in the boiling point are engineered by progressively adding solute and thus changing the concentration. In this case, with a reactive solute, this is inconvenient, and it was decided to alter the concentration by adding solvent. Injecting progressively known amounts through the septum inlet is an easy and effective way of accomplishing this.

Along the connecting glass tube were placed four take offs: ballast, vacuum, nitrogen and a manometer. A ballast (20 litre aspirator) was necessary to alleviate the small fluctuations in pressure which



EBULLIOMETRIC SYSTEM

FIG. IV. 6

occur when boiling is performed in a small closed system.

Ebulliometric Theory

The temperature dependence of vapour pressure is given by the Clausius-Clapeyron equation

$$d\ln P/dT = \Delta H_{vap}/RT^2$$

Combining this with Raoult's Law, according to which the addition of solute lowers the vapour pressure, the following relationship is established.

$$\Delta T = \frac{RT_o^2}{\Delta H_{vap}} \cdot M_a W_b / M_b W_a$$

ΔT = Difference in boiling point between solvent and solution

R = Gas constant

T_o = Boiling temperature of the solvent

ΔH_{vap} = Latent heat of vapourization of the solvent

M = Molecular weight of solvent (a) and solute (b)

W = Weight (gms.) of solvent and solute in system

For standard bead thermistors

$$\text{Resistance } (r) = a\, e^{b/T} \qquad \text{....(5)}$$

IV.5.

Thus

$$\ln r = a' + b/T$$

$$r_1 = ae^{b/T_1} \quad : \quad r_o = ae^{b/T_o}$$

$$\ln r_1/r_o = b[1/T_o - 1/T_1]$$

$$\Delta T = T_1 - T_o = \ln r_1/r_o . T_o T_1/b$$
$$\simeq \ln r_1/r_o . T_o^2/b$$

Defining;

$$r_1 = r_o + \Delta r$$
$$\therefore \quad \ln r_1/r_o = \ln(1+\Delta r/r_o) \simeq \Delta r/r_o$$

and substituting for ΔT;

$$M_b = \frac{R.b}{\Delta H_{vap}} . \frac{r_o}{\Delta r} . \frac{M_a W_b}{W_a} \qquad ....(6)$$

This procedure was first used by Stokes and Pugh in 1963.[51] From equation (6) it can be seen that in order to obtain a value for M_b, the b coefficient of the thermistor must be known, and so, before embarking on molecular weight measurements, it is necessary to determine this parameter for the solution thermistor. Initially the apparatus was pumped out using a rotary oil pump to approximately 10 Nm^{-2}. The tap to the vacuum pump was then closed and high purity nitrogen (C.I.G. specifications <01% O_2/H_2O) bled in until half atmospheric pressure in the system was attained. Cyclohexane was then introduced by injection into the lefthand (solution) ebulliometer vessel, and heated to boiling by passing current through the heating wire. The resistance of the thermistor was then measured.

Resistance was measured using a Wheatstone bridge circuit incorporating two standard mica card resistors (± 05%, temp coeff 5p.p.m.), and a Cambridge Instruments 0-11,000Ω decade resistance box (minimum 0.1Ω) in addition to the thermistor to form the four sections of the bridge (Fig. IV.7). D.C. was supplied to the circuit by a 1.35 volt Mercury Mallory cell (RM-42R) via a precision potentiometer to enable the current passing through the bridge, and hence the sensitivity, to be varied. Current across the bridge was detected with a Leeds and Northrup Electronic Null Detector (Model 9834). At maximum sensitivity, a full scale deflection on this instrument corresponds to a voltage of 0.6μV. At the null point the resistance of the thermistor is given by

$$r = \text{decade box resistance} \times \frac{69993}{4999} \text{ ohms}$$

On completion of each resistance reading, enough nitrogen was bled in to increase the pressure by about 1 cm Hg. After the solvent had reached

THERMISTOR RESISTANCE MEASUREMENT

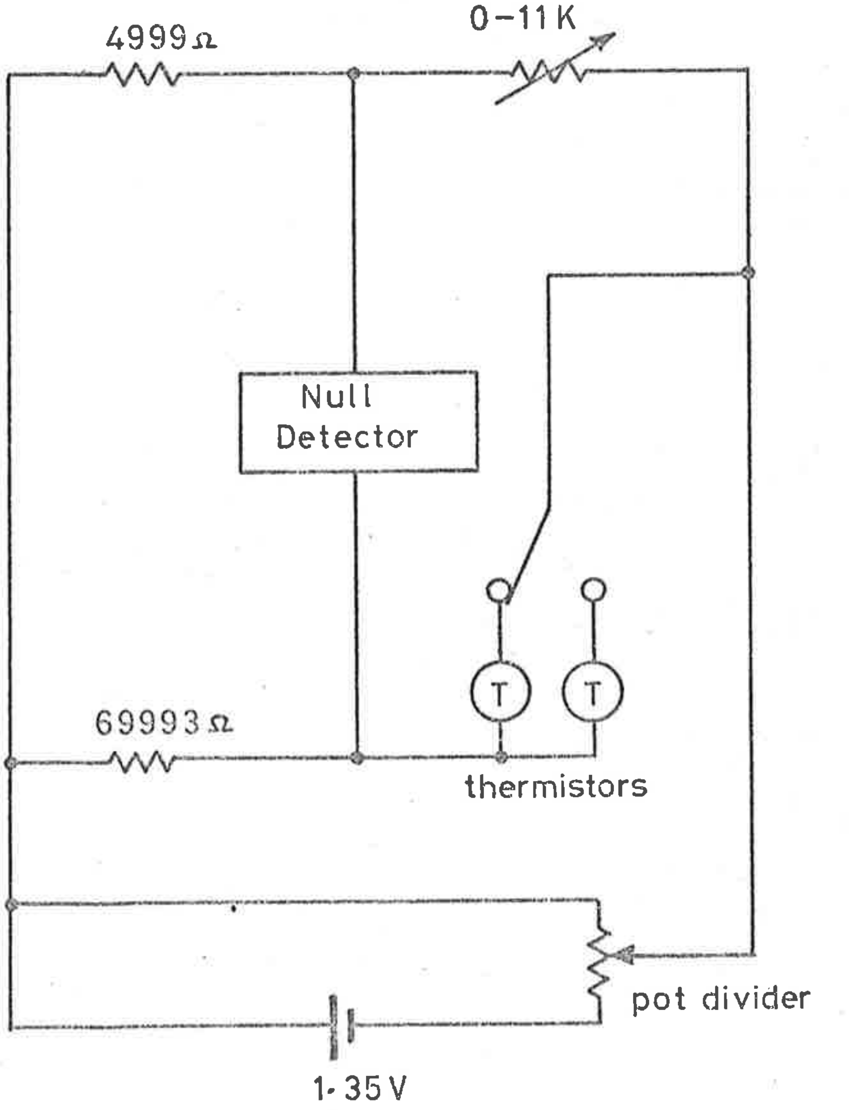


FIG. IV 7

equilibrium at its new boiling point (approximately 2 mins.), the new pressure was noted, and the resistance again taken. This procedure was repeated until the pressure in the system was approximately 1½ atmospheres. The data for cyclohexane can be represented to a good approximation by an Antoine equation[52]

$$\ln P = 17.256 - 3889.2/T$$

P = pressure in mm Hg

T = Temp in degrees K

Combining this with the equation (5)

$$\ln r = -b/3889.2 \ln P + const.$$

A plot of $\log_{10} r$ against $\log_{10} P$, therefore, has a slope of $-b/(2.303 . 3889.2\mathrm{K})$ (Fig. IV.8). The b coefficient for the solution thermistor was calculated to be 4124K. In some thermistors this co-efficient can be altered due to the occurrence of the so called "self heating effect", which arises from the fact that the thermistor is a resistance, and so uses up power according to the equation $w = i^2 r$. Use of this wattage will contribute heat to the thermistor and thus decrease its apparent resistance. This was overcome here by using pre-aged thermistors. Pre-aging, as its name implies, consists of heating and cooling the thermistor a number (~25) of times, after which the resistance is stable for long

DETERMINATION OF β COEFFICIENT

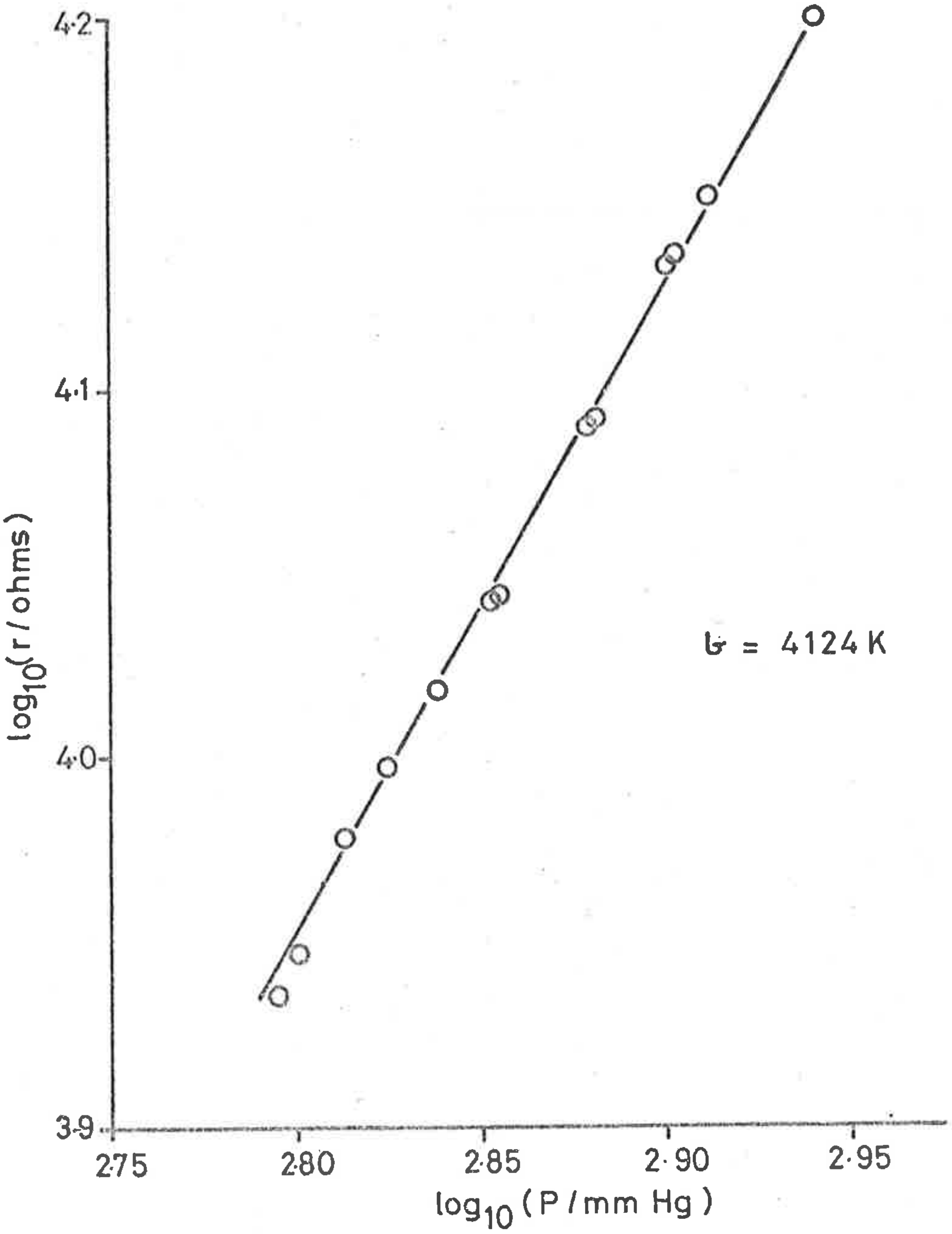


FIG. IV 8

periods of time under normal voltages.

It is theoretically possible to use the $\log_{10}r$ vs $\log_{10}P$ plot to determine r_o (equation (6)) for molecular weight calculations, necessitating the use of only one ebulliometer vessel. In practice, however, this technique is not possible because the manometer is not accurate enough: a change in pressure of 0.1 mm changes the r value by about 12Ω, and values of r need to be known to 0.2Ω to give reproducible results. To produce the accuracy required is the reason for incorporating the solvent (righthand) ebulliometer vessel.

Cyclohexane was introduced into each vessel and the resistances of both thermistors measured at various pressures to 1½ atmospheres. The two thermistors used were a matched pair (very similar b co-efficients) and so the relationship between them can be expressed as a straight line

$$r_1 = m\, r_2 + c$$

During a molecular weight determination, therefore, r_o for equation (6) was obtained by measuring the resistance of the solvent thermistor (2), and the solution thermistor (1) at the same pressure, and applying the above relationship to obtain r_o.

In this apparatus a known mass of solvent is injected, but unfortunately not all of it is in solution during the measurements; some is present as vapour and some as a film of liquid on the walls of the ebulliometer vessel and condenser. It is therefore necessary to determine the mass of solvent in the liquid phase by calibration. For this purpose pure naphthalene was used as a solute.

The apparent molecular weight of naphthalene was determined at pressures between ½ and 1½ atmospheres. Since naphthalene is not strictly involatile at the temperature of boiling cyclohexane, (it has a vapour pressure of 6.6 mm at 81°C),[52] equation (6) was corrected by multiplying the right hand side by $(1-p_1/p_o)$, where p_1 is the vapour pressure of naphthalene and p_o is the vapour pressure of cyclohexane (760 mm). From equation (6) it can be seen that

$$\frac{MW_{\text{app}}}{MW_{\text{true}}} = \frac{\text{Wt.solvent added}}{\text{Wt.solvent in liquid phase}}$$

Results from four different naphthalene concentrations show that the solvent holdup at 0.5 atm. = 0.59 gms.,rising linearly to 0.72 gms. at 1.5 atm.

Since no vapour pressure data is available for the two triethylaluminium-amine complexes, a preliminary experiment was necessary to see if equation (6) need be modified for solute vapour pressure in these systems. For this purpose, the apparatus shown in Fig. IV.9 was constructed. After evacuation for 1 hr at 10^{-1} Nm^{-2}, the taps to the vacuum system were closed, the breakseals containing equimolar quantities of each component (1ml Al_2Et_6, 1.02 ml NEt_3 or 1.17 ml NBu_3) were broken,

VAPOUR PRESSURE OF $Et_3Al \leftarrow NR_3$

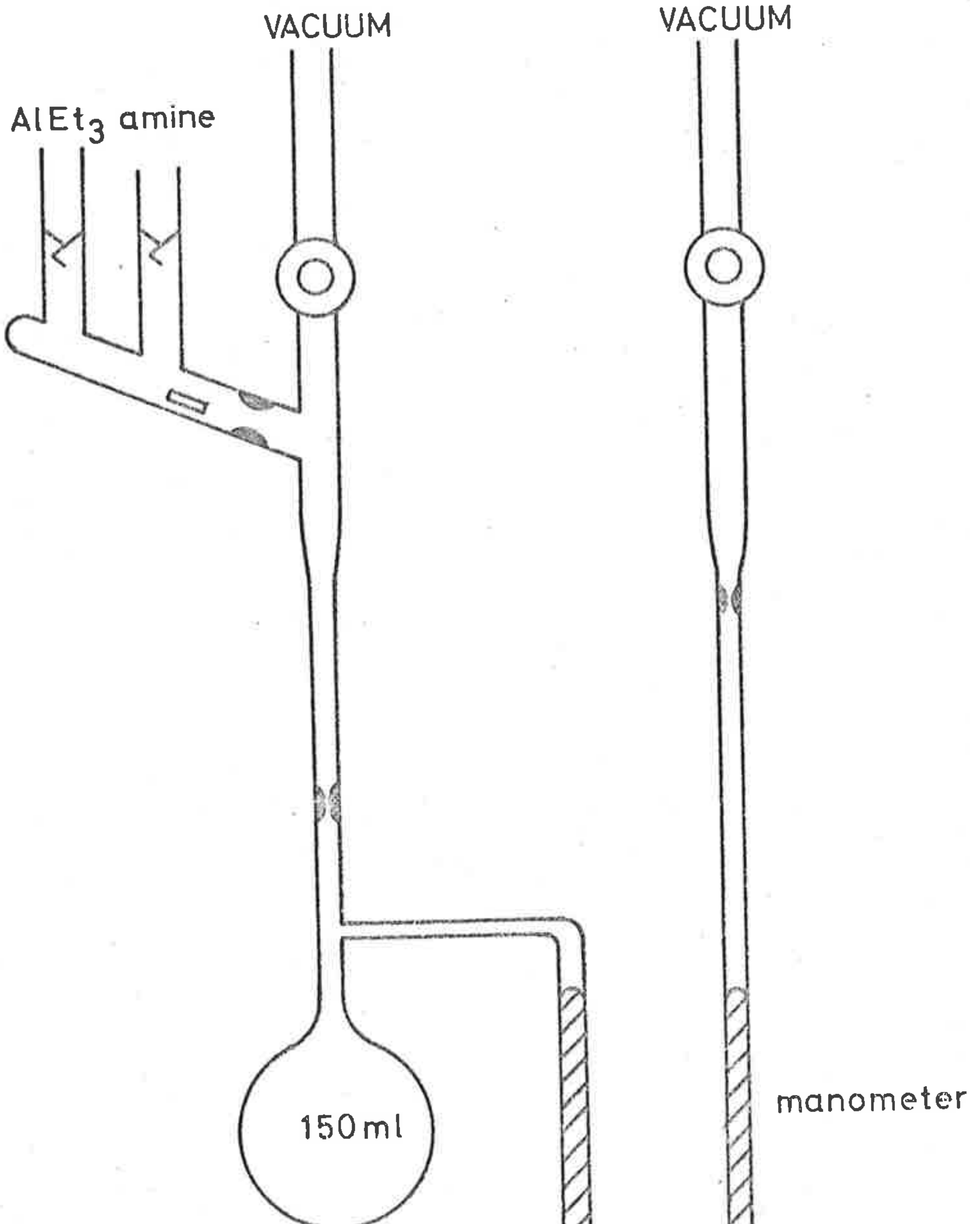


FIG. IV. 9

and the liquid frozen in the flask using liquid nitrogen, before the constrictions were sealed. The whole apparatus was placed in a glass oil bath containing silicone 200 oil at 293K and the height of the inner column of mercury read on a cathetometer. The temperature of the oil bath was raised in progressive steps to 410K, measuring the mercury height each time. In the case of $Et_3Al{\leftarrow}NBu_3$, no change in height of the mercury could be detected over this temperature range, and it was concluded that, under these conditions, the vapour pressure of this complex was negligible. A rise in pressure could, however, be detected for $Et_3Al{\leftarrow}NEt_3$. As only a small change in mercury height could be observed on heating the complex from 77K to 294K, and this can be accounted for by degassing, it was assumed that the vapour pressure of the complex was negligible at 294K, and the Antoine equation was calculated on this basis. The observed pressures between 294K and 410K can be represented by the equation

$$\log_{10}P = 5.501 - 1738.6/T$$

The apparent molecular weight determination of the triethylaluminium-amine complexes was conducted under an inert atmosphere of nitrogen. This was obtained by evacuating the ebulliometer to 10 Nm^{-2} using the rotary oil pump, closing the vacuum tap (Fig. IV.6), and bleeding in high purity nitrogen until atmospheric pressure was regained. This flushing process was repeated three times to ensure the removal of all air. After the pressure was reduced to 0.5 atm. a breakseal containing

IV.5.

2.0 mls. of complex in 7 mls. of cyclohexane was broken. All liquid was forced into the solution ebulliometer vessel by cooling the bottom of the condenser with liquid nitrogen soaked cotton wool, while heating the rest of the glass apparatus with a hair dryer. 10 mls. of cyclohexane were injected into the solvent ebulliometer vessel using septum inlet (2).

In order to assist in boiling and to prevent excessive frothing in the solution, 0.2 gms. of coarse powdered glass were placed in the vessel before assembly. Thermistor resistances of the boiling solution and solvent were recorded at several pressures in the range 0.5-1.5 atm. The vacuum tap was then opened to enable the pressure to drop back to 1 atm. and this was followed by the injection of 2.0 mls. of cyclohexane through the septum inlet (1). Thermistor resistances were again measured for the boiling solutions between 1.0-1.5 atm. Pressures less than one atmosphere could not be used in these subsequent determinations because obtaining the reduced pressure would take an appreciable amount of cyclohexane from solution. The determinations were repeated with two subsequent 2.0 mls. cyclohexane additions. Apparent molecular weights were calculated from equation (6), modified for solute vapour pressure in the case of the triethylaluminium-triethylamine complex, with the result displayed in Figs. IV.10a&b. Examination of these figures indicates that both complexes exist in cyclohexane solution as monomer over the temperature range covered. The slight slope is probably due to errors in the solvent holdup determination.

APPARENT MOLECULAR WEIGHT

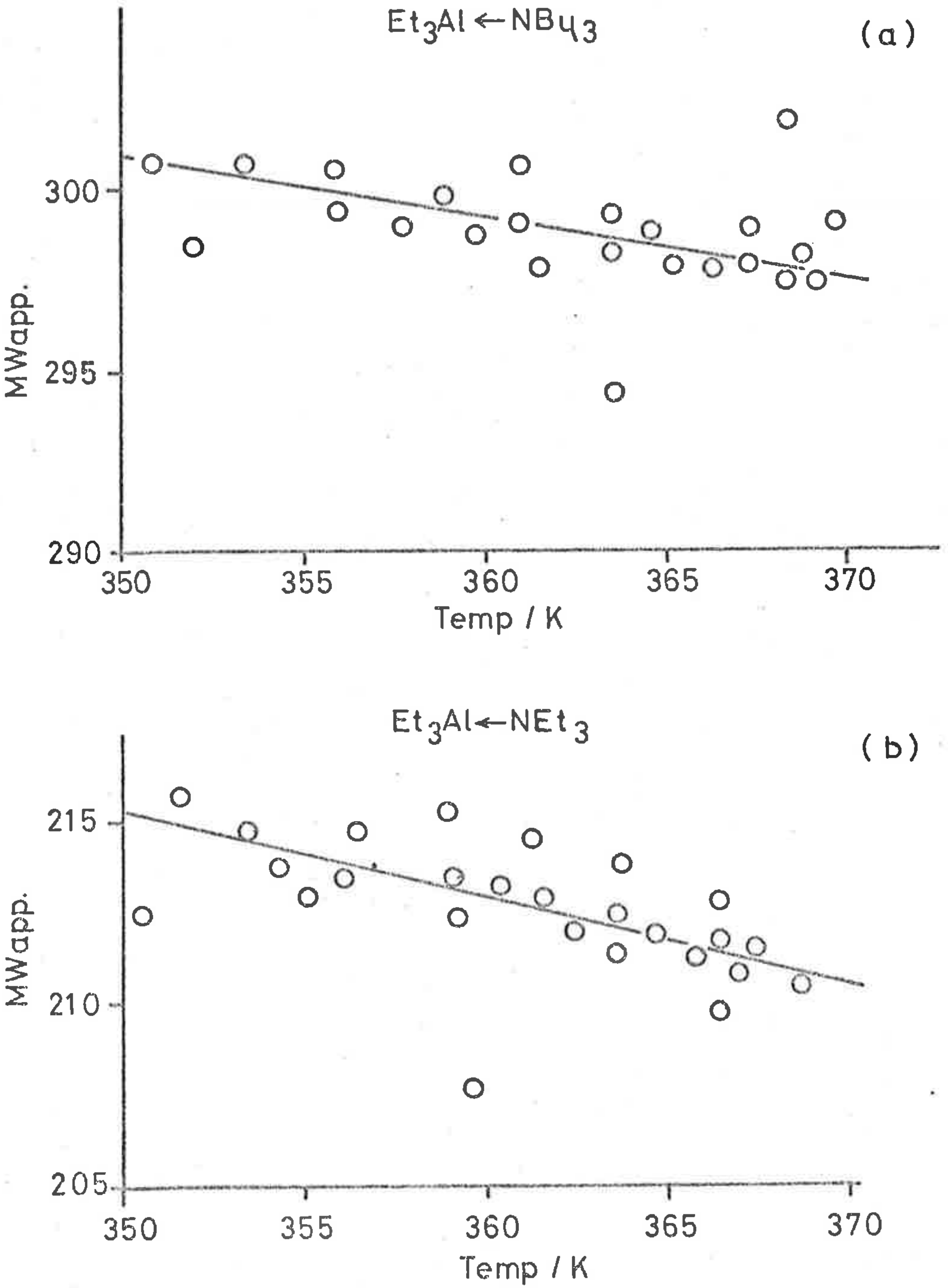


FIG. IV 10

IV.5.

The monomeric nature of both complexes in solution was confirmed by determining the apparent molecular weight of each in boiling n-heptane (b.p. 367K compared with 354K for cyclohexane). Molecular weights obtained in both solvents were, within experimental error, identical.

As a result of these p.m.r. and ebulliometric investigations, it was concluded that no appreciable concentration of triethylaluminium-amine dimer exists in the reaction medium with phenylacetylene, ruling out mechanism (2).

5.2. Triethylaluminium-trialkylamine-phenylacetylene complex.

If such a ternary complex exists, the p.m.r. spectra of phenylacetylene should change in the presence of the $Et_3Al{\leftarrow}NR_3$ complex. Two n.m.r. tube/flasks were prepared using the method outlined in Section III.2.1 and the apparatus shown in Fig. III.1, containing $Al.N/C_8H_6$ molar ratios of 1/15 and 15/1 in cyclohexane. The recorded spectrum is shown in Fig. IV.11. At 303K, the acetylenic peak was 83.3 Hz downfield from cyclohexane in the presence of triethylaluminium-triethylamine, but only 80.2 Hz downfield from cyclohexane when phenylacetylene was the only solute present. The concentration of phenylacetylene was identical in both samples to eliminate solvent shift (see Section III.2.1). The corresponding shift values for the phenylacetylene aromatic protons were 346.1 and 344.4 Hz.

P.M.R. SPECTRUM OF $AlEt_3/NBu_3$/PHENYLACETYLENE
in cyclohexane

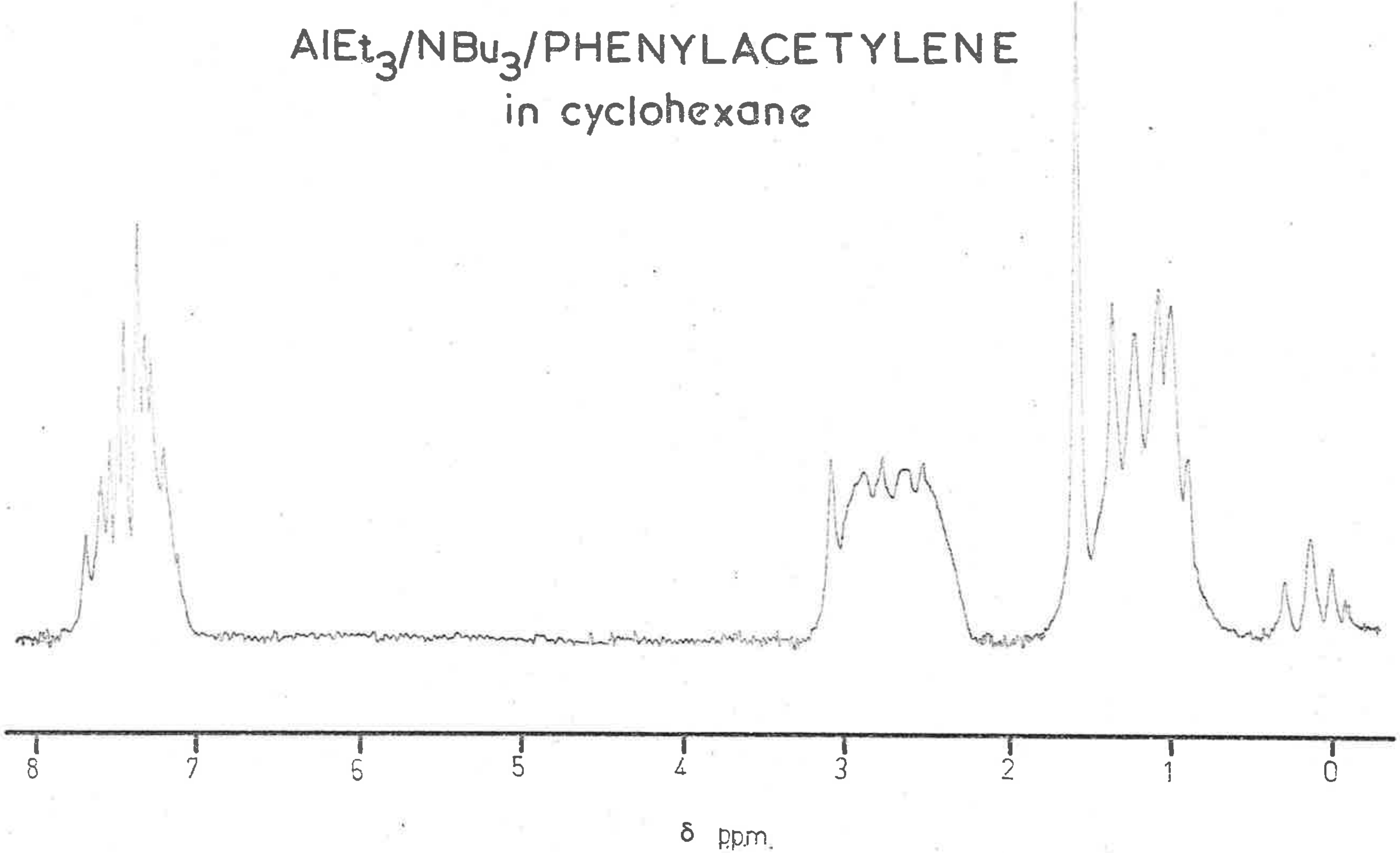


Fig IV. 11

IV.5.

These results indicate that there is an interaction between phenylacetylene and the triethylamine complex of triethylaluminium, but the size of the shifts, when compared to those noted for the triethylaluminium-phenylacetylene complex (7.6 Hz) show that the equilibrium constant for formation of the ternary complex is small. (i.e. $<.064\ M^{-2}$). If only a small concentration of ternary complex is present, the observed orders of reaction with respect to $Et_3Al \leftarrow NR_3$ can only be explained as two simultaneous reaction steps, (mechanism (4)) involving reaction of the Et_3Al complex with phenylacetylene in addition to the ternary complex dissociating.

IV.6.

6. KINETIC RESULTS

The presence of simultaneous reactions in mechanism (4) can be confirmed to a certain extent by showing that the ternary complex is not the sole reactant.

$$\begin{array}{ccccc} 2Et_3Al\leftarrow NR_3 & + & C_8H_6 & \rightleftarrows & (Et_3Al\leftarrow NR_3)_2\cdot C_8H_6 \\ 2\alpha & & b+\alpha & & a-\alpha \\ & & & & \downarrow \\ & & & & \text{products} \end{array} \qquad \text{....(7)}$$

If this is the sole reaction path, α can be estimated from the observed order of reaction with respect to triethylaluminium complex using the method developed for styrene (Section II.3). Thus

$$a^n = (2\alpha)^2 + a-\alpha \qquad \text{....(7a)}$$

where n is the observed order of reaction. Following the procedure laid down in Section II.3 values for α for each kinetic run were calculated. According to mechanism (7),

$$v^o = k(a-\alpha)$$

and thus a plot of v^o against $a-\alpha$ should be a straight line passing through the origin. Fig. IV.12 shows such a plot for $Et_3Al\leftarrow NBu_3$ at 343K, and it is obvious that the product is not formed solely by mechanism (7).

INITIAL RATE v [TERNARY COMPLEX]
MECHANISM (7)

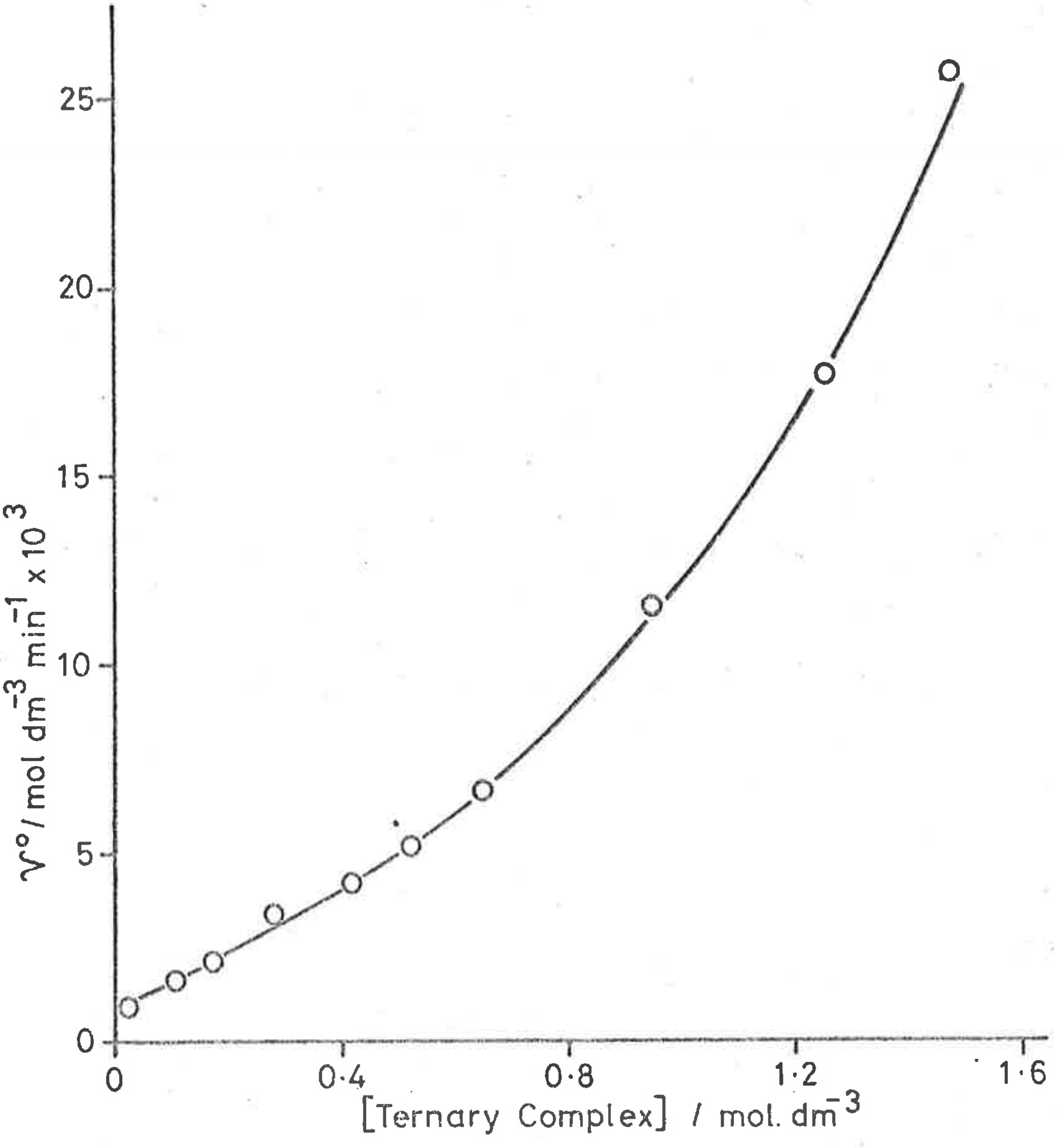


FIG. IV 12

IV.6.

The simultaneous reaction path mechanism (4) gives a rate equation of the form

$$v^{\circ} = d[EtH]/dt = k_1[Et_3Al{\leftarrow}NR_3]_o[C_8H_6]_o + k_2K_E[Et_3Al{\leftarrow}NR_3]_o^2[C_8H_6]_o \quad ....(8)$$

and thus a plot of $v^{\circ}/[Et_3Al{\leftarrow}NR_3]_o[C_8H_6]_o$ against $[Et_3Al{\leftarrow}NR_3]_o$ should be a straight line of slope k_1, intercept k_2K_E. Figs.IV.13a&b show these plots for the triethylamine and tri-n-butylamine complexes respectively. Values of k_1 and k_2K_E are tabulated in Table IV.1.

TABLE IV.1.

Rate Co-efficients

	Temp/K	$k_1/M^{-1}\ min^{-1}$	$k_2K_E/M^{-2}\ min^{-1}$
$Et_3Al{\leftarrow}NEt_3$	333	.00102	.00278
	343	.00199	.0118
	353	.00477	.0204
	363	.00528	.0660
	373	.0125	.124
$Et_3Al{\leftarrow}NBu_3$	343	.00293	.0121
	353	.00450	.0319
	363	.0162	.0628
	373	.0462	.1035
	378	.0642	.1207
$Et_3Al{\leftarrow}N(C_6H_5)Et_2$	353	.0021	.0175
$Et_3Al{\leftarrow}$pyridine	353	no reaction	
$Et_3Al{\leftarrow}$THF	353	no reaction	

Note: The linear least squares regression error is in the last significant figure for each value.

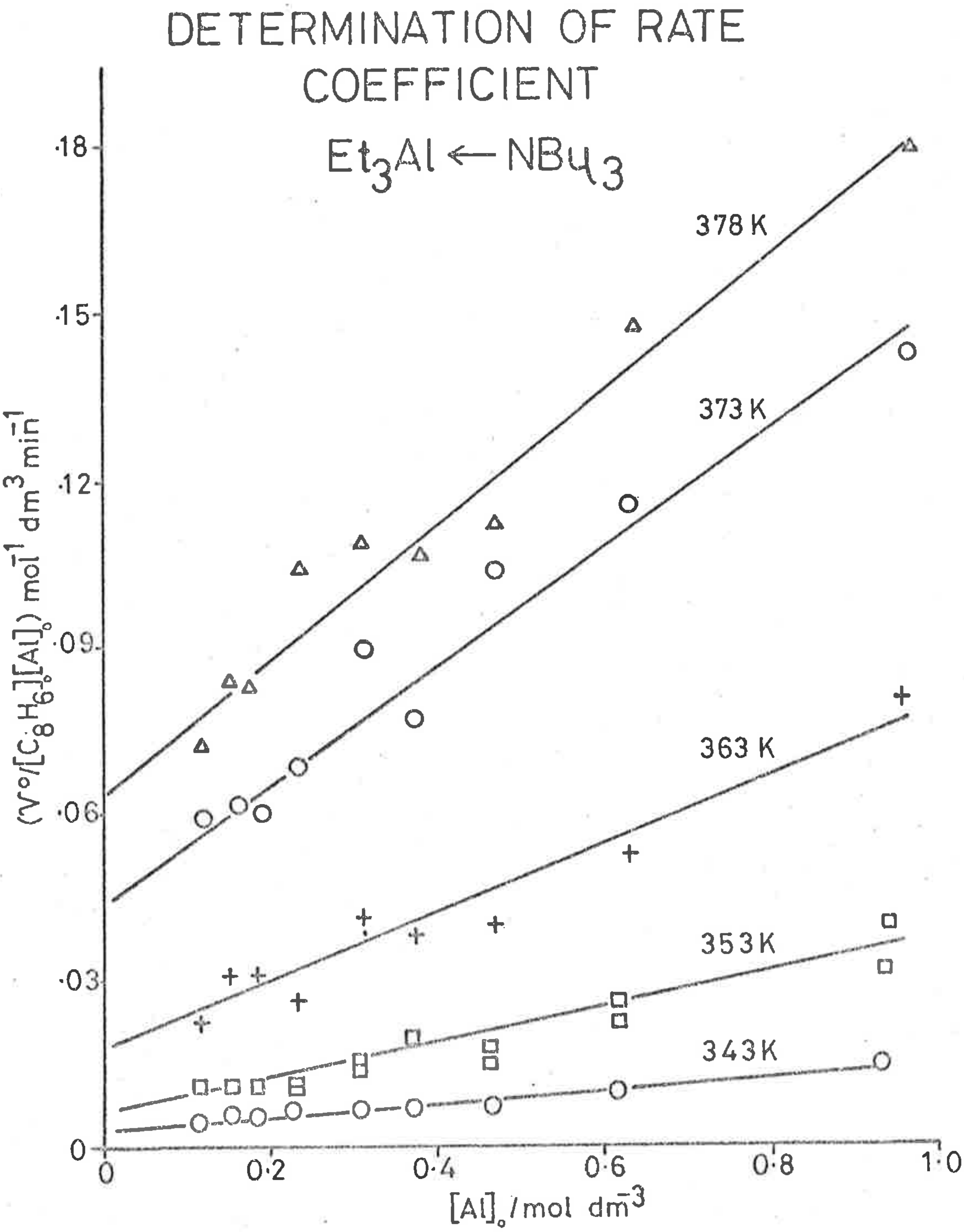
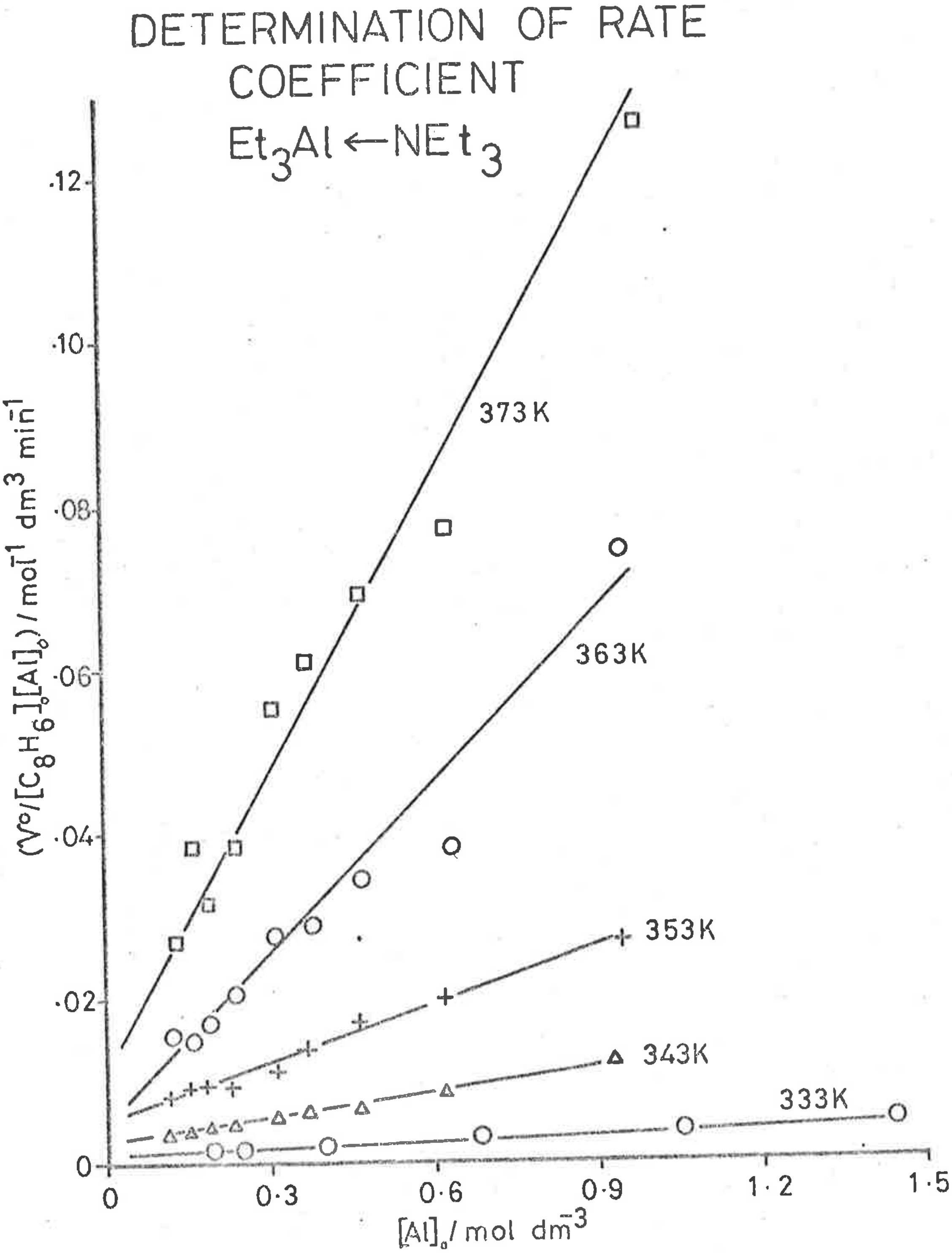

DETERMINATION OF RATE COEFFICIENT
$Et_3Al \leftarrow NBu_3$
378 K
373 K
363 K
353K
343K
$(V^o/[C_8H_6]_o[Al]_o)$ mol^{-1} dm^3 min^{-1}
·18
·15
·12
·09
·06
·03
0
0
0·2
0·4
0·6
0·8
1·0
$[Al]_o$/mol dm^{-3}

FIG. IV 13(a)



DETERMINATION OF RATE COEFFICIENT $Et_3Al \leftarrow NEt_3$

FIG. IV 13 (b)

IV.6.

Arrhenius plots for each trialkylamine complex are shown in Fig. IV.14 and the derived Arrhenius parameters are shown in Table IV.2.

TABLE IV.2.

Arrhenius Parameters

	$\log_{10}A/\mathrm{s}^{-1}$	$E/\mathrm{kJ\ mol}^{-1}$
$\mathrm{Et_3Al{\leftarrow}NEt_3}$	4.9	61.
$\mathrm{Et_3Al{\leftarrow}NBu_3}$	11.1	101.

It is pointless to try and calculate Arrhenius parameters for the ternary complex because any determined parameter depends on K_E, whose value is unknown. The value calculated using a single reaction path (mechanism (7)) is not valid as equation (7a) is not valid if a multiple reaction is occurring.

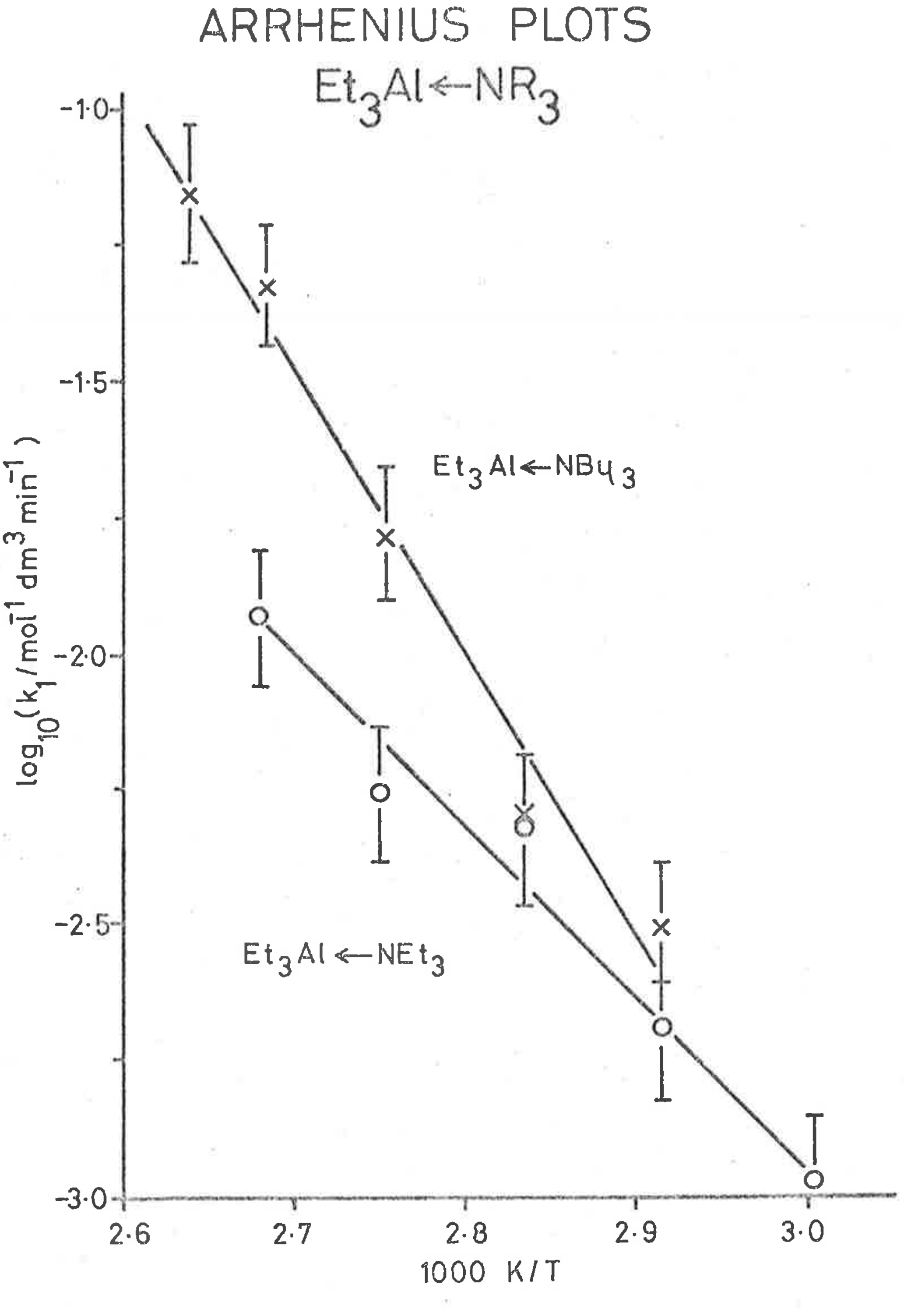
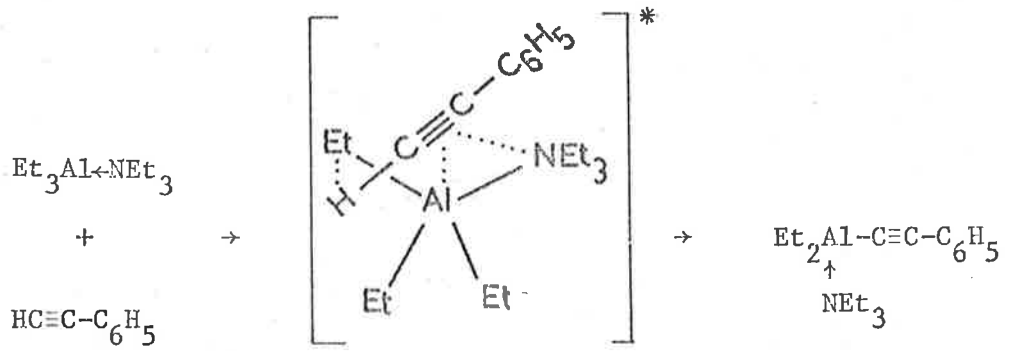

ARRHENIUS PLOTS
$Et_3Al \leftarrow NR_3$
$Et_3Al \leftarrow NBu_3$
$Et_3Al \leftarrow NEt_3$
$\log_{10}(k_1/mol^{-1}\,dm^3\,min^{-1})$
-1·0
-1·5
-2·0
-2·5
-3·0
2·6
2·7
2·8
2·9
3·0
1000 K/T

FIG. IV 14

7. DISCUSSION OF MECHANISM

Firstly, it can be seen that the overall reaction rate increases as the proton basicity of the amine increases in the order; pyridine $<$N,N,Diethylaniline$<NR_3$, thus confirming that the proton exchange rate is a function of the polarity of the aluminium-alkyl bond. How this correlates with the fact that additions are inhibited will be discussed in Section V.2. Secondly, the very large change in *A* factor and the substantial change in the energy of activation of the bimolecular reaction on changing from a triethylamine to a tri-n-butylamine donor suggest to us that the increased steric hindrance of the butyl group around the nitrogen forces a change in mechanism of the proton exchange.

It is suggested that for the bi-molecular triethylaluminium-triethylamine reaction with phenylacetylene a tight transition state is formed:



This is analogous to the four centre transition state postulated to exist for the lower alkene homologues when they react with triethylaluminium, and the similarity in the *A* factors is thereby accounted for.

Energies of activation are also of comparable values.

The high *A* factor for the $Et_3Al{\leftarrow}NBu_3$ bimolecular reaction with phenylacetylene is much harder to explain. Very little data are available on proton exchange reactions in non aqueous solutions, making direct comparisons impossible. It is nevertheless suggested that in non-interacting solvents, the proton exchange reaction between two molecules can be directly compared with hydrogen atom exchange. The latter are reasonably well documented, and while most hydrogen atom abstractions appear to have *A* factors around 10^{8-9}, Benson has estimated some to have *A* factors around 10^{11}. Such a reaction is the hydrogen exchange between ethane and ethylene:

$$C_2H_6 + C_2H_4 \rightarrow 2C_2H_5\cdot$$

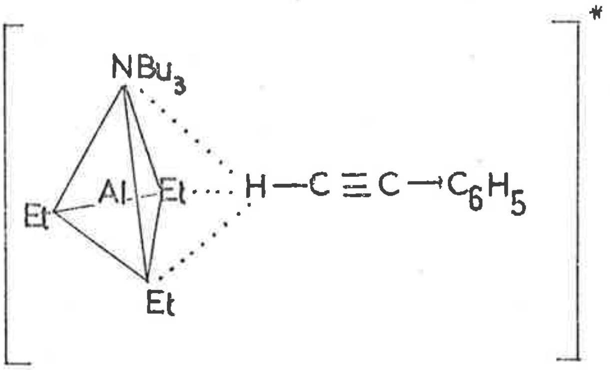
Recently Pacey[53] has also determined that the reaction

$$neoC_5H_{12} + CH_3^{\cdot} \rightarrow CH_4 + C_5H_{11}^{\cdot}$$

has an Arrhenius *A* factor of $10^{10.5}$. The high *A* factor in these hydrogen atom exchanges is explained by postulating a loose long range transition state involving change separation in which few, if any, degrees of freedom are lost. It is suggested that in the $Et_3Al{\leftarrow}NBu_3$ bimolecular reaction with phenylacetylene a similar situation exists.

IV.7.

$Et_3Al \leftarrow NBu_3$ + $HC{\equiv}C{-}C_6H_5$ →

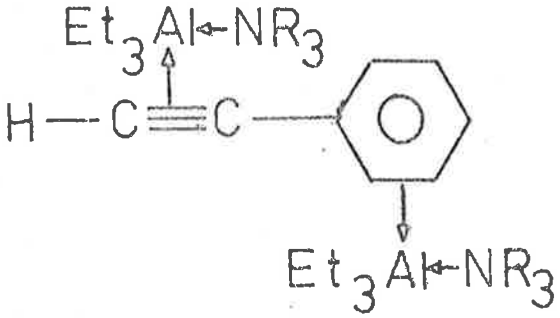


↓

$Et_2Al{-}C{\equiv}C{-}C_6H_5$ + EtH

The steric hindrance associated with the increased size of the butyl group is suggested to account for the non-formation of the tight transition state.

Not very much can be deduced about the reaction proceeding through the ternary complex from this kinetic study. A possibility for the structure of the complex is based on the fact that phenylacetylene has two electron donating areas.



IV.7.

This again postulates pentaco-ordinate aluminium, and while this is not entirely unknown, it is fairly rare. However, it seems impossible to visualize a complex containing both amine and alkyne without invoking a co-ordination number for aluminium of more than four.

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SECTION V

CONCLUSION

General summary - a summary of the data determined and mechanistic conclusions formed in the treatise.

Effect of complexing on the reactivity of organometallics with unsaturated compounds - The effect is different depending on which nucleophilic attack is rate determining. With lithium, the rate determining step is R^- attack on substrate. With aluminiums some rate determining steps appear to be the attack of substrate on Al. A published mechanism for the reaction of LiBu with ethylene in TMEDA is shown to be incorrect.

Conclusion - The reliability of data determined is discussed and several suggestions for further work are proposed.

V.1.

1. GENERAL SUMMARY

In this treatise, the kinetics of reactions occurring between triethylaluminium and alkenyl and alkynyl hydrocarbons have been examined, and mechanisms proposed. The reaction study of triethylaluminium with alkynes has been extended to include trialkylamine complexes of triethylaluminium.

In hydrocarbon solution it has been shown that alkynes and alkenes with an aromatic substituent form donor complexes with triethylaluminium. The complex has been characterized for phenylacetylene, and has been established as a π-donation from the alkynyl bond in both hex-3-yne and phenylacetylene. This previously unestablished postulate is thus confirmed.[20] The complex with styrene has been shown to be an aromatic π donation, which proved to be a general effect in mixtures of aromatic compounds and triethylaluminium. Unfortunately the experimental technique used to detect these complexes (p.m.r. spectroscopy) is not very sensitive. It was possible to estimate the enthalpy of formation for the phenylacetylene/triethylaluminium complex (32 kJ mol^{-1}), but it has not been possible to perform the extrapolation necessary to calculate the entropy with any degree of confidence. In the case of the styrene-triethylaluminium complex, not even the equilibrium constant could be determined from p.m.r. spectroscopic data, and it was necessary to evaluate it from deviations of kinetic relationships from simple limiting forms.

V.1.

The existence of a complex in the reaction solution introduces a three stage equilibrium prior to any possible reaction.

$$\begin{tikzcd}
\text{reaction} & A + B \arrow[l] \arrow[rr, shift left] \arrow[dr, shift left] & & C \arrow[ll, shift left] \arrow[r] \arrow[dl, shift left] & \text{reaction} \\
& & D + B \arrow[ul, shift left] \arrow[ur, shift left] \arrow[d] & & \\
& & \text{reaction} & &
\end{tikzcd}$$

The detailed kinetics of this type of system are quite complicated. We believe that the method developed to deal with this and other complicated systems involving multiple equilibrium calculations and numerical integration techniques on a large scientific computer, is the most comprehensive so far developed. A method proposed by Ball and Groenweghe[1] is superficially similar, but detailed examination reveals that their method uses numerical integration of each rate equation with approximate rate co-efficients as a first step, followed by a minimization procedure to obtain the least difference in the various calculated and experimental concentrations. Our method combines these two steps, and has the added advantage that complex equilibria, which have variables that cannot be separated, are easily accounted for.

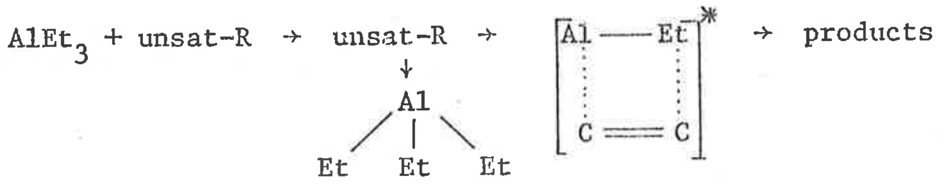
Rate parameters for the addition of triethylaluminium to the substrates investigated here are

V.1.

TABLE V.1.

	A	E/kJ mol^{-1}
styrene	$10^{4.5\pm0.3}$ dm^3 mol^{-1} s^{-1}	66.7
2-methyl-hept-1-ene	$10^{7.6\pm0.6}$ dm^3 mol^{-1} s^{-1}	95.0
phenylacetylene	$10^{11.6\pm0.9}$ s^{-1}	94

These and other published data on alkenes have been interpreted in terms of a π complex preceding a four-centre transition state. Formation of either can form the rate determining step.



It should be mentioned at this time that the chemical reaction paths have all been rationalized in terms of the Transition State Theory. While this is by far the best of the theories proposed, it is still not wholly secure. Many transition state models proposed to explain certain reaction systems cannot be extended to other, related, systems. For example, several alkyl radical reactions, presumably proceeding by similar mechanisms, have A factors differing by as much as 10^3.[2] Differences are usually explained as polar or steric effects. All kinetic data presented here, therefore, should be viewed in this light, and are thus subject to review should a more acceptable version of transition state theory appear.

These criticisms notwithstanding, we believe that the explanation presented here for the observed reaction rates for addition to alkenes and alkynes satisfactorily correlates the experimental parameters of each system.

2. EFFECT OF COMPLEXATION ON THE REACTIVITY OF ORGANOMETALLICS WITH UNSATURATED COMPOUNDS

The effect of co-ordinating solvents on the reactions of triethylaluminium were examined in Section IV, and it was shown that complexation effectively prevents the normal addition reactions occurring. Only in amines is the donating effect of the donor molecule strong enough to polarize the Al-Et bond to an extent large enough to offset the increased steric hindrance, and allow proton exchange to take place. On the other hand, complexation retards the addition. No evidence has been obtained that donor complexes of triethylaluminium react to add to unsaturated hydrocarbons, the reduced reaction rates in these systems arising from the small concentration of uncomplexed triethylaluminium present.

This mechanism for the reactions of triethylaluminiums with unsaturates hydrocarbons in co-ordinating solvents has been used as an analogy for the reaction of n-butyllithium with ethylene in the presence of N,N,N',N',-tetra-methylethylenediamine (TMEDA).[3] In order to examine the merits of this claim, it is necessary to first examine the general effect of solvation on reactions of metal alkyl compounds.

All reactions of the metals alkyls of groups I, II and III can be regarded as the full or partial heterolytic dissociation of the metal carbon bond, either as part of the reaction step or as a preliminary formation of ion pairs prior to reaction. For example, rearrangement of the triethylaluminium π complex to the four-centre complex can be regarded as a supplementary attack of a nucleophilic ethyl group to the carbon of the unsaturated molecule.

The energy of dissociation of the metal-carbon bond into its respective ions decreases with increasing polarity of the bond, and on this basis it can be seen that, if co-ordinating solvents increase the polarity of the metal-carbon bond, all reactions involving the dissociation of this bond as the rate determining step will have an increased rate in co-ordinating solvents. An increased polarity on solvation is, however, by no means a fully proven point. Rochow[4] *et al* state "Normally the effect of solvation is to decrease bond polarity by contribution of electrons from the electronegative donor atom of the solvent to the metal, but solvolytic dissociation into ion pairs may occur." However, it now appears that on solvation an increase in bond polarity occurs. Pauling[5] formulated this effect and stated that on specific solvation of the positive end of a dipole (metal) there is a change in valence of the metal atom, which is accompanied by a change in the spatial configuration of the molecule, interatomic distances, angles etc., the net result being an increase in the length of the metal-carbon bond, accompanied by the corresponding increase in bond polarity. Pauling's physical data relate to inorganic lattices, but the argument can still be applied to organometallic compounds. The second, and more definite effect of solvation on a metal-carbon bond, is that co-ordination favours the formation of ion pairs, and free ions.

V.2.

$$\overset{\delta+}{M} - \overset{\delta-}{R} \overset{K}{\rightleftarrows} M^{+}R^{-} \overset{K'}{\rightleftarrows} M^{+} + R^{-}$$

Solvation of the free ion stabilizes the charged species with respect to the polar bond, thus increasing the concentrations of ion pairs and free ions. It may also lead to charge separation in the transition state so that the entropy of activation in polar solvents is less negative.[6]

Thus, where the reaction involves the nucleophilic attack of a carbanion or alkyl group of the organometallic compound, the rate will be increased in complexing solvents. When the rate determining step is not a carbanionic attack, but a nucleophilic attack by the π electrons of the substate on the metal, the same argument does not apply. As mentioned previously, the donor molecule blocks the acceptor site on the metal and reaction via this mechanism is inhibited.

Lithium is less electronegative than aluminium or magnesium, and so covalent carbon-metal bonds will be more polar with lithium than aluminium or magnesium and ionic species will be more prevalent. Therefore carbanionic or nucleophilic attack of the alkyl group on the substrate is more likely, and nucleophilic attack of the substrate on the metal is less likely with alkyllithiums than with their magnesium and aluminium counterparts. Thus, with certain similar types of reaction, the effect of donor solvents on the reaction may be different in alkyllithiums (faster) and alkylaluminiums or alkylmagnesium compounds (slower), due to the occurrence of the first and second mechanisms respectively.

These views are substantiated by examples. The displacement reaction

$$nC_4H_9Li + RBr \rightarrow LiBr + nC_4H_9R$$

is 10^3 times faster in ether than in hexane.[7] The increased rate is probably due in part, as the authors claim, to the conversion of the hexamer to the dimer of n-butyllithium on complex formation, but this decrease in the degree of association cannot be the complete reason, as nucleophilic substitution reactions of R_2Zn and R_2Cd, which are monomeric, are also faster in ethers. The best example of this is metallation. Alkyl cadmium and zinc compounds metallate phenylacetylene faster in THF than in heptane or anisole.[8] This is similar to the alkyllithiums as the metallating ability of these compounds decreases in the solvent series THF>Et_2O> hydrocarbon.[9] In Section IV it was shown that the metallating ability of triethylaluminium complexes increases with increasing proton basicity of the donor. A similar situation also exists in alkyl magnesiums and Grignards.[10]

Most, if not all reactions of the main group metal alkyls with substrates that have low electron donating ability can thus be rationalized in terms of carbanionic attack and thus are favoured in co-ordinating solvents.

V.2.

Addition reactions of metal alkyls to unsaturated hydrocarbons do not appear to follow the same straightforward course as substitutions. The addition of n-butyllithium to diphenylacetylene takes place in diethylether, but not in pentane.[11] n-Butyllithium also adds to 1,1-diphenylethylene faster in THF than in hydrocarbons[18] and is accompanied by the development of a red colour, indicating the presence of a 1,1 diphenylalkyl anion.[12] The rates of initiation of styrene polymerization by n-butyllithium are also faster in ethers than in hydrocarbons.[14] Only one mol of ethylene adds to t-butyllithium in hydrocarbon, but in a ditertiary amine further ethylene molecules react.[13] All these increased rates have again been attributed to a breakdown of the BuLi hexamer on complexing. While this undoubtedly takes place, it is by no means the complete explanation. Other factors must be present. The additions of n-butyllithium to 1,1-diphenylethylene in 0.4% ether in benzene solution and THF have the same order of reaction with respect to n-butyllithium (0.5) in both solvents indicating that the position of the dissociation equilibria are similar. Nevertheless the overall rate co-efficients differ by 10^4, and so there must be a direct kinetic solvent effect acting on at least one of the elementary reaction steps involved.[15]

Aluminium alkyls have a decreased rate of reaction towards addition to unsaturated hydrocarbons in co-ordinating solvents (v.s.). It has also been shown that the donor complexes are completely unreactive

V.2.

towards addition to alkenes and alkynes. Data on the addition of Grignards to alkenes are scarce but it seems that a similar situation to aluminium exists. For example, RMgX polymerizes ethylene at 373K-393K in anisole, but no reaction occurs in ether.[16] Diethylmagnesium mixed with ethylene at 373K at high pressure left 63% $MgEt_2$ unreacted in ether solution but in hydrocarbon at 373K all the ethylene was polymerized to long chain hydrocarbon.[17]

Recently, Hay *et al* have postulated that the increase in reaction rate occurring when N,N,N',N'-tetramethylethylenediamine (TMEDA) is added to the n-butyllithium-ethylene system arises from reaction occurring via a small concentration of uncomplexed n-butyllithium. This is analogous to the mechanism that we proposed for the reaction of triethylaluminium with n-oct-1-ene in diphenylether solution. We believe argument by analogy is a dangerous principle in organometallic chemistry, especially as the mechanism of a given reagent is liable to change through a series of substrates, as is observed with triethylaluminium and alk-1-enes (Section II). In the light of the arguments presented here, we are convinced that this particular analogy is a false one. In the case of triethylaluminium, co-ordinating solvents retard or suppress the reaction because the concentration of uncomplexed, unassociated reagent ($AlEt_3$) is depressed by the addition of solvent, while the complex is unreactive. This explanation cannot be used to explain the *acceleration* of the reactions of n-butyllithium in the presence of TMEDA. This point is supported by the observation that some of the experimental results pre-

V.2.

sented are inconsistent with the published conclusion.

It is claimed that a zero order dependence of reaction rate (uptake of C_2H_4) on TMEDA concentration can be explained by assuming a reactive, undissociated monomeric lithium butyl species. Thus

$$\underset{C}{\text{LiBu TMEDA}} \overset{K}{\rightleftarrows} \underset{B}{\text{LiBu}_{\text{mon}}} + \underset{A}{\text{TMEDA}} \qquad \ldots.(1)$$

$$\text{LiBu}_{\text{mon}} + nC_2H_4 \xrightarrow{k} \text{Bu}(CH_2)_{2n}\text{Li}$$

and

$$K = [B][A]/[C]$$

$$d[D]/dt = k[B][D]$$

First order dependences on $[\text{LiBu}]_o$ and $[C_2H_4]_o$ were observed. If in fact the species LiBu_{mon} is reacting, the rate would depend on [TMEDA] at molar ratios LiBu>TMEDA as the varying concentrations of TMEDA will affect equilibrium (1), thus altering [B]. The equilibrium explanation presented for zero-order dependence presented is cyclic, proving nothing.

An unexplained solid appears when [LiBu]>[TMEDA] and the constant rate of ethylene uptake quoted does not arise until after this complex has been dissolved. A great deal could be occurring in the reaction system during this time, and it seems likely that the role of the unidentified intermediate cannot be ignored. Zero-order kinetics are not established in the early stages of the reaction when a simple mechanism involving only the prime reactants might be occurring. In addition, if any one of these possible species in the system is reactive at molar ratios LiBu>TMEDA, equilibrium (1) would still be affected, and so it is difficult to see how a zero order could arise under these conditions.

The Arrhenius parameters for the rate constant characterized by

$$-d[C_2H_4]/dt = k[C_2H_4][LiBu]_o$$

are erroneous, as the "true" rate constant proposed would be given by

$$-d[C_2H_4]/dt = k[C_2H_4][LiBu_{mon}]$$

It is well known that amine complexes of metal alkyls are very strong; thus the concentration of $LiBu_{mon}$ must be very small. Even if $[LiBu_{mon}]/[LiBu]_o$ is as high as 10^{-3}, the pre-exponential factor is raised from $10^{7.6}$ to $10^{10.6}$, which is very high for bimolecular reaction of this type. If, on the other hand, the LiBu-TMEDA complex is assumed to react, the pre-exponential factor as quoted ($10^{7.6}$) stands. This is more acceptable.

It can be argued that the ethylene complexes with $LiBu_{mon}$ and a unimolecular rearrangement takes place. The *A* factor for this reaction is the same as the bimolecular reaction because the concentration of ethylene in the system never varies a great deal from unity. $10^{10.6}$ s^{-1} is a reasonable *A* factor for this reaction (see Sections II, III). This explains the initial rapid uptake of ethylene but in no way explains the acceleration of the reaction in TMEDA.

Considering all of the arguments, it is difficult to escape the conclusion that the reactive species is a TMEDA complex of n-butyllithium. It appears probably that there are many equilibria present in solution, and their relationships will be very complicated, but there seems no reason for rejecting the concept of the high reactivity of chelate on kinetic grounds. This concept is well established. In discussing the TMEDA complex of n-butyllithium, Coates[19] states "The metal carbon bond is so strongly polarized that the complex may be regarded as the best source of highly reactive soluble carbanions currently available." The strong chelating ability of TMEDA will also increase the concentration of ion pairs and free ions, in addition to polarizing the M-R bond. The high reactivity of chelated n-butyllithium is thus accounted for.

V.3.

3. CONCLUSION

In this treatise, an attempt has been made to understand the factors influencing the reactivity of triethylaluminium. As is usual in most scientific investigations, more questions have been posed than answered.

It is felt that the reaction between triethylaluminium and alkenes has been characterized as completely as possible at the present stage of scientific knowledge. There is no reason to suppose that further work would seriously alter the conclusions given in Section II. Rate parameters for the reaction of triethylaluminium with cyclohexene appear to be anomalous, and further studies on this system are obviously warranted. The final establishment of numerical values of the kinetic parameters for any reactions involving dissociation of the triethylaluminium dimer, requires a third, completely independent, determination of the dissociation constant to resolve the continuing dichotomy of opinion that exists between Hay and Smith. This determination should be in both the liquid and vapour phase, and should be performed by an experimental method compatible with the two phases. Such a method could be a spectroscopic determination in the low frequency IR/high frequency microwave region.

The reaction of triethylaluminium with phenylacetylene has been kinetically characterized and the mechanism proposed is in keeping with that expected by analogy with alkenes. Further mechanistic proof should be obtained by studying the reaction between triethylaluminium and a non-terminal alkyne, so that no proton exchange can take place.

V.3.

On the other hand, the study of the reactions of triethylaluminium complexes carried out can at best be classified as preliminary. Much work has still to be done on the steric and electronic factors influencing proton exchange in non-aqueous solvents, as well as a complete characterization of aromatic π complexes with triethylaluminium. The only really quantitative work done in connection with the latter are the experiments performed by Smith[21] with triethylaluminium in mesitylene. Other nucleophilic substitutions of triethylaluminium complexes, such as reaction of alkyl halides should also be studied to aid the characterization of the Al-C bond. The mechanism for proton exchange must therefore be regarded as incomplete, and as such must be subjected to a critical review when other kinetic data become available.

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APPENDIX I - Polynomial Curve Fitting

General

This routine computes the nth degree polynomial of best fit (least squares criterion) to arbitrarily chosen data points $(x_i y_i)$ iterating on n from 1 to any desired maximum. The points may be weighted arbitrarily and the results may be printed or returned to the calling program. The algorithm is due to G.E. Forsythe, *J. Soc. Ind. Appl. Maths*, 5, (1957), 74. The routine may be obtained from the Program Library, University of Adelaide under the name LSQPOL.

Algorithm

The program computes iteratively the orthogonal polynomials defined by the distribution of $\{x_i\}$ thus;

$$Q_o(x_i) \equiv 1$$

$$Q_{k+1}(x_i) = (x_i - a_{k+1})Q_k(x_i) - b_{k+1}Q_{k-1}(x_i)$$

where

$$a_{k+1} = J_{k+1}/I_{k+1}, \quad b_{k+1} = I_{k+1}/I_k$$

$$I_{k+1} = \sum_i w_i \, [Q_k(x_i)]^2$$

$$J_{k+1} = \sum_i w_i \cdot x_i \, [Q_k(x_i)]^2$$

and if

$$Q_{k+1}(x) = \sum_{j=0}^{k+1} C_j^{k+1} \, x^j$$

then

$$C_j^{k+1} = C_{j-1}^k - a_{k+1} C_j^k - b_{k+1} C_j^{k-1}$$

where

$$0 < k$$

$$0 < j < k+1 \text{ and } C_o^o = 1$$

$$C_m^n = 0 \text{ if } n>m \text{ or } n<0 \text{ or } m<0$$

then

$$\sum_i w_i Q_k(x_i) Q_j(x_i) = \delta_{jk} I_{k+1}$$

and the required polynomials are: $P_k(x)$ where

$$P_k(x) = \sum_{j=0}^{k} d_j Q_j(x)$$

$$d_j = K_{j+1}/I_{j+1}$$

$$K_{j+1} = \sum_i w_i y_i Q_j(x_i)$$

The iterative formula for the sum of squares of the deviations is

$$E_{-1} = \sum_i w_i y_i^2$$

$$E_j = E_{j-1} - (K_{j+1})^2/I_{j+1}$$

APPENDIX II - Alkene Rate Co-efficients

The first part of this program computes the numerical solution to give $x = f(y)$ while the second part calculates the rate co-efficient for the addition of triethylaluminium to 2-methylhept-1-ene from the initial concentrations of each component in the system and the series p.m.r. integrals of each component with time.

The algorithm is based on the standard integrals;

$$\int \frac{\mathrm{d}x}{(ax^2+bx+c)(fx+g)} = \frac{1}{2(cf^2-gbf+g^2a)} \cdot \left[f.\ln\left[\frac{(fx+g)^2}{(ax^2+bx+c)}\right]\right]$$

$$+ \frac{2ga-bf}{2(cf^2-gbf+g^2a)} \cdot \int \frac{\mathrm{d}x}{(ax^2+bx+c)}$$

$$\int \frac{\mathrm{d}x}{(ax^2+bx+c)} = \frac{1}{(b^2-4ac)^{\frac{1}{2}}} \ln\left[\frac{2ax+b-(b^2-4ac)^{\frac{1}{2}}}{2ax+b+(b^2-4ac)^{\frac{1}{2}}}\right] \quad (b^2<4ac)$$

$$= \frac{2}{(4ac-b^2)^{\frac{1}{2}}} \arctan\left[\frac{2ax+b}{(4ac-b^2)^{\frac{1}{2}}}\right] \quad (b^2<4ac)$$

$$= -\frac{2}{2ax+b} \qquad (b^2=4ac)$$

The program then computes the 90% confidence limits for each kinetic run (Subroutine NINTYC) and, in addition to printing the data, also displays it as a line printer plot (Subroutine QIKPLT).

```
      PROGRAM KINT(INPUT,OUTPUT)
      DIMENSIONVINM(20),ALM(20),Y(40),YI(40),FN(20),YCL1(20),YCL2(20),TI
     2ME(20),Z(20,3 ),ZI(20,3),FN5(20),YCL3(20),YCL4(20)
     $,X(20),YC(20)
      COMMON A,C(21),D(200),TITLE(7)
      COMMON/PARAS/T(20),W(200)
      DATA(W(I),I=1,200)/200.,199*1./
      DATA(T(I),I=1,12)/6.31,2.92,2.35,2.13,2.01,1.94,1.89,1.86,1.83,1.8
     $1,1.80,1.78/
      REAL NAPM,NAP,NAPWT
       INTEGER TN
   63 READ104,TITLE
        IF(TITLE(1).EQ. 10H          )  GO TO99
  104 FORMAT(7A10)
      READ101,AK33,N
C   N IS NO OF TUBES AT THIS TEMP
      DO1KL=1,N
      READ 102,NAPWT,HT,TN
  101 FORMAT(F10.2,I2)
  102 FORMAT(2F10.2,I2)
      VOL=0.1353*HT
      NAPM=NAPWT/160*1000/VOL
      READ103,NAP,VINT,ALINT,TIME(1)
      VINM(1)=NAPM*VINT/NAP*2.5
      ALM(1)=NAPM*ALINT/NAP*0.83333
      DO2J=2,15 /
      READ103,NAP,VINT,        TIME(J)
  103 FORMAT(4F5.2)
      IF(NAP.EQ.0)GO TO 5
    2 VINM(J)=NAPM*VINT/NAP*2.5
    5 J=J-1
      CALLLSQPOL(J,TIME,VINM,W,1,33,4,0,2,0)
      DO7I=1,J
      YI(I)=VINM(I)
    7 YI(I+J)=D(1)
      IF(D(1).LE.D(2)) CALLLSQPOL(J,TIME,VINM,W,1,33,4,0,1,0)
      VINM(1)=C(1)
      TOT=ALM(1)+VINM(1)+NAPM
      AK3=AK33*TOT
       AX=(-1.+SQRT(1.+4.*(2./AK3*ALM(1))))/(2.*(2./AK3))
      FN(1)=0.
      X(1)=YC(1)=0.
      DO 10 I=2,J
      YC(I)=VINM(1)-VINM(I)
   10 CONTINUE
      NN=1
       DO20 I=1,J
       IF(YC(I)) 20,21,21
   21 X(NN)=X(I)
      YC(NN)=YC(I)
      CON=AX-YC(NN)
      B=2*CON+AK3/2
      CX=-AK3*((ALM(I)-AX)/2)+CON**2
      IF((B**2-4*CX).LT.0 ) GO TO 20
       X(NN )=(-B+SQRT(B**2-4*CX))/2
      NN=NN+1
   20 CONTINUE
       J=NN-1
      CALL LSQPOL(J,YC,X,W,1,33,4,0,2,1)
      IF(C(3).LT.0) GO TO 44
       AAA=C(3) $ BB=C(2)-1
       CC=AX+C(1)     $   FF=-1
       GG=VINM(1)
        DO 11 I=1,J
      XX=AAA*YC(I)**2+BB*YC(I)+CC
      FN1=1/(2*(CC+GG*BB+GG**2*AAA))
      FN2=FF*ALOG((FF*YC(I)+GG)**2/XX)
      FN3=(2*GG*AAA-BB*FF)*FN1
       DEL=BB**2-4*AAA*CC
       IF(DEL)13,14,15
   13 FN11=2/SQRT(-DEL)
      FN12=ATAN((2*AAA*YC(I)+BB)/SQRT(-DEL))
      FN4=FN11*FN12
      GO TO  11
   14 FN4=-2/(2*AAA*YC(I)+BB)
      GO TO 11
   15 FN11=1/SQRT(DEL)
      FN12=2*AAA*YC(I)+BB-SQRT(DEL)
      FN13=2*AAA*YC(I)+BB+SQRT(DEL)
      FN4=ALOG(FN12/FN13)*FN11
        FN5(I)=FN1*FN2+FN3*FN4
         IF(I.EQ.1) GO TO 11
         FN(I)=FN5(I)-FN5(1)
   11 CONTINUE
        GO TO 49
   44 CALL LSQPOL(J,YC,X,W,1,33,4,0,1,1)
      AA=C(2)-1
       BB=AX
        DD=VINM(1)
       DO45I=1,J
       FN1=1/(-BB-AA*DD)
      FN2=ALOG((-YC(I)+DD)/(AA*YC(I)+BB))
      FN5(I)=FN1*FN2
       IF(I.EQ.1) GO TO45
       FN(I)=FN5(I)-FN5(1)
   45 CONTINUE
   49 CALLNINTYC(TIME,FN,J,1,YCL1,YCL2,SPE)
      SLO=C(2)
      PRINT29,TITLE,TN,ALM(1),VINM(1),NAPM
   29 FORMAT(1H1,47X,7A10/54X,*TUBE*,4X,I2/42X,*INITIAL CONCENTRATIONS-M
     2OLES/LITRE*///23X,*ORGANOMETALLIC*,10X,*ALKENE*,11X,*COMPLEXER*,1
     31X,*INERT SOLVENT*//25X,3(E10.3,10X)//28X,*KINETIC RESULTS*/7X,*TI
     $ME*,1
     45X,*ALKENE*,,15X,*PRODUCT*,11X,*INTEGRATED FN*,11X,*90 PC CONFIDEN
     5CE LIMITS*/7X,*HRS*,15X,*M/L*,18X,*M/L*/10X,*COMPLEX KINETICS*)
      DO8I=1,J
    8 PRINT27,TIME(I),YI(I),FN(I),YCL1(I),YCL2(I)
   27 FORMAT(4X,2(E12.5,8X)20X,3(E12.5,8X))
      PRINT28,SLO
   28 FORMAT(//46X,*SLOPE-INTEGRATED FN VS TIME =*,G12.5)
      CALL QIKPLT(TIME,FN,J,-1,11H*TIME(HRS)*,11H*INTEGR.FN*)
    1 CONTINUE
      GO TO 63
   99 STOP
      END
      NOLIST
      SUBROUTINE NINTYC(X,Y,N,IS,YCL1,YCL2,SPE)
      DIMENSIONX(1),Y(1),YCL1(1),YCL2(1),YA(20)
      COMMON/PARAS/T(20),W(200)
      COMMON A,C(21),D(200),TITLE(7)
      CALLLSQPOL(N,X,Y,W,1,33,4,0,1,15)
      SUMX=SUMY=SUMX2=SUMXY=SUMD=SUMT=0
      DO1I=1,N
      SUMX=SUMX+X(I)
      SUMY=SUMY+Y(I)
      SUMX2=SUMX2+X(I)**2
    1 SUMXY=SUMXY+X(I)*Y(I)
      SPE=(N*SUMXY-SUMX*SUMY)/(N*SUMX2-SUMX**2)
        SPE=C(2)
      AVX=SUMX/N
      AVY=SUMY/N
      DO2I=1,N
```

```
      YA(I)=AVY+C(2)*(X(I)-AVX)
      DIF=(ABS(Y(I)-YA(I)))**2
    2 SUMD=SUMD+DIF
      S=SQRT(SUMD/N)
      M=N-2
      DO3I=1,N
    3 SUMT=SUMT+(X(I)-AVX)**2
       DO 33 I=1,N
      YCL1(I)=YA(I)+T(M)*S*SQRT((1./N)+(X(I)-AVX)**2/SUMT)
   33 YCL2(I)=YA(I)-T(M)*S*SQRT((1./N)+(X(I)-AVX)**2/SUMT)
      RETURN
      END
```

APPENDIX III - Alkyne Rate Co-efficients

LSQMN, FFORM, YGRAPH, LSQMIN, LINMIN and CALFUN, comprise the standard non linear least squares package written by E.A. Beals at UCLA, U.S.A. in 1965. We modified the package as follows.

Subroutine KIN does the calculations necessary to give values of z, x and y, as functions of time. This was performed using the standard IBM subroutine POLRT which computes the real and complex roots of a real polynomial.

FFORM contains the function form to be fitted. In this case it is the integrated form of equations (12), (13), or (17) in Section III. These integrals have no algebraic solution and so the numerical integration subroutine RK2 calculates and supplies values for the integrated form of the rate equation. RK2 uses the function DYDX to provide the differential equation to be integrated.

```
      PROGRAM LSQMN (INPUT,OUTPUT,TAPE2=INPUT,TAPE3=OUTPUT)
      LOGICAL IWRITE
      COMMON A,C(21),D(200),TITLE(7),AYC(21),YA(21),COM,ALM,PA,AKA
      COMMON /MIN/ W
      COMMON /FUN/ Y,WI,T,M1
      DIMENSION X(20),E(20),F(200),Y(200),WI(200),W(4850),T(10,500)
      DIMENSION YC(200),CHAR(12),S(20),XBEST(20)
      DIMENSION AY(30),TIME(30)
    1 READ (2,5) N,INDP,M,IWGT,ISCALE,IPRINT,IDIFER,IGRAPH,IPERT,MAXFUN
      IF(EOF,2)57,58
   57 STOP
   58 CONTINUE
      READ(2,15) TEMP
    5 FORMAT (16I5)
      KS=0
      IDF=IDIFER
      IGP=IGRAPH
      IWRITE=.FALSE.
      IF (IPRINT .LE. 0) GO TO 6
      IPRINT=IPRINT-1
      IWRITE=.TRUE.
    6 READ(2,7)  TITLE
      READ(2,15)    EK,R,VTOT,ALM,PA,AK,AKA
      EK1=EK-VTOT
      CONS=EK1/22.41*(273+TEMP)/273/76*2/VTOT
    7 FORMAT(7A10)
      MAXFUN=1000-MAXFUN
      ESCALE=10.0**(6-ISCALE)
      M1=2
   15 FORMAT (8E10.0)
       DO2I=2,M
      READ(2,15) HT,RAT,T(1,I)
      AY(I)=RAT*PA*2.5/11.416
      TIME(I)=T(1,I)
       WI(I)=1.0
    2 Y(I)=(HT-R)*CONS
       TIME(1)=0.
       AY(1)=0.
      WI(1)=1.0
       Y(1)=T(1,1) =0.
   30 CONTINUE
      CALL LSGPOL(M,TIME,AY,V,1,33,4,0,6,0)
      DO16I=1,7
   16 AYC(I)=C(I)
      CALL KIN(M,TIME,CONS,AY,Y,PA,ALM,AK,COM)
   50 READ (2,15) (X(I),I=1,N)
      WRITE (3,55)
   55 FORMAT (21H0THE INITIAL GUESS IS)
      WRITE (3,75) (X(I),I=1,N)
      DO 10 I=1,N
      XBEST(I)=X(I)
      E(I)=1.0/ESCALE
   10 CONTINUE
      E(I)=X(I)/ESCALE
      M1=1
      DUMMY=FFORM(X,T,M1)
      M1=2
      CALL CALFUN (M,N,F,X)
      WRITE (3,60)
   60 FORMAT (21H0AT THE INITIAL GUESS)
   63 CONTINUE
      IF (IDIFER .EQ. 0) GO TO 70
      WRITE (3,65)
   65 FORMAT (78H0INDEPENDENT VARIABLE--DATA VALUE--CALCULATED VALUE--WE
     *IGHT--DIFFERENCE--RATIO)
   70 CHISQ=0.0
      DO 80 K=1,M
      CHISQ=CHISQ+F(K)*F(K)
      DIFFER=F(K)/WI(K)
      YC(K)=Y(K)-DIFFER
      RATIO=DIFFER/YC(K)
      IF (IDIFER .NE. 0) WRITE (3,75) (T(I,K),I=1,INDP),Y(K),YC(K),WI(K)
     *,DIFFER,RATIO
   75 FORMAT (10E13.5)
   80 CONTINUE
      WRITE (3,85) CHISQ
   85 FORMAT (11H0AND CHISQ=,E13.5)
      IF ((IGRAPH .NE. 0) .AND. (INDP .EQ. 1)) CALL YGRAPH(M,T,Y,YC)
   87 IF (M1 .EQ. 3) GO TO 100
      IF (M1 .EQ. 4) GO TO 1
      FBEST=CHISQ
   88 CALL LSGMIN (M,N,F,X,E,ESCALE,IPRINT,MAXFUN)
      M1=3
      DUMMY=FFORM(X,T,M1)
      IF (IWRITE) GO TO 89
      IDIFER=0
      IGRAPH=0
      GO TO 63
   89 WRITE (3,90)
   90 FORMAT (20H1AT THE FINAL VALUES)
      WRITE (3,95) KS
   95 FORMAT (37H0THE PARAMETERS AT THE MINIMUM OF THE,I3,9H STEP ARE)
      WRITE (3,320) (X(I),I=1,N)
      GO TO 63
  100 IF (CHISQ .GE. FBEST) GO TO 200
      FBEST=CHISQ
      DO 110 I=1,N
      XBEST(I)=X(I)
  110 CONTINUE
  200 IF (KS .GE. IPERT) GO TO 300
      KS=KS+1
      MM=(KS+1)/2
      SUM=0.0
      DO 210 I=1,N
      MN=MOD(I,MM)+MOD(KS,2)
      S(I)=2*MOD(MN,2)-1
      SUM=SUM+S(I)*S(I)
  210 CONTINUE
      SUM=1.0/SQRT(SUM)
      DO 220 I=1,N
      X(I)=X(I)*(1.0+.001*S(I)*SUM)
  220 CONTINUE
      IF (.NOT. IWRITE ) GO TO 88
      WRITE (3,225) KS
  225 FORMAT (16H1PERTURBED X FOR,I3,4H TRY)
      WRITE (3,320) (X(I),I=1,N)
      GO TO 88
  300 IDIFER=IDF
      IGRAPH=IGP
      M1=4
      CALL CALFUN (M,N,F,XBEST)
      WRITE (3,310)
  310 FORMAT (24H1AT THE BEST FINAL STEP /9H0XBEST IS)
      WRITE (3,320) (XBEST(I),I=1,N)
  320 FORMAT (10E13.5)
      GO TO 63
      END
      FUNCTION DYDX(X,Y,AK)
       DIMENSION AK(2)
      COMMON A,C(21),D(200),TITLE(7),AYC(21),YA(21),COM,ALM,PA,AKA
      ADY=AYC(1)+AYC(2)*X+AYC(3)*X**2+AYC(4)*X**3+AYC(5)*X**4+AYC(6)*X**
```

```
     $5+AYC(7)*X**6
       Z=C(1)+C(2)*X+C(3)*X**2+C(4)*X**3+C(5)*X**4+C(6)*X**5+C(7)*X**6
      DYDX=AK(I)*(ALM-COM/2-Z/2-Y/2)*(PA-COM-ADY-Z-Y)
      RETURN  $END
       SUBROUTINE KIN(N,TIME,CONS,ADD,ETH,PA,ALM,AK,COM)
       DIMENSION TIME(30),ETH(30),ADD(30),Z(30),XCOF(4),COF(4),ROOTR(3),
     $ROOTI(3)
      COMMON A,C(21),D(200),TITLE(7)
      AAX=-2*ALM-2*PA+2/AK
      BBX=4*ALM*PA+PA*PA
      CCX=-2*ALM*PA*PA
      XCOF(1)=CCX$XCOF(2)=BBX$XCOF(3)=AAX$XCOF(4)=1.
      CALL POLRT(XCOF,COF,3,ROOTR,ROOTI,IER        )
       COM=ROOTR(1)
       PRINT104,TITLE,PA,ALM,COM
  104 FORMAT(1H1,30X,7A10//20X*INITIAL CONCS*//50X*PHEN ACET*5X*ALET3*3X
     $*COMPLEX*5X*Z*//50X,3E10.3/20X*REACTION CONCS*)
        DO13I=2,N
      AX=ALM-COM/2-ETH(I)/2
      BX=PA-COM-ETH(I)-ADD(I)
      CX=COM-ADD(I)
       AAX=-2*BX-2*AX+2/AK
      BBX=4*AX*BX+BX*BX+4*CX/AK
      CCX=-2*AX*BX*BX+2*CX*CX/AK
      XCOF(1)=CCX$XCOF(2)=BBX$XCOF(3)=AAX$XCOF(4)=1.
      CALL POLRT(XCOF,COF,3,ROOTR,ROOTI,IER ,      )
        Z(I)=ROOTR(1)
      AXX=AX+Z(I)/2$BXX=BX+Z(I)    $CXX=CX-Z(I)
   13 PRINT105 ,I,BXX,AXX,CXX,Z(I),TIME(I)
        Z(1)=0.
  105 FORMAT(46X,I2,2X,5E10.3)
      CALL LSGPOL(N,TIME,Z,W,1,33,4,0,6,0)
      RETURN
      END
      FUNCTION FFORM(X,T,M1)
      DIMENSION  X(2)
       DIMENSION VEC(1)
      COMMON A,C(21),D(200),TITLE(7),AYC(21),YC(21),COM,ALM,PA
      EXTERNAL DYDX
      H=T/20
      CALL RK2(DYDX,H,0.,0., 20,1,VEC,X)
      FFORM=VEC(1)+X(2)
      RETURN$END
      SUBROUTINERK2(FUN,H,XI,YI,K,N,VEC,XX)
     DIMENSION VEC(1)    ,XX(2)
     COMMON A,C(21),D(200),TITLE(7),AYC(21),YC(21),COM,ALM,PA
      H2=H/2
     Y=YI
     X=XI
     DO2I=1,N
     DO1J=1,K
     T1=H*FUN(X,Y,XX)
     T2=H*FUN(X+H2,Y+T1/2.,XX)
     T3=H*FUN(X+H2,Y+T2/2.,XX)
     Y=Y+(T1+2.*T2+2.*T3+T4)/6.
    1 X=X+H
    2 VEC(I)=Y
     RETURN$END
     SUBROUTINE YGRAPH(M,X,Y,YFIT)
     DIMENSION X(10,1),Y(1),YFIT(1)
     DATA IFFF,IBBB,IOOO,IPPP/1HF,1H ,1HO,1HP/
     YMIN=Y(1)
     YMAX=Y(1)
     DO 3 I=1,M
     IF(YMIN .GT .  Y(I))  YMIN=Y(I)
     IF(YMAX .LT. Y(I))  YMAX=Y(I)
```

```
      IF (YMIN .GT. YFIT(I)) YMIN=YFIT(I)
      IF (YMAX .LT. YFIT(I)) YMAX=YFIT(I)
    3 CONTINUE
      WRITE (3,1005) YMIN,YMAX
 1005 FORMAT (1H1,15X,E13.5,87X,E13.5/19X,101HIIIIIIIIIIIIIIIIIIIIIIIII
     1IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII
     1IIIIIIIIII    )
      DO 1100 I=1,M
      IO=1.0+100.0*(Y(I)-YMIN)/(YMAX-YMIN)
      IO=MAX0(MIN0(IO,100),1)
      IP=1.0+100.0*(YFIT(I)-YMIN)/(YMAX-YMIN)
      IP=MAX0(MIN0(IP,100),1)
      IF (IO .NE. IP) GO TO 1030
      IF (IO .NE. 1) GO TO 1020
      WRITE (3,1010) X(1,I),IFFF
 1010 FORMAT (1X,E13.5,6H     -,100A1)
      GO TO 1100
 1020 K=IO-1
      WRITE (3,1010) X(1,I),(IBBB,J=1,K),IFFF
      GO TO 1100
 1030 IPP=IPPP
      IOO=IOOO
      IF (IP .GT. IO) GO TO 1040
      IPP=IOOO
      IOO=IPPP
      IDUMMY=IO
      IO=IP
      IP=IDUMMY
 1040 IF (IO .GT. 1) GO TO 1060
      IF (K .GT. 0) GO TO 1050
      WRITE (3,1010) X(1,I),IOO,IPP
      GO TO 1100
 1050 CONTINUE
      WRITE (3,1010) X(1,I),IOO,(IBBB,J=1,K),IPP
      GO TO 1100
 1060 K1=IO-1
      K2=IP-IO-1
      IF (K2 .GT. 0) GO TO 1070
      WRITE (3,1010) X(1,I),(IBBB,J=1,K1),IOO,IPP
      GO TO 1100
 1070 CONTINUE
      WRITE (3,1010) X(1,I),(IBBB,J=1,K1),IOO,(IBBB,J=1,K2),IPP
 1100 CONTINUE
      WRITE (3,1110) YMIN,YMAX
 1110 FORMAT (19X,101HIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII
     1IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII  /16X,E13.5,87
     2X,E13.5)
      WRITE (3,1120)
 1120 FORMAT (33HOP REPRESENTS THE PREDICTED POINT/28H00 REPRESENTS THE
     1DATA POINT/73H0F REPRESENTS BOTH THE DATA AND THE PREDICTED POINTS
     2 IF THEY LIE TOGETHER/1H1)
      RETURN
      END
C       LSQMIN
      SUBROUTINE LSQMIN (M,N,F,X,E,ESCALE,IPRINT,MAXFUN)
      DIMENSION F(1),X(1),E(1),W(4850)
      COMMON /MIN/ W
      LOGICAL STOP,MAXCAL,CONTIN,FIRST
C  D(I,J)=W(KST+(I-1)*(N+M)+J)  LINEARLY IN DEPENDENT DIRECTION
C  G(I,K)=W(KST+(I-1)*(N+M)+N+K)  APPROXIMATE COMPONENT OF THE GRADIENT
C        IN THE DIRECTION OF D(I,J)
C  G-1(I,J)=W(KINV+I-1+(J-1)*N-J*(J-1)/2)  I GREATER EQUAL J   INVERSE
C         OF G*GT
C  Q(I)  COMPONENT OF D(I,J) IN THE DIRECTION OF SEARCH
C  STEP(I)=SUM OF Q(J)*D(J,I) J=1,N  DIRECTION OF SEARCH
```

```
C     P(I)=-SUM OF G(I,K)*F(K) K=1,M
C     INITIALIZE
      STOP=.FALSE.
      MAXCAL=.FALSE.
      IPP=IPRINT*(IPRINT-1)
      ITC=0
      IPC=0
      MPLUSN=M+N
      KST=N+MPLUSN
      NPLUS=N+1
      KINV=NPLUS*(MPLUSN+1)
      KSTORE=KINV-MPLUSN-1
      NN=N+N
      K=NN
C     INITIAL FUNCTION EVALUATION
      CALL CALFUN (M,N,F,X)
      MC=1
      FF=0.0
      DO 1 I=1,M
      K=K+1
      W(K)=F(I)
      FF=FF+F(I)*F(I)
    1 CONTINUE
      FOLD=FF
  100 FIRST=.TRUE.
      K=KST
      I=1
C     COMPUTE THE COMPONENTS OF THE GRADIENT IN THE COORDINATE DIRECTIONS
    2 XDUMMY=X(I)
      ISMALL=0
      DUMMY=ABS(X(I)*1.E-6)+E(I)
    5 X(I)=X(I)+DUMMY
      CALL CALFUN (M,N,F,X)
      MC=MC+1
      X(I)=XDUMMY
      DO 3 J=1,N
      K=K+1
      W(K)=0.
      W(J)=0.
    3 CONTINUE
      SUM=0.
      KK=NN
      DO 4 J=1,M
      KK=KK+1
C     FPLUS-FBEST
      F(J)=F(J)-W(KK)
      SUM=SUM+F(J)*F(J)
    4 CONTINUE
      IF (SUM .GT. FF*1.E-12) GO TO 6
      WRITE (3,7) I
    7 FORMAT (5X,3HTHE,I3,58H-TH COMPONENT OF THE INITIAL STEP WAS TO
     1MALL  DOUBLE IT)
      DUMMY=2.0*DUMMY
      ISMALL=ISMALL+1
      K=K-N
      IF (ISMALL .LT. 15) GO TO 5
      ITC=0
      K=NN
      DO 8 I=1,M
      K=K+1
      F(I)=W(K)
    8 CONTINUE
      GO TO 10
C     SUM IS USED TO NORMALIZE G(I,K) AND D(I,J)
    6 SUM=1.0/SQRT(SUM)
      ISMALL=0
      J=K-N+I
C     W(J) IS D(I,I)  NOTE D(I,J)=0.0 J NOT EQUAL TO I
      W(J)=DUMMY*SUM
      DO 9 J=1,M
      K=K+1
C     W(K) IS G(I,K) IN THE COORDINATE DIRECTIONS
      W(K)=F(J)*SUM
      KK=NN+J
      DO 11 II=1,I
      KK=KK+MPLUSN
C     W(II) IS G*GT(I,II)
      W(II)=W(II)+W(KK)*W(K)
   11 CONTINUE
    9 CONTINUE
      ILESS=I-1
      IGAMAX=N+I-1
      INCINV=N-ILESS
      INCINP=INCINV+1
      IF (ILESS .GT. 0) GO TO 14
C     INVERSE OF G*GT(II,JJ) II,JJ=1,I  BY HOUSEHOLDER METHOD
C           RECALL (I-1)X(I-1) UPPER BLOCK ALREADY DONE
      W(KINV)=1.0
      GO TO 15
   14 B=1.
      DO 16 J=NPLUS,IGAMAX
      W(J)=0.
   16 CONTINUE
      KK=KINV
      DO 17 II=1,ILESS
      IIP=II+N
C     W(IIP)=W(N+II) IS THE SUM OF G-1(II,J)*G*GT(J,I) J=1,N
      W(IIP)=W(IIP)+W(KK)*W(II)
      JL=II+1
      IF (JL .GT. ILESS) GO TO 19
      DO 20 JJ=JL,ILESS
      KK=KK+1
      JJP=JJ+N
      W(IIP)=W(IIP)+W(KK)*W(JJ)
      W(JJP)=W(JJP)+W(KK)*W(II)
   20 CONTINUE
C     B IS G*GT(I,I)-SUM OF G*GT(I,II)*G-1(II,JJ)*G*GT(JJ,I)
C           WHICH IS A0
   19 B=B-W(II)*W(IIP)
      KK=KK+INCINP
   17 CONTINUE
      B=1./B
      KK=KINV
      DO 21 II=NPLUS,IGAMAX
      BB=-B*W(II)
      DO 22 JJ=II,IGAMAX
C     W(KK) IS G-1(II,JJ)  WHICH EQUALS A1-1+A1-1*A2*A0-1*A3*A1-1
      W(KK)=W(KK)-BB*W(JJ)
      KK=KK+1
   22 CONTINUE
C     W(KK) IS G-1(I,II) WHICH EQUALS -A0-1*A3      WHICH EQUALS G-1(II,I)
      W(KK)=BB
      KK=KK+INCINV
   21 CONTINUE
C W(KK) IS G-1(I,I) WHICH EQUALS A0-1
      W(KK)=B
   15 IF ( .NOT. FIRST) GO TO 27
      I=I+1
      IF ( I .LE. N) GO TO 2
C     0-TH ITERATION INITIALIZATION
      FIRST=.FALSE.
```

```
      ISAME=0
      FF=0.
      KL=NN
      DO 26 I=1,M
      KL=KL+1
      F(I)=W(KL)
      FF=FF+F(I)*F(I)
   26 CONTINUE
      CONTIN=.TRUE.
   27 IPC=IPC-IPRINT
      IF (IPC .GE. 0) GO TO 29
C  ITERATION PRINTOUT
   28 WRITE (3,30) ITC,MC,FF
   30 FORMAT (//5X,9HITERATION,I4,I9,16H CALLS OF CALFUN,5X,2HF=,E24.9/
     15X,9HVARIABLES)
      WRITE (3,31) (X(I),I=1,N)
   31 FORMAT (5E24.9)
   32 FORMAT (5X,9HFUNCTIONS)
      WRITE (3,32)
      WRITE (3,31) (F(I),I=1,M)
      IPC=IPP
      IF (STOP) GO TO 33
C  CONVERGENCE TESTS
C  1 N+1 VALUES OF F ARE THE SAME
C  2  MAXIMUM OF STEP(I)/E(I)  LESS THAN OR EQUAL TO 1.0  (CONTIN FALSE)
C  3  MAXIMUM OF THE I-TH COMPONENT OF THE ACTUAL STEP TAKEN / E(I)
C        LESS THAN OR EQUAL TO 1.0         CHANGE LESS THAN OR EQUAL TO 1
   29 IF (CHANGE .NE. 0.0) ISAME=0
      ISAME=ISAME+1
      IF (ISAME .LE. N) GO TO 291
      IF (IPRINT .LE. 0) GO TO 33
      WRITE (3,295)
  295 FORMAT (//5X,28HN+1 VALUES OF F ARE THE SAME)
      IF (FF .GE. FOLD) GO TO 10
      FOLD=FF
      K=NN
      DO 293 I=1,M
      K=K+1
      W(K)=F(I)
  293 CONTINUE
      GO TO 100
  291 IF (CONTIN) GO TO 34
      IF (CHANGE .GT. 1.0) GO TO 36
   10 IF (IPRINT .LE. 0) GO TO 33
C  TERMINAL PRINTOUT
      WRITE (3,38)
   38 FORMAT (//5X,46HLSQMIN FINAL VALUES OF FUNCTIONS AND VARIABLES)
      STOP=.TRUE.
      GO TO 28
   33 RETURN
   36 CONTIN=.TRUE.
C  START NEXT ITERATION
   34 ITC=ITC+1
      K=N
      KK=KST
C  CALCULATION OF P
      DO 39 I=1,N
      K=K+1
      W(K)=0.
      KK=KK+N
      W(I)=0.
      DO 40 J=1,M
      KK=KK+1
C  W(I) IS THE SUM OF G(I,K)*F(K) WHICH IS -P(I)
      W(I)=W(I)+W(KK)*F(J)
   40 CONTINUE
   39 CONTINUE
      DM=0.
      K=KINV
C  CALCULATION OF Q
      DO 41 II=1,N
      IIP=II+N
C  W(IIP)=W(N+II) IS THE SUM OF G-1(II,J)*(-P(J)) 4=1,N  WHICH IS -Q(I)
      W(IIP)=W(IIP)+W(K)*W(II)
      JL=II+1
      IF (JL .GT. N) GO TO 43
      DO 44 JJ=JL,N
      JJP=JJ+N
      K=K+1
      W(IIP)=W(IIP)+W(K)*W(JJ)
      W(JJP)=W(JJP)+W(K)*W(II)
   44 CONTINUE
      K=K+1
C  MAXIMUM OF P(I)*Q(I)      KL INDEX OF THE DIRECTION OF D(I,J)
C        TO BE REPLACED BY STEP(J)
   43 IF (DM .GE. ABS(W(II)*W(IIP))) GO TO 41
      DM=ABS(W(II)*W(IIP))
      KL=II
   41 CONTINUE
      II=N+MPLUSN*KL
      CHANGE=0.
      DO 46 I=1,N
      JL=N+I
      W(I)=0.
      DO 47 J=NPLUS,NN
      JL=JL+MPLUSN
C  W(I) IS THE SUM OF (-G(J))*D(J,I) J=1,N   WHICH IS -STEP(I)
      W(I)=W(I)+W(J)*W(JL)
   47 CONTINUE
      II=II+1
C  INTERCHANGING KL AND N ROWS OF D(I,J) PUT XBEST IN D(N,J)
      W(II)=W(JL)
      W(JL)=X(I)
C  CHANGE IS THE MAXIMUM OF ABS(STEP(I)/E(I))
      IF (ABS(E(I)*CHANGE) .GT. ABS(W(I))) GO TO 46
      CHANGE=ABS(W(I)/E(I))
   46 CONTINUE
      DO 49 I=1,M
      II=II+1
      JL=JL+1
C  INTERCHANGING KL AND N ROWS OF G  PUT FBEST IN G(N,K)
      W(II)=W(JL)
      W(JL)=F(I)
   49 CONTINUE
      FC=FF
      ACC=0.1/CHANGE
      IT=3
      XC=0.
      XL=0.
      IS=3
      XSTEP=-AMIN1(0.5,ESCALE/CHANGE)
      IF (CHANGE .LE. 1.0) CONTIN=.FALSE.
C  LINEAR SEARCH
   51 CALL LINMIN (IT,XC,FC,6,ACC,0.1,XSTEP)
      IF (IT .NE. 1) GO TO 53
      MC=MC+1
      IF (MC .LE. MAXFUN) GO TO 54
      WRITE (3,56) MAXFUN
   56 FORMAT (5X,I6,16H CALLS OF CALFUN)
      MAXCAL=.TRUE.
      GO TO 53
   54 XL=XC-XL
```

```
      DO 57 J=1,N
      X(J)=X(J)+XL*W(J)
   57 CONTINUE
      XL=XC
      CALL CALFUN (M,N,F,X)
      FC=0.
      DO 58 J=1,M
      FC=FC+F(J)*F(J)
   58 CONTINUE
      IF (IS .NE. 3) GO TO 59
      K=N
C  DETERMINATION OF SECOND BEST POINT
      IF (FC-FF) 61,51,62
   61 IS=2
      FMIN=FC
      FSEC=FF
      GO TO 63
   62 IS=1
      FMIN=FF
      FSEC=FC
      GO TO 63
   59 IF (FC .GE. FSEC) GO TO 51
      K=KSTORE
      IF (IS .EQ. 2) GO TO 74
      K=N
   74 IF (FC-FMIN) 65,51,66
   66 FSEC=FC
      GO TO 63
   65 IS=3-IS
      FSEC=FMIN
      FMIN=FC
   63 DO 67 J=1,N
      K=K+1
      W(K)=X(J)
   67 CONTINUE
      DO 68 J=1,M
      K=K+1
      W(K)=F(J)
   68 CONTINUE
      GO TO 51
   53 K=KSTORE
      KK=N
C  IF IS=2  XBEST AND FBEST LIE IN W(N+   ) SECOND BEST X AND X LIE IN
C  W(KSTORE+    )=D(N,J)  AND G(N,K)
C  IF IS IS NOT 2 XBEST AND FBEST LIE IN W(KSTORE+    )AND THE SECOND BES
C        LIE IN W(N+     )
      IF (IS .NE. 2) GO TO 69
      K=N
      KK=KSTORE
   69 SUM=0.
      DM=0.
      JJ=KSTORE
      DO 71 J=1,N
      K=K+1
      KK=KK+1
      JJ=JJ+1
C  XBEST INTO X
      X(J)=W(K)
C  XBEST-XSECOND INTO D(N,J)
      W(JJ)=W(K)-W(KK)
   71 CONTINUE
      DO 72 J=1,M
      K=K+1
      KK=KK+1
      JJ=JJ+1
C  FBEST INTO F
      F(J)=W(K)
C  FBEST-FSECOND  INTO G(N,K)
      W(JJ)=W(K)-W(KK)
      SUM=SUM+W(JJ)*W(JJ)
      DM=DM+F(J)*W(JJ)
   72 CONTINUE
      IF (MAXCAL) GO TO 10
      J=KINV
      KK=NPLUS-KL
      DO 76 I=1,KL
      K=J+KL-I
      J=K+KK
C  INTERCHANGE KL AND N ROWS OF G-1
      W(I)=W(K)
      W(K)=W(J-1)
   76 CONTINUE
      IF (KL .GE. N) GO TO 78
      KL=KL+1
      JJ=K
      DO 79 I=KL,N
      K=K+1
      J=J+NPLUS-I
      W(I)=W(K)
      W(K)=W(J-1)
   79 CONTINUE
      W(JJ)=W(K)
      B=1./W(KL-1)
      W(KL-1)=W(N)
      GO TO 88
   78 B=1./W(N)
   88 K=KINV
C  DETERMINE A1-1 FROM G-1  FOR USE IN CALCULATING NEW G-1
      DO 80 I=1,ILESS
      BB=B*W(I)
      DO 81 J=I,ILESS
C  W(K) IS G-1(I,J) WHICH IS A1-1=B1-B2*B4-1*B3
      W(K)=W(K)-BB*W(J)
      K=K+1
   81 CONTINUE
      K=K+1
   80 CONTINUE
      IF (FMIN .LT. FF) GO TO 82
      CHANGE=0.0
      GO TO 84
   82 FF=FMIN
C  CHANGE IS THE MAXIMUM OF THE COMPONENTS OF THE ACTUAL STEP TAKEN
C        DIVIDED BY THE COMPONENTS OF E
      CHANGE=ABS(XC)*CHANGE
   84 XL=-DM/FMIN
C  SUM IS USED TO NORMALIZE G(N,K) AND D(N,J)
      SUM=1.0/SQRT(SUM+DM*XL)
      K=KSTORE
      DO 85 I=1,N
      K=K+1
C  W(K) IS D(N,J) THE STEP TAKEN PROPERLY NORMALIZED
      W(K)=SUM*W(K)
      W(I)=0.
   85 CONTINUE
      DO 86 I=1,M
      K=K+1
C  W(K) IS G(N,K) WHICH IS (FBEST-FSECOND+(SUM OF (FBEST-FSECOND)*FBEST/
C        FMIN)*FBEST)  NORMALIZED
      W(K)=SUM*(W(K)+XL*F(I))
      KK=NN+I
      DO 87 J=1,N
```

```
      KK=KK+MPLUSN
C  W(J) IS THE N-TH ROW OF G*GT
      W(J)=W(J)+W(KK)*W(K)
   87 CONTINUE
   86 CONTINUE
      GO TO 14
      END
C       LINMIN
      SUBROUTINE LINMIN(ITEST,X,F,MAXFUN,ABSACC,RELACC,XSTEP)
      GO TO (1,2,2),ITEST
    2 IS=6-ITEST
      ITEST=1
      IINC=1
      XINC=XSTEP+XSTEP
      MC=IS-3
      IF (MC) 4,4,15
    3 MC=MC+1
      IF (MAXFUN .GE. MC) GO TO 15
      ITEST=4
   43 X=DB
      F=FB
      IF (FB .LE. FC) GO TO 15
      X=DC
      F=FC
   15 RETURN
    1 GO TO (5,6,7,8),IS
    8 IS=3
    4 DC=X
      FC=F
      X=X+XSTEP
      GO TO 3
    7 IF (FC-F) 9,10,11
   10 X=X+XINC
      XINC=XINC+XINC
      GO TO 3
    9 DB=X
      FB=F
      XINC=-XINC
      GO TO 13
   11 DB=DC
      FB=FC
      DC=X
      FC=F
   13 X=DC+DC-DB
      IS=2
      GO TO 3
    6 DA=DB
      DB=DC
      FA=FB
      FB=FC
   32 DC=X
      FC=F
      GO TO 14
    5 IF (FB .LT. FC) GO TO 16
      IF (F .GE. FB) GO TO 32
      FA=FB
      DA=DB
   19 FB=F
      DB=X
      GO TO 14
   16 IF (FA .LE. FC) GO TO 21
      XINC=FA
      FA=FC
      FC=XINC
      XINC=DA
      DA=DC
      DC=XINC
   21 XINC=DC
      IF ((D-DB)*(D-DC) .LT. 0.0) GO TO 32
      IF (F .GE. FA) GO TO 24
      FC=FB
      DC=DB
      GO TO 19
   24 FA=F
      DA=X
   14 IF (FB .GT. FC) GO TO 29
      IINC=2
      XINC=DC
      IF (FB .EQ. FC) GO TO 45
   29 D=(FA-FB)/(DA-DB)-(FA-FC)/(DA-DC)
      IF (D*(DB-DC) .LT. 0.0) GO TO 33
      D=0.5*(DB+DC-(FB-FC)/D)
      IF ((ABS(D-X) .GT. ABS(ABSACC)) .AND. (ABS(D-X) .GT. ABS(D*RELACC)
     1)) GO TO 36
      ITEST=2
      GO TO 43
   36 IS=1
      X=D
      IF ((DA-DC)*(DC-D)) 3,26,38
   38 IS=2
      GO TO (39,40),IINC
   33 IS=2
      GO TO (41,42),IINC
   39 IF (ABS(XINC) .GE. ABS(DC-D)) GO TO 3
   41 X=DC
      GO TO 10
   40 IF (ABS(XINC-X) .GT. ABS(X-DC)) GO TO 3
   42 X=0.5*(XINC+DC)
      IF ((XINC-X)*(X-DC) .GT. 0.0) GO TO 3
      GO TO 26
   45 X=0.5*(DB+DC)
      IF ((DB-X)*(X-DC) .GT. 0.0) GO TO 3
   26 ITEST=3
      GO TO 43
      END
C       CALFUN
      SUBROUTINE CALFUN (M,N,F,X)
      DIMENSION X(1),F(1),Y(200),WI(200),T(10, 500)
      COMMON /FUN/ Y,WI,T,M1
      DO 10 K=1,M
      F(K)=(Y(K)-FFORM(X,T(1,K),M1))*WI(K)
   10 CONTINUE
      RETURN
      END
```

APPENDIX IV - Plotting Programm PLOTT

PLOTT is a versatile program designed to produce any size plots within the limits of the Calcomp 10" Plotter. Any number of functions containing up to 100 prints can be plotted as a line or as symbols. Up to 12 different types of symbols may be used in any one function for composite plots. The routine provides automatic scaling and choice of origin. The co-ordinate axes are annotated and the user may specify titles for each axis as well as a main and a subsidiary title. The user may also elect to have the plot produced on blank paper and with a Rapidograph pen.

Each function can be displayed in many ways:

1) A point plot for the function (symbols only)

2) A point plot, plus a 3rd order spline-interpolated, nth order, polynomial-fitted line. The spline interpolation is necessary because at high degrees a polynomial tends to oscillate between data points.

3) A point plot plus a 3rd order spline fitted line (through all the points).

4) A 3rd order spline interpolated nth order polynomial fitted line only.

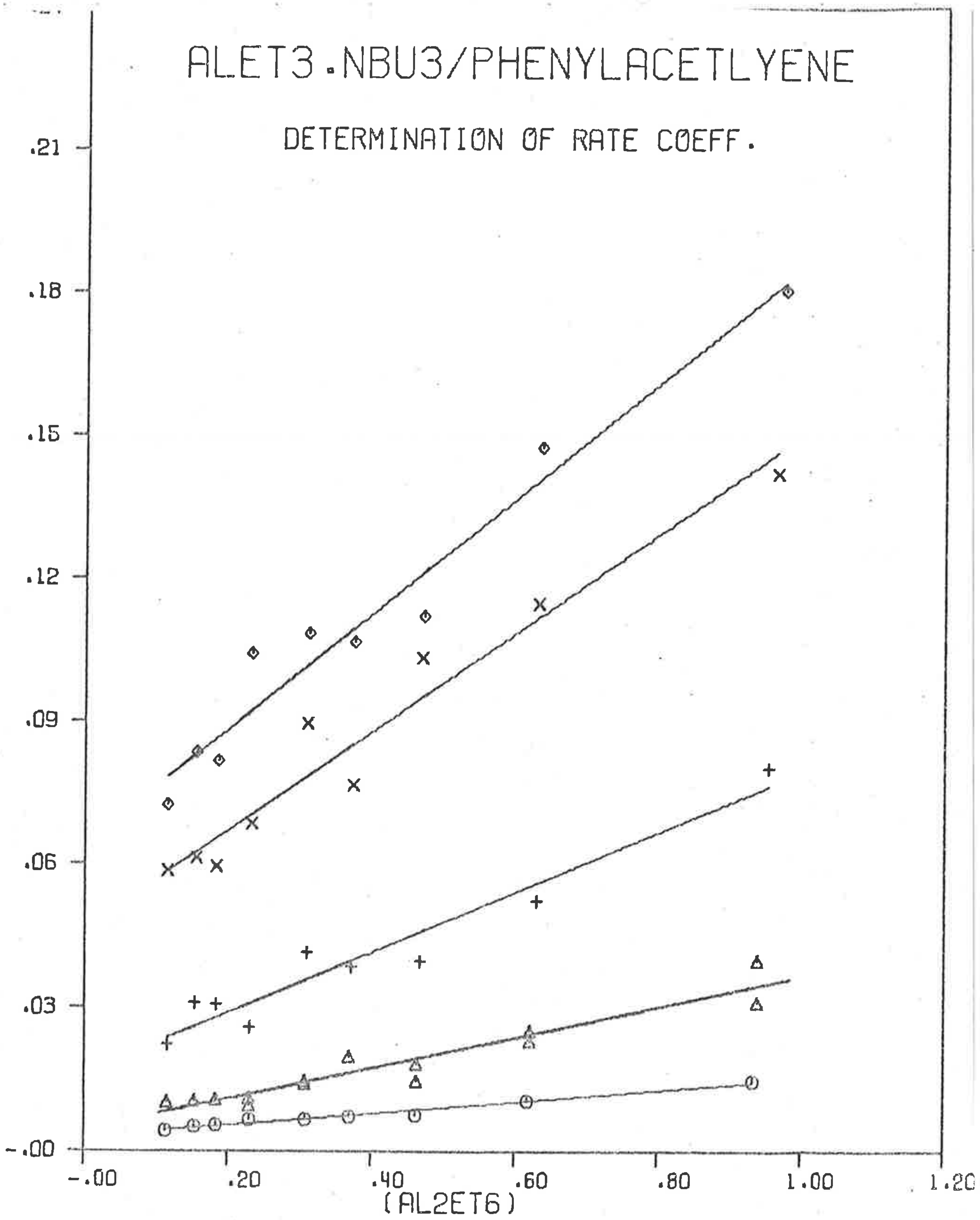
5) A 3rd order spline fitted line only.

Each function on the graph may also be described in a legend alongside the plot.

```
      PROGRAM PLOTT(INPUT,OUTPUT)
C
C     PLOTT IS A VERSITILE PLOTTING PROGRAM TO PRODUCE PLOTS ON A 10
C     INCH CALCOMP PLOTTER. FOR A FULL EXPLAINATION OF VARIABLES AND
C     OPTION USE CONSULT THE WRITE UP.  WRITTEN BY R LOUGH 1971.
C
      DIMENSION XTITLE(7),YTITLE(7),STITLE(7),GTITLE(7),XBCD(7),
     1YBCD(7),SBCD(7),GBCD(7),XM(4),YM(4),X(100),Y(100),XX(100),YY(100),
     2XC(2000),YC(2000),NOP(12),S(110),SX(100),SY(100),ZBCD(7),ZTITLE(7)
      COMMON A,C(21),D(200),TITLE(7)

C
C     READ NO OF JOBS AND CONTROL PARAMETER
C     CONTROL=0. - GRAPH AND BIRO PEN    CONTROL=1. - BLANK PAPER AND
C     BLACK INK PEN
C
      READ1,NJ,PLOTYPE
    1 FORMAT(40I2)
      CALL PLOTS(5HSCJGM,5)
      XK=40.0*(NJ+1)
      CALL XLIMIT(XK)
      IF(PLOTYPE.EQ.0) GO TO 20
      CALL PAUPLOT(26HBLNK PPR,0.3MM,BLK INK PLS,26)
C
C     START OF LOOP FOR EACH PLOT
C
   10 DO 130 J=1,NJ
C
C     READ LENGHS OF AXES AND NO OF LINES ON GRAPH
C
      READ2,XAXIS,YAXIS,NL
    2 FORMAT(2F4.1,I2)
C
C     READ TITLES OF X,Y AXES AND MAIN TITLE
C
      READ3,XTITLE,YTITLE,STITLE ,ZTITLE
    3 FORMAT(4(7A10/))
      CALL INKHAR(XTITLE,XBCD,NX)
      CALL INKHAR(YTITLE,YBCD,NY)
      CALL INKHAR(STITLE,SBCD,NS)
      CALL INKHAR(ZTITLE,ZBCD,NZ)
      DO 20 IT=1,7
   20 TITLE(IT)=STITLE(IT)
      READ4,XM(1),XM(2),YM(1),YM(2),HT
    4 FORMAT(8F10.0)
C
C     READ MIN AND MAX VALUES OF X,Y AXES RESPECTIVLY AND HEIGHT OF
C     CHARACTERS IN MAIN TITLE
C
      CALL SCALE(XM,XAXIS,2 ,1)
      CALL SCALE(YM,YAXIS,2 ,1)
      CALL AXIS(0.,0.,XBCD,-NX,XAXIS,0.,XM(3),XM(4),0)
      CALL AXIS(0.,0.,YBCD,NY,YAXIS,90.,YM(3),YM(4),-1)
      XLEG=XAXIS+2.0
      YLEG=YAXIS/2
      HT1=0.66*HT
      SSZ=(NZ-1)*(6*HT1/7)+4*HT1/7
      SM=(NS-1)*(6*HT/7)+4*HT/7
      SZ=(XAXIS-SM)/2
      SSZ=(XAXIS-SSZ)/2
      YA=YAXIS-0.5
      YY1=YA-0.5
      CALL SYMBOL(SZ,YA,HT,SBCD,0.,NS)
      CALL SYMBOL(SSZ,YY1,HT1,ZBCD,0.,NZ)
      CALL SYMBOL(XLEG,YLEG,0.1,6HLEGEND,0.,6)
      XLEG=XLEG-1.0
      YLEG=YLEG-0.25
      M=0
C
C     START OF LOOP FOR EACH LINE ON PLOT
C
      DO 120 J=1,NL
C
C     READ NO OF TYPES OF POINTS ON NTH LINES,POLYNOMIAL ORDER OF FIT
C     IF APPLICABLE,SWITCH FOR FIT THROUGH ORIGIN OR NOT,KEY FOR
C     COMINATION OF LINE AND SYMBOLS REQUIRED AND WHETHER POLYNOMIAL,
C     3RD ORDER SPLINE OR NO FIT IS REQUIRED ON THIS LINE
C
      READ1,NTP,NPOL,IS,ISYM,IFIT
      IF(J.AND.NTP.GT.1 ) YLEG=YLEG-0.1
      READ1,(NOP(I),I=1,NTP)
      NA=0
      DO 30 I=1,NTP
   30 NA=NA+NOP(I)
C
C     READ IN VALUES OF X,Y FOR THIS LINE
C
      READ4,(X(I),I=1,NA)
      READ4,(Y(I),I=1,NA)
      N=0
C
C     START OF LOOP FOR EACH TYPE OF POINT ON LINE
C
      DO 60 K=1,NTP
      L=NOP(K)
      DO 40 KA=1,L
      N=N+1
      XX(KA)=X(N)
   40 YY(KA)=Y(N)
      XX(L+1)=XM(3)
      XX(L+2)=XM(4)
      YY(L+1)=YM(3)
      YY(L+2)=YM(4)
      M=M+1
      IF(ISYM.EQ.1)GO TO 50
      CALL LINE(XX,YY,NOP(K),1,-1,M)
C
C     READ IN TITLE FOR LEGEND IDENTIFICATION
C
   50 READ5,GTITLE
    5 FORMAT(7A10)
      CALL INKHAR(GTITLE,GBCD,NG)
      YLEG =YLEG-0.15
      XXLEG=XLEG+2.5
      CALL SYMBOL(XLEG,YLEG,0.07,GBCD,0.,NG)
   60 CALL SYMBOL(XXLEG,YLEG,0.07,M,0.,-1)
      IF(IFIT)100,70,80
   70 CALL LSQPOL(NA,X,Y,W,1,00,4,0,NPOL,IS)
      GO TO 100
   80 DO 90 NI=1,NA
   90 D(NI)=Y(NI)
      CALL FIT(NA,X,D,S,SX,SY,100,XC,YC)
  100 NC=(NA-1)*100+1
      XC(NC+1)=XM(3)
      XC(NC+2)=XM(4)
      YC(NC+1)=YM(3)
      YC(NC+2)=YM(4)
      IF(ISYM)120,110,110
  110 CALL LINE(XC,YC,NC,1,0,0)
```

```
  120 CONTINUE                                                          PLT  655
      CALL PLOT(0.,YAXIS,3)                                             PLT  660
      CALL PLOT(XAXIS,YAXIS,2)                                          PLT  665
      CALL PLOT(XAXIS,0.,2)                                             PLT  670
      PLB=YAXIS/2.+0.3                                                  PLT  675
      PLA=XAXIS+0.7                                                     PLT  680
      PLC=PLA+3.1                                                       PLT  685
      PLD=YLEG-0.25                                                     PLT  690
      CALL PLOT(PLA,PLB,3)                                              PLT  695
      CALL PLOT(PLA,PLD,2)                                              PLT  700
      CALL PLOT(PLC,PLD,2)                                              PLT  705
      CALL PLOT(PLC,PLB,2)                                              PLT  710
      CALL PLOT(PLA,PLB,2)                                              PLT  715
      PLX=XAXIS+5.0                                                     PLT  720
  130 CALL PLOT(PLX,0.,-3)                                              PLT  725
      STOP                                                              PLT  730
      END                                                               PLT  735
      SUBROUTINEINKHAR(ATITLE,ABCD,N)                                   INK   05
C                                                                       INK   10
C     A SUBROUTINE FOR CODING THE TITLES FOR PLOT PRIOR TO USE BY       INK   15
C     SYMBOL                                                            INK   20
C                                                                       INK   25
      DIMENSION ATITLE(7),ABCD(7)                                       INK   30
      M=MTEST=10H                 $ N=0                                 INK   35
      CALL ZERO(ABCD,7)                                                 INK   40
      MTEST=KHAR(ATITLE,1)                                              INK   45
      DO1I=2,122                                                        INK   50
      M=KHAR(ATITLE,I)                                                  INK   55
      IF(M.EQ.MTEST)GO TO 2                                             INK   60
      N=N+1                                                             INK   65
    1 CALL KHIN(ABCD,I-1,M)                                             INK   70
    2 RETURN                                                            INK   75
      END                                                               INK   80
      SUBROUTINE ZERO(ABCD,N)                                           ZER   05
C                                                                       ZER   10
C     A SUBROUTINE TO BLANK THE TITLE HOLDING ARRAYS USED BY INKHAR      ZER   15
C                                                                       ZER   20
       DIMENSION ABCD(12)                                               ZER   25
      DO1 I=1,N                                                         ZER   30
    1 ABCD(I)=10H                                                       ZER   35
      RETURN                                                            ZER   40
      END                                                               ZER   45
```



TYPICAL OUTPUT FROM
PLOTT

APPENDIX V

Published Papers

THE INFLUENCE OF COORDINATING SOLVENTS AND COMPLEXING AGENTS ON THE ADDITION REACTIONS OF ORGANOMETALLIC COMPOUNDS

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(Received March 20th, 1973)

SUMMARY

The influence of coordinating solvents on the addition reactions of trialkylalumiums, where the reaction is retarded, and alkyllithium, where reactivity is enhanced, is discussed. Since the mechanisms of the reaction of the two reagents are different, analogies drawn are likely to be misleading.

The addition reactions of trialkyaluminiums with alkenes are inhibited in coordinating solvents. We have recently shown[1] that the reaction of triethylaluminium with 1-octene in diphenyl ether (one of the few which forms a complex weak enough for reaction to be observed) proceeds from the small concentration of uncomplexed monomeric Et_3Al in equilibrium with the complexed species.

On the other hand, it is well known that the addition reactions of alkyllithiums with alkenes are faster in coordinating basic solvents[2-6]. Complexes of alkyllithiums with chelating diamines are reputed to be the most reactive organolithium compounds available[6].

Our mechanism for the reactions of triethylaluminium with alkenes in diphenyl ether solutions has been used as analogy for the reaction of n-butyllithium with ethylene in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA)[5]. We believe argument by analogy is a dangerous principle in organometallic chemistry. The reaction mechanism of a given reagent is liable to change through a series of substrates, as we have observed with triethylaluminium and unsaturated hydrocarbons[7,8]. We are convinced that this particular analogy is a false one. In the case of triethylaluminium, coordinating solvents retard (or suppress) the reaction, because the concentration of the uncomplexed, unassociated reagent (Et_3Al) is depressed by the addition of the solvent (Sv) and the complexed reagent ($Et_3Al \leftarrow Sv$) is unreactive. This explanation cannot be used to explain the *acceleration* of the reactions of butyllithium in the presence of TMEDA. The mechanism proposed[5], that uncomplexed, unassociated reagent (BuLi) is responsible for the reaction, is untenable since its concentration will be depressed in the presence of TMEDA due to the formation of the complex BuLi · TMEDA.

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On consideration of basic reactivities it is difficult to escape the conclusion that the reactive species is a TMEDA complex of butyllithium. It appears probable that there are a number of such complexes and the equilibrium relationships will be most complicated. Only simple cases have been tested so far, or indeed could be tested against the limited kinetic data at present available. There is thus no reason for rejecting the well-established concept of the high reactivity of chelated complexes on kinetic grounds.

The difference of behaviour of alkylaluminium and lithium compounds on the addition of coordinating solvents is not surprising. In the former case it is well-established that the addition reaction with alkenes proceeds through a π-complex in a reaction step which either precedes[8,10] or constitutes[8] the rate-controlling step. This appears to be the only reaction path available when the reaction is an insertion in a covalent metal–carbon bond, and it is obviously not open when the vacant coordination on Al is occupied as is the case in $Et_3Al \leftarrow Sv$. Where the reaction involves a carbanion or paired carbanion, different factors are involved. In general coordinating solvents will increase the concentration of free carbanions and the looser, more reactive ion pairs, thereby increasing the overall reaction rate. This is probably the explanation of the high reactivity of the chelated butyllithium.

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