KINETICS OF REACTIONS BETWEEN TRIETHYLALUMINIUM AND 1-ALKENES

A Thesis submitted by

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This thesis is a record of research work investigated in the Department of Physical and Inorganic Chemistry at the University of Adelaide between February 1966 and August 1969. The material contained within this thesis is original throughout, except where due reference has been made.

Alan E. Byers

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SYNOPSIS

A review of reactions between trialkylaluminiums and 1-olefins has been attempted, with particular emphasis on the kinetic information of the growth reaction, derived by previous workers. Some criticism has been levelled at previous authors on the basis of errors in practical and theoretical technique.

The kinetics of the addition reaction between triethylaluminium and 1-octene has been studied in detail, utilising proton magnetic resonance spectroscopy as the kinetic tool. Reaction rate constants were evaluated at five temperatures between 95° and 120°C and the Arrhenius parameters calculated.

An investigation of the monomer-dimer equilibrium of triethylaluminium has been performed. An applied ebulliometric technique was used to estimate the dimer dissociation constant, K_d, at several temperatures in the range 80° to 125°C. The knowledge of both K_d and the derived heat of dissociation has enabled correction of the pure system rate constants and Arrhenius parameters for dimer dissociation.

A kinetic study of the complexed triethylaluminium and 1-octene reaction has been performed with rate constants at five temperatures between 100° and 120°C and accompanying Arrhenius parameters tabulated.

The stoichiometry of the triethylaluminium-ether complex used above has been determined by proton magnetic resonance and the equilibrium constant for complex formation derived.

CHAPTER I - GENERAL INTRODUCTION

The Importance of Trialkylaluminiums

Although organoaluminium compounds were prepared[1] in the mid nineteenth century, their true contribution to scientific research and technology was not realised until the nineteen fifties. In 1955, K. Ziegler[2] developed the direct synthesis of aluminium alkyls by one or two stage processes.

(a) $Al + \frac{3}{2} H_2 + 3\ C_nH_{2n} \rightarrow Al(C_nH_{2n+1})_3$

(b) $Al + \frac{3}{2} H_2 + 2\ AlR_3 \rightarrow 3\ R_2AlH$

$3\ R_2AlH + 3\ C_nH_{2n} \rightarrow 3\ R_2AlC_nH_{2n+1}$.

These methods provided economically feasible syntheses for commercial use. Combined academic and industrial research illustrated the value of trialkylaluminiums as:

compounds for the synthesis of hitherto difficult-to-prepare organic compounds, such as starting materials for the synthesis of other alkyl compounds by processes which are economical compared with Grignard reactions;

intermediate catalysts, e.g. for ethylene oligomerisation;

co-catalyst with transition metal compounds for stereo-regular polymerisation (the Ziegler-Natta Catalyst);

catalysts, cocatalysed by water or quinones, for vinyl polymerisation and copolymerisation.

Bonding in Organoaluminium Compounds

The bonding configurations of organoaluminium compounds are unusual and could not be immediately solved by conventional theory. The aluminium M shell has four orbitals occupied by three electrons, which tends to produce compounds in which the shell of the metal atom is unsaturated. Thus aluminium, with its lack of d electrons and limited tendency to form multiple bonds, can adopt a variety of bonding situations to compensate for its electron deficiency and unsaturated coordination. The octet-configuration stability can be achieved by the direct acceptance of electrons from donor molecules, by the formation of bridging compounds, with an electron donating atom as part of the bridge or by dimerisation by formation of electron deficient (Al-C-Al) bridge bonds. These electron deficient bonds are covalent and contain less than two electrons per bond. These three centre bonds were a departure from classical valence theory, but are now generally accepted and are believed to be responsible for metal-metal bonding in certain classes of compound.

The reactivity of organoaluminium compounds is a result of the electronegativity of the aluminium atom itself. To clarify, aluminium is assigned a Pauling electronegativity of 1.5. This is reflected in the reactivity of the aluminium-carbon bond, which is intermediate between that in the highly reactive alkyl compounds of elements of Groups I(A) and II(A) and the more unreactive alkyls of elements in the II(B), III(B), IV(B) and V(B) sub-groups. The former are more electropositive ranging from about 0.8 to the more electronegative at around 2.0. As a generalisation, the intermediate reactivity group may be said to comprise the alkyls of elements with Pauling electronegativities in the range 1.0-1.5 which includes Si, Be, Mg, Al and possibly some transition metals which form thermally unstable alkyl compounds, and which as yet have been little studied. The importance of this group of compounds lies with their reasonably high reactivity, but not so high that the reagents are highly unselective. It is in this group of compounds that it is possible to select conditions of solvent and reagent by which an element of control can be exerted over the reaction course and products.

The aluminium-carbon bond is believed to be polarised but essentially a covalent bond. There is no evidence for the formation of simple carbanions in any solution. The conductivity of certain solutions, if not due to impurities, arises from complex ions of the AlR_4^-, AlR_2^+ type.

The tendency of trialkylaluminiums to dimerise through three centre bonds is common only to tri-n-alkylaluminiums of which trimethyl and triethylaluminiums are typical. Alkyl groups branched in the α or β position appear too bulky and sterically hinder dimerisation. Hence alkylaluminiums with α and β branched groups such as isopropyl and isobutyl are unassociated.

The Reactions of Trialkylaluminiums with 1-Olefins

The reaction of organoaluminium compounds with unsaturated hydrocarbons was discovered by K. Ziegler.[3] The growth or "aufbau" reaction as it was called, involved the combination of trialkylaluminiums with ethylene at a pressure of 100 atmospheres and a temperature of 100°C, resulting in the formation of unbranched long chain trialkylaluminiums. The best example of the growth reaction is the combination of triethylaluminium and ethylene. The yield is long chain trialkylaluminiums with an even number of carbon atoms in each chain.

The mechanism of the growth reaction is:

$$\text{R-al} + n\text{-}C_2H_4 \rightarrow \text{R}(C_2H_4)_n\text{-al} \qquad (1)$$

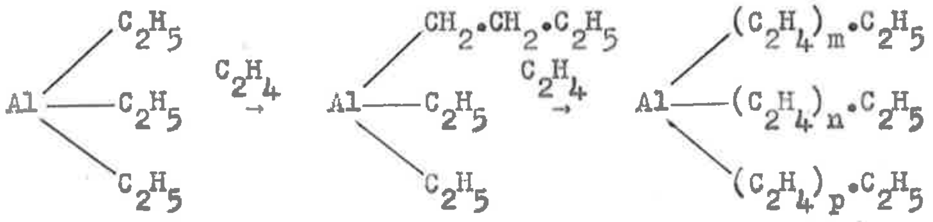
(where $\text{al} = \frac{1}{3}\text{Al}$),

or

$$\text{al-}CH_2\text{-}CH_2\text{-R} \rightarrow \text{al-H} + CH_2\text{=}CH\text{-R} \qquad (2)$$

$$\text{al-H} + CH_2\text{=}CH_2 \rightarrow \text{al-}C_2H_5 \qquad (3)$$

Schematically



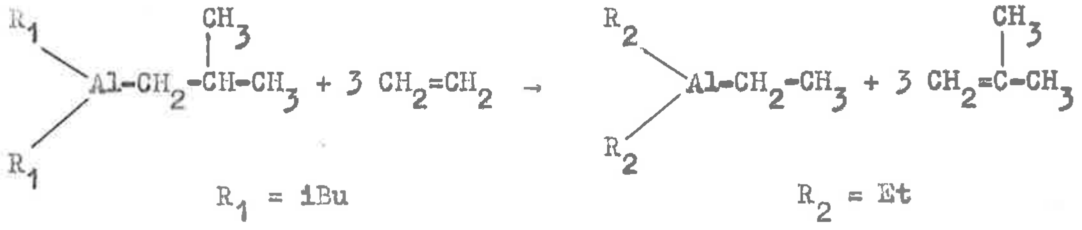
Reactions (2) and (3) constitute the displacement ("verdrangung") reaction which is in competition with the growth reaction, the displacement rate increasing with the bulk of the attached alkyl group. β-branched groups are displaced more readily than straight chain groups. The rate of addition of 1-alkene to the Al-H bond (reaction (3)) decreases with substitution of the vinyl carbons.[4]

$$CH_2{=}CH_2 > RCH{=}CH_2 > R_2C{=}CH_2 > R{-}CH{=}CH{-}R$$

In this case the diminished reactivity towards nucleophilic addition arises out of the increasing electron density in the π system with alkyl substitution. Any steric effect is also enhanced by this alkyl substitution.

The rate of displacement (reactions (2) and (3)) is independent of ethylene pressure. This implies that reaction (2) above is rate controlling and that reaction (3) follows rapidly. Thus the most important factor influencing the displacement reaction is the stability of the alkyl group of the reagent towards hydride-elimination (reaction (2)). As mentioned above, the group is not stable in small n alkyl compounds (e.g. ethyl) and least stable in p branched groups (e.g. isobutyl) where a reactive H atom $-CH_2\underline{CH}(CH_3)_2$ is favourably placed sterically for interaction with a vacant orbital on the aluminium atom.

The increased rate of the growth reaction and the independence of the rate of displacement on pressure means that optimum yields of growth products are only obtained at high pressures. Also, the growth reaction is entirely uncompetitive with the displacement reaction when β-branched trialkylaluminiums react with ethylene, e.g.

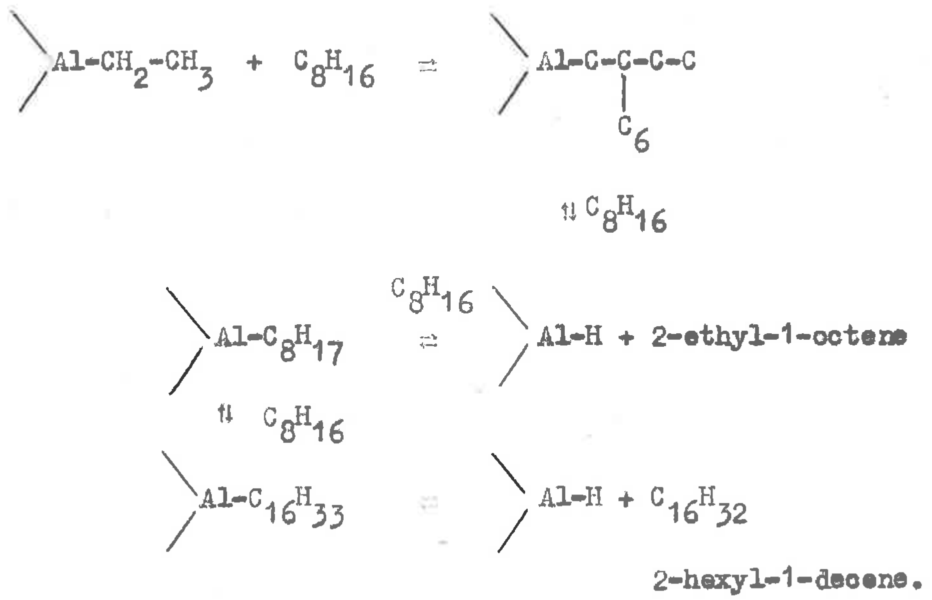


The product of displacement is always a 2-alkyl-1-alkene. The reaction also occurs with branched or straight chain trialkylaluminiums and higher n-1-alkenes.

The growth reaction is slow at low temperatures even under optimum conditions of high ethylene pressure. This places the process under considerable commercial disadvantage. At higher temperatures (above 120°C), the presence of side reactions such as chain rupture and alkene dimerisation become prominent. Heat generated by the reaction has to be removed to prevent unwanted side reactions. Zosel[5] solved these problems and improved the efficiency of the addition reaction by conducting it in spiral copper reactors. The short residence time of the reactants within the reactor permitted temperatures of up to 160°C. The products are mainly straight chain trialkylaluminiums with only about 1-4% branched trialkylaluminiums present as impurity. Naturally, the reaction is faster at the higher temperature and the rate compares well with many long established technical processes.

High Conversion Reactions of Triethylaluminium and 1-Octene

Perry and Ory[6] forced the reaction between triethylaluminium and 1-octene beyond the stages of reaction (3) above. A mechanism was established from the products identified. The mixture corresponded to 1.2 moles of octene per ethyl group and was allowed to react under argon at temperatures ranging from 145° to 190°C. Among the products were 2-ethyl-1-octene and 2-hexyl-1-decene, compounds mentioned only briefly in the literature to that time and for which no reliable physical constants were available. The former of these products was unequivocally confirmed by carbon and hydrogen analysis, cryoscopic molecular weight measurements and I.R. spectroscopy. This product is to be expected from the scheme of reactions (2) and (3). However, in addition they found the 2-hexyl-1-decene. Their deduced reaction scheme, to explain the product isolated is as follows:



This mechanism has recently been confirmed.[7] Again, triethylaluminium and n-1-octene were mixed, the reaction pushed to high conversions and the products extracted and identified. They were 2-ethyl-1-octene, a hexa-decene, n-octyl-, 2-ethyloctyl-, and hexadecyl-aluminium compounds.

Previous Kinetic Studies

The mechanism of the addition reaction was first attempted by Ziegler,[8] who discussed the question whether reactions of trialkylaluminiums involve the dimeric species or dissociated monomer

$$\begin{tikzcd}[column sep=small] (Al_2Et_6) \arrow[dr] & \rightleftharpoons & 2(AlEt_3) \arrow[dl] \\ & \text{Reaction} \arrow[d] & \\ & {} & \end{tikzcd}$$

The problem was briefly investigated by Ziegler and Söll,[9] using kinetic measurements. They found the rate of ethylene absorption per aluminium atom increased when the aluminium trialkyl solution was diluted with inert hydrocarbon solvents. The reaction conditions were arranged such that the displacement reaction giving 2-butene was suppressed and only the addition reaction was present.

$$Al(C_2H_5)_3 + C_2H_4 \rightarrow Al(C_2H_5)_2.C_4H_9$$

The ratio of absorption rates for 1M and 0.01M solution of triethylaluminium was approximately 10. Hence the rate of absorption per mole of triethylaluminium dimer was proportional to the square root of its concentration. The data implies that the monomers of trialkylaluminiums are the reactive species in the addition mechanism according to

$$Al_2Et_6 \overset{K_d}{\rightleftharpoons} 2\ AlEt_3$$

$$AlEt_3 + C_2H_4 \xrightarrow{k} Et_2AlC_2H_4.Et$$

and Rate = $K_d^{\frac{1}{2}} k[Al_2Et_6]^{\frac{1}{2}}[C_2H_4] \simeq K_d^{\frac{1}{2}} k\, C_{Al}^{\frac{1}{2}}[C_2H_4]$

when K_d is small.

Cal = total concentration of alkyl in gram atoms of aluminium per mole.

Natta et al.[10] measured both the rate of ethylene consumption and the rate of product formation in solutions of trialkylaluminium. They found the rate of ethylene absorption to be proportional to "the number of moles of aluminium alkyl present" and to the concentration of ethylene in the liquid phase. Arrhenius parameters were calculated from rate constants for the growth reaction, the energy of activation being 21.3 kcal/mole. However, they did not consider the association equilibria of trialkylaluminiums and the observed activation energy contains no correction for the heat of dimer dissociation prior to reaction as a monomeric species. Their treatment of results implies that the reaction involves the predominant dimeric species and their first order dependence on C_{Al} supports this. The pre-exponential factor calculated from Natta's results was 10^8 litres per mole sec; calculated from second order rate constants, first order in triethylaluminium and ethylene. The implication that the dimeric species is active in the addition reaction is contrary to the kinetic scheme of Ziegler et al.

This inconsistency prompted Allison et al.[11] to re-examine the reaction kinetics. The replacement of ethylene by a higher olefin homologue n-1-hexene, allowed a study of the liquid phase kinetics at slower rates and avoided any errors associated with the technique of gas absorption. Briefly, their experimental technique required the filling of reaction tubes with known concentrations of triethylaluminium and 1-hexene, heating the samples for a desired time period, hydrolysing the reaction mixture, extracting the products, and determining the concentration of product 2-ethyl-1-hexene formed, by gas-liquid partition chromatography. The rate was measured in terms of product yield with respect to time rather than reactant consumption. The order with respect to triethylaluminium was determined from a plot of product (2-ethyl-1-hexene) yield versus initial triethylaluminium concentration. Second order integrated rate equations, first order with respect to both reactants were straight lines passing through the origin. The kinetic evidence indicates the dimer participates in the addition reaction and as it is the dominating species in the liquid phase, it determines the kinetic equation. As stated by the authors, the precision of their results did not permit distinction between a mechanism of sole dimer participation and a mechanism in which dimer and monomer react in parallel. They also conceded that methods of gas absorption were probably more accurate than their rate of product formation measurements. The evidence for dimer participation is kinetic and is substantiated by an improbable value of the pre-exponential factor, calculated on a monomer only basis. The A factor for dimer participation was a credible value within the range of bimolecular association reactions. These Arrhenius parameters depend on values of K_d extrapolated from Laubengayer and Gilliam's[12] data. It now seems likely that this data was misinterpreted.

The still conflicting evidence and the inaccuracy of the above results prompted Hay et al.[13] to re-examine the kinetics, by gas absorption and dilatometry. The systems examined were triethylaluminium with 1-propene, 1-butene, 1-pentene and 1-hexene. The gas absorptions were followed by the rate of volume decrease of the alkene over a solution of triethylaluminium in decalin, but only to 5% conversions, to limit any side reactions. A dilatometric study was employed with 1-hexene where the low vapour pressure at room temperature rendered the gaseous absorption method insensitive. The overall reaction rates, measured by volume contraction, were standardised by product (2-ethyl-1-hexene) analysis using gas chromatography. Utilising the same procedure as before, they found in this case, that the initial rates were proportional to the square root of the total aluminium concentration:

i.e. Reaction Rate $\propto C_{Al}^{\frac{1}{2}}$

The Arrhenius parameters obtained from an integrated rate equation, first order in 1-alkene concentration and half order in dimer, were corrected for the heat of dimer dissociation prior to the addition step. ΔH_d was also calculated from the vapour pressure data of Laubengayer and Gilliam.[12] More recently, Hay, Hooper and Robb[14] have re-examined the dissociation of the triethylaluminium dimer, using vapour density and pressure measurements in the temperature range 60-120°C. Their experimental technique appeared more satisfactory than that of Laubengayer and Gilliam, although their results were in good agreement.

Equilibrium constants with respect to pressure, K_p, were derived and calculated from the vapour pressure measurements. The corresponding dissociation constants were then calculated and used to determine the Arrhenius parameters for the addition reaction between triethylaluminium and a range of 1-alkenes. There was little difference between the Arrhenius parameters, corrected for dimer dissociation, using Laubengayer and Gilliam's data and their own vapour pressure data.

1-alkene	Activation Energy		Pre-exponential Factor	
	*	**	*	**
1-propene	15.7 ± 2.0	15.4 ± 0.8	$10^{5.6-7.2}$	$10^{5.0-6.0}$
1-butene	16.7 ± 2.0	16.4 ± 0.8	$10^{6.0-7.6}$	$10^{5.3-6.3}$
1-pentene	19.0 ± 2.0	18.4 ± 0.8	$10^{7.1-8.7}$	$10^{6.3-7.3}$
1-hexene	18.8 ± 1.0	18.2 ± 1.0	$10^{7.3-8.9}$	$10^{6.5-7.5}$

* from rate constants for the addition reaction, corrected using Laubengayer and Gilliam's data.

** from rate constants, corrected by their own (Hay et al.) data.

Criticism of Previous Efforts

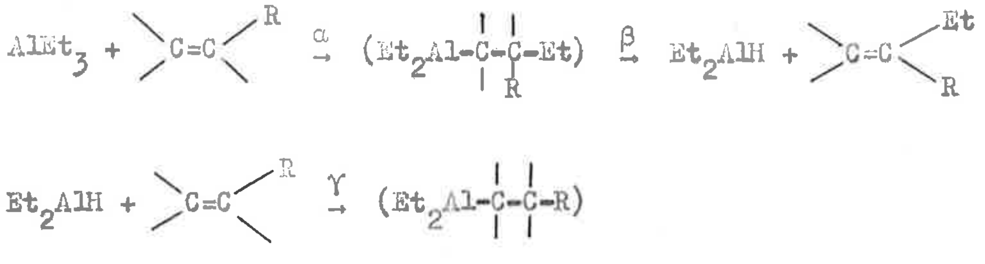
Gas absorption methods are suspected on experimental grounds because of handling errors. The rate of reaction may be a function of the surface area and certainly depends on the rate of stirring. Ziegler studied the addition reaction at one temperature only and reported no Arrhenius parameters.

Natta et al., although estimating Arrhenius parameters for the alkene absorption, did not take into account the prior dissociation of dimer to monomer.

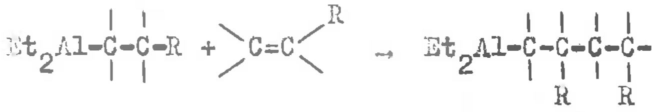
Allison et al. initially used sampling methods of studying the kinetics of addition. However, methods in which the reactant decay is followed continuously, _in situ_, are always preferred to sampling methods. This is emphasised in importance in examples where reactants are very sensitive to atmospheric contamination, e.g. trialkylaluminiums. Quantitative extraction of products from a reaction mixture must also be a difficult procedure and could explain the inaccuracy in Allison's results. The pre-exponential factor which appeared to rule out a monomer mechanism was based on an incorrect estimate of the heat of dimer dissociation from Laubengayer's data. Overall, the rate determined by product formation is related to that determined by reactant consumption by the stoichiometric coefficients. No discrepancy should arise from this source if the stoichiometric equation is correctly determined.

Hay et al. have reverted to the direct techniques of gas absorption and dilatometry. Dilatometry is a "blind" method and can be misleading unless the reaction is completely characterised. For effective dilatometry, a contraction in reaction volume or decrease in the number of molecules from reactants to products, is required. Although a fundamental technique in polymerisation reactions where there is a large reduction in free molecules (monomers) to form polymers, dilatometry must be treated with caution when applied to the reaction between trialkylaluminiums and higher 1-alkenes.

Schematically the mechanism is:



and possibly at high conversion,



When considered as a combination of addition reaction (α), hydride elimination (β) and hydride addition (γ), the mechanism decreases in molecule number from four to three. Represented above, dilatometry would depend on the rate of reaction γ relative to the addition rate (α) and on the lifetime of the adduct (in brackets and shown later to be a transient species). The method would also depend on the state of association of all the alkyl species present. Tri-n-alkylaluminiums are known to be dimeric and di-alkylaluminium hydrides form trimers. Finally, the Arrhenius parameters are corrected with a ΔH_d value calculated from vapour pressure data in the gaseous phase.[12] This vapour pressure data is inapplicable to liquid phase reactions. We also believe that methods used to estimate equilibrium constants from Laubengayer and Gilliain's raw data depend on unjustified assumptions concerning the way in which the measurements were made (see Chapter IV).

Selection of a Kinetic Technique

The indecision surrounding monomer or dimer participation in the addition step of a growth mechanism prompted a re-investigation of this problem. To explore the uncertainty fully, we desired a method of studying the reaction that would be devoid of all inaccuracies encountered by previous workers. The most suitable technique is proton magnetic resonance spectroscopy. The n.m.r. tube itself can be used as the reactor and the reaction can be followed without withdrawing samples and the inherent errors thereby introduced are eliminated. It is a direct method providing easy and simultaneous measurement of reactant decay and product formation by integrated peak areas which are proportional to the concentration of the species they characterise. In a similar fashion, one can measure any reaction intermediate which attains a reasonable concentration. The method incorporates the use of high vacuum conditions. Reactants can be sealed in n.m.r. tubes and therefore conditions of maximum purity can be obtained as the tubes remain sealed throughout all measurements. Complete control of the reaction is maintained at all times. The sample tube as a whole can be removed from the heating medium and thermally quenched to stop the reaction where a reading is to be taken. It also enables the reaction to be followed using small reactant concentrations.

The main disadvantage of the p.m.r. method lies in the time required to obtain enough samples (usually eight for a particular kinetic run) under vacuum in n.m.r. tubes; the preparation of glassware, dispensing vessels, calibrated breakseals and the purification of alkyl, 1-alkene and solvents for vacuum distillation. At first sight, the errors associated with a p.m.r. method are dispensing errors that are always present when operating under high vacuum (e.g. an error in distilling or tipping to or from calibrated vessels) an instrument error, in this case an integration error which is quoted as ± 2% of the integrated peak area and may be larger in poorly resolved peaks.

The disadvantages can be summarised as pre-experimental inconvenience and errors that will normally be less than those encountered by most kinetic methods (except dilatometry, where the measurement is precise, but the relation of the measurement to the rate is open to ambiguity).

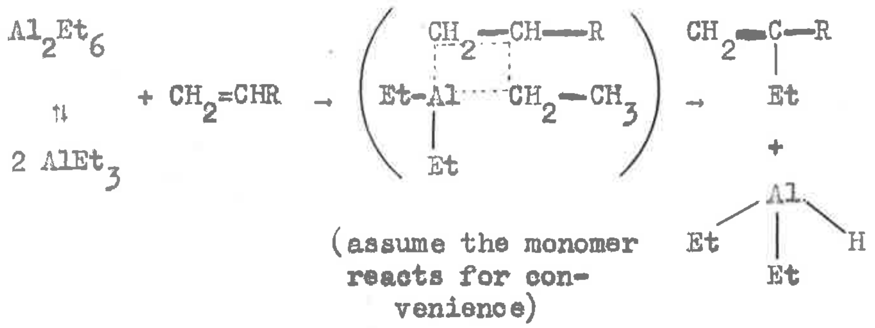
We considered advantages to outweigh disadvantages and selected p.m.r. spectroscopy as the kinetic technique.

CHAPTER II - PRELIMINARY EXPERIMENTS

Introduction

The conjecture arising out of the work of previous authors revolves around the true identity of the trialkylaluminium species responsible for the addition step with 1-alkenes. Specifically, we require the order of reaction with respect to triethylaluminium and knowing this, the correct mechanism of the reaction with its definitive reaction parameters.

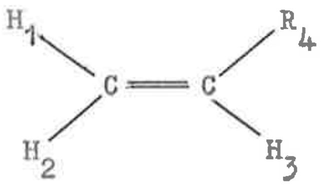
The addition step can be initially represented as



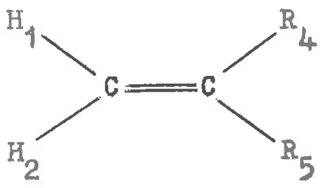
(assume the monomer reacts for convenience)

The most obvious structural change is the loss of a proton from the alkene vinyl group which is gained by the aluminium to give the product molecules diethylaluminium hydride and 2-ethyl-1-octene. In an analogous fashion to the ethylene growth reaction, the above addition involves the insertion of an ethyl group into the vinyl system of the 1-alkene. However, the product molecular weight is far less than the ethylene polymerisation because of steric blocking of the β branched alkylaluminium adduct which prevents further addition. The C-2 vinyl proton of the olefin disappears in the reaction and this should be easily detected by p.m.r. spectroscopy. Using this method the rate of octene consumption can be equated to the rate of disappearance of this single proton. In p.m.r. terms the octene decay rate is equal to the rate of decrease in peak area characteristic of this proton or to the integrated peak area.

Another predicted structural change is a result of the change in environment of the terminal vinyl ($CH_2=$) protons. Although these protons remain static in number throughout the addition, their magnetic environment does change. A comprehensive description of this effect on the p.m.r. structure of 1-alkenes is included in a paper by Bothner-By and Naar-Colin.[15] Briefly, within the reactant 1-octene there is a magnetic asymmetry in the vinyl group; the two terminal protons are not p.m.r. equivalent and the result is a complex triplet signal pattern.



reactant olefin



product olefin

R_4 = n hexyl

R_5 = ethyl

In the product olefin, insertion of the bulkier group R_5 in place of the proton H_3 produces a similar magnetic field around each of the terminal protons and the environments are now described as magnetically equivalent. Thus they resonate at the same applied field frequency and their chemical shifts are identical. The literature[16,17] shows this equivalent terminal group signal as a possible p.m.r. singlet peak at 4.7 p.p.m., some 0.05 p.p.m. upfield from the end of the non-equivalent terminal $CH_2=$ signals.

In total these structural and magnetic environmental changes provide three methods of observing the reaction by p.m.r. spectroscopy: the rate of disappearance of the reactant vinyl terminal ($CH_2=$) pattern with time; the rate of disappearance of the multiplet signal of the vinyl ($-\underset{H}{C}=$) proton with time; the rate of formation of the product vinyl terminal ($CH_2=$) singlet pattern.

From experience, the latter two methods were rejected in practice except when the formation rate was used as a stoichiometric check. The method of recording rate of disappearance of the single proton, involves considerable error because of the complexity of the multiplet pattern. It was difficult to determine the start and finish of this absorption and errors in integrated peak areas would be exaggerated. The product formation method was inaccurate at initial conversions because of the small size of the product peak. Again integration errors would be considerable. This method only appears suitable when measuring at larger reaction times and extrapolating a log concentration versus time plot to zero time, i.e. using extrapolated concentrations at small conversions instead of attempting to measure them.

The concentration of octene at any time t by the accepted method is

$$\frac{\dfrac{(I_{CH_2=})_{t=t}}{(I_{BENZ})_{t=t}}}{\dfrac{(I_{CH_2=})_{t=0}}{(I_{BENZ})_{t=0}}} \times [\text{octene}]_{t=0} = [\text{OCTENE}]_{t=t}$$

$I_{CH_2=}$ is the integrated peak area of the vinyl $CH_2=$ triplet,

I_{BENZ} is the integrated peak area of the benzene singlet.

The explanation of this ratio relationship is as follows:

The internal and external conditions of an n.m.r. spectrometer can change from day to day and integrals of a particular peak need not be the same at different measurement times. For this reason and because we were measuring a decreasing integral, it was necessary to use benzene as an integral constant. All concentrations of 1-octene were measured relative to this constant benzene concentration.

Purification of Materials

(a) Triethylaluminium

Bulk samples were obtained in lecture bottles from the Ethyl

Corporation, New York. The alkyl is stored in the cylinder under a positive pressure of nitrogen.

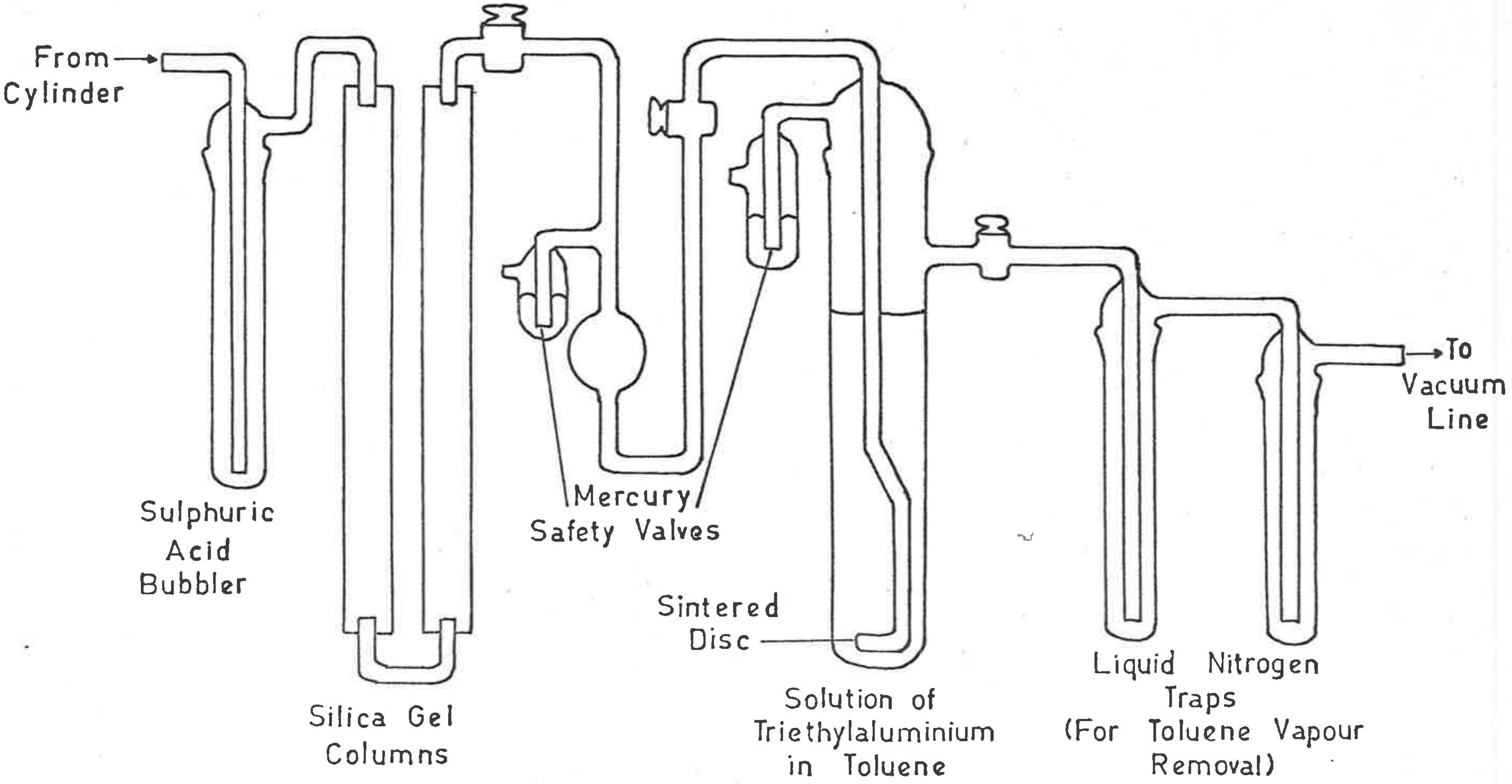
The previously accepted methods of handling the alkyl were either within a nitrogen dry box or by dispensation from an hypodermic syringe. Dry box techniques are susceptible to impurity formation because of the nitrogen drying methods. Syringes are also prone to contamination because of the impossibility of obtaining a completely airtight seal. In brief, both methods are vulnerable to the reaction of moisture and oxygen traces with the alkyl, forming diethylaluminium ethoxide and hydroxide. The resulting sample is impure before any accurate measurement has commenced.

The formation of diethylaluminium hydride occurs in small amounts in the synthesis of triethylaluminium. Any purification method we might consider had to ensure removal of the hydride and prevent formation of the oxy-impurities. Use of high purity nitrogen during the removal of the alkyl from the bulk container and high vacuum conditions plus a distillation step in the subsequent purification should eliminate the impurities.

The dry oxygen free nitrogen was obtained (see Fig. 1) by bubbling C.I.G. nitrogen (oxy-free) through a concentrated sulphuric acid solution, silica gel columns and a solution of triethylaluminium in toluene. The nitrogen stream then passed

NITROGEN PURIFICATION APPARATUS.

FIG 1



through a liquid nitrogen trap to remove any toluene vapours, and finally into the purification vessel.

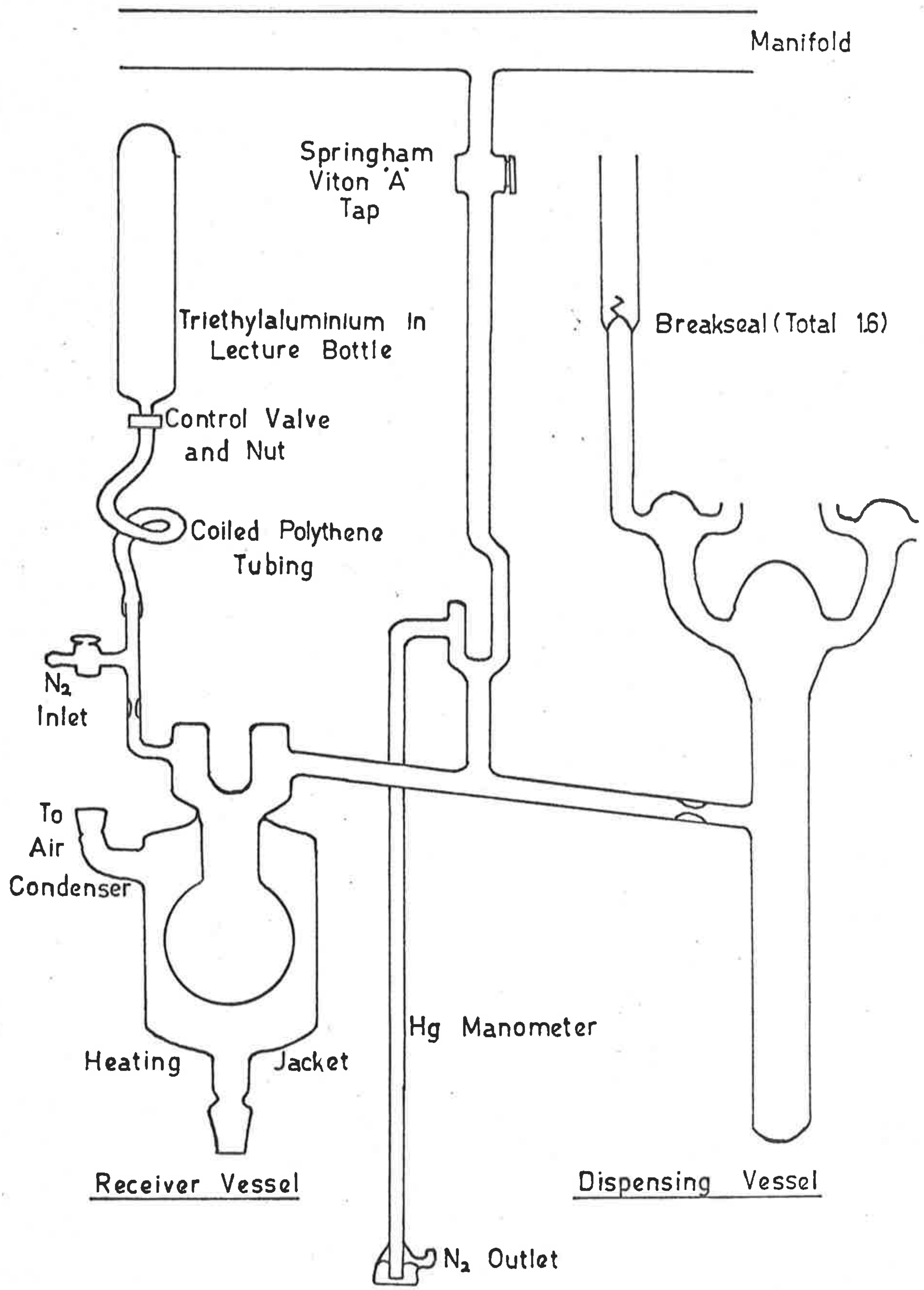
The vacuum line was composed of an Edwards single-stage rotary oil pump (as a backing pump) coupled to a three-stage mercury diffusion pump and then to the manifold and take-offs. Liquid nitrogen traps were present on the manifold and between each pump. These were an essential part of the vacuum line for their assistance to the pumps is obtaining the required vacua and for their prevention of diffusion of mercury vapour and other contaminants, either "back" into the manifold or "forward" into the oil pump. The vacuum pressure was measured by the combination of an Edwards Pirani gauge and a Pirani 65C-2 gauge head.

The alkyl purification apparatus (Fig. 2) consists of a supported lecture bottle connected via a control unit and polythene tubing to a receiving vessel; this in turn being connected to a dispensing vessel with sixteen breakseals attached.

The whole system was initially purged with dry oxy-free nitrogen for about ten minutes. The gas was admitted via the tap indicated in the diagram and out through the manometer reservoir. The N_2 inlet tap was closed and the apparatus evacuated to a pressure of $\leq 10^{-4}$ torr. This purging and evacuation procedure was repeated twice until the final situation was a pure nitrogen

TRIETHYLALUMINIUM PURIFICATION.

FIG 2

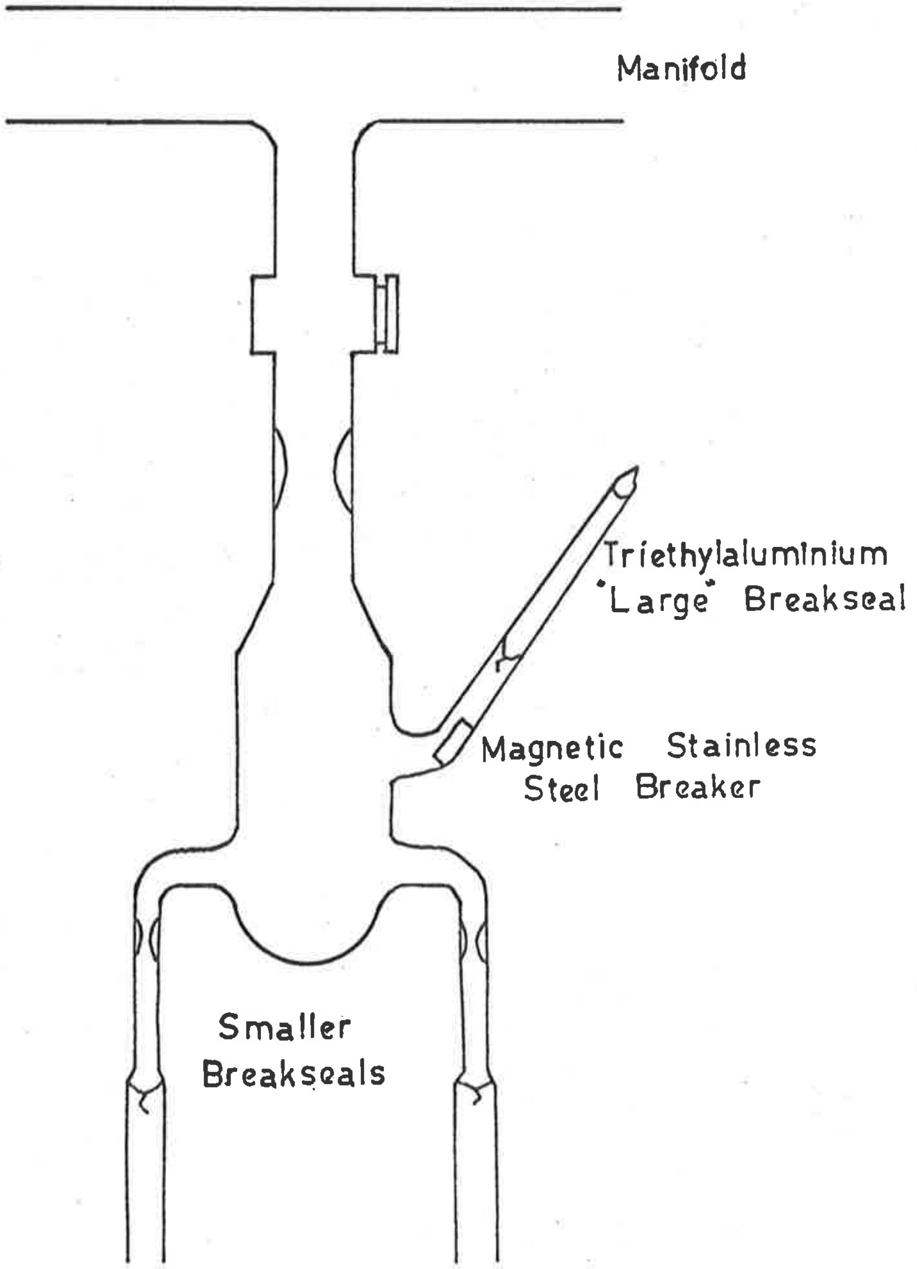


atmosphere remaining within the apparatus. This pressure was then slightly reduced to facilitate the flow of the alkyl from the lecture bottle. With both the N_2 inlet and manifold taps closed, the triethylaluminium was allowed to slowly trickle into the receiving vessel. Careful manipulation of the control nut and valve was required in order that the volume of alkyl dispensed did not exceed two thirds of the total bulb volume of the receiving vessel (a precaution necessary for the degassing procedure to follow). The alkyl was frozen within the bulb by liquid nitrogen, the constriction below the inlet tap sealed off and the lecture bottle and delivery tube removed for cleaning and storage.

The apparatus containing the now frozen alkyl was pumped out to a pressure of $\leq 10^{-4}$ torr and then thawed with a warm heptane bath. Degassing was repeated twice until a good vacuum was present to enable an efficient distillation. The distillation of the alkyl was initiated by externally heating the receiver bulb with boiling heptane vapour. The combination of temperature and reduced pressure forced the alkyl to boil, the vapours passing up and out of the receiver, and down a slanted connecting tube to the dispensing vessel. Cooling the dispenser with liquid nitrogen assisted the distillation. The connecting tube was slanted to ensure that any prior condensate flowed into the dispensing vessel (particularly from the constriction region). The distillation was stopped when at least 80% of the distillate had been collected and the residue started to colour (yellowish-brown). Both the residue and distillate vessels were frozen with liquid nitrogen and pumped out to $\leq 10^{-4}$ torr. The dispensing vessel was sealed off while pumping; the alkyl thawed and tipped into the sixteen breakseals which were all sealed off in turn and stored in vermiculite. The residue remaining in the receiver was deactivated by distilling in heptane from an external source and then cutting this vessel and its contents from the manifold. The heptane contains traces of dissolved oxygen and water which allow the controlled oxidation and hydrolysis of any residual alkyl. Because of its pyrophoric nature and for the sake of purity, the triethylaluminium was always handled carefully within breakseals under high vacuum conditions. The main disadvantage of the purification technique was the time factor, i.e. approximately one week's work from start to finish. A minor disadvantage was the usually "large" amount of alkyl per breakseal. Normally, around 35.0 ml. of distillate was obtained which results in over 2.0 ml. of alkyl per breakseal. In general, (especially with p.m.r. work) smaller volumes of alkyl were required and these were obtained using a "breakdown" vessel (Fig. 3). The "large" breakseal was sealed on to the trunk of the vessel as a sidearm. After pumping out this vessel to a good vacuum, it was removed from the manifold

BREAKDOWN APPARATUS.

FIG 3



by sealing off at the constriction. The "large" alkyl breakseal was ruptured by forcing a magnetic stainless steel breaker (sometimes glass-coated steel) onto the needle-like point of the breakseal. The alkyl was allowed to drain into the vessel base and the required amount tipped into each calibrated breakseal. The breakseals and contents were sealed off at the take-off constriction and stored in vermiculite.

(b) Normal 1-octene

"Purum" grade (99%) from the Aldrich Chemical Co. U.S.A.

The olefin was first dried over calcium hydride for twenty four hours and then triply degassed on the vacuum line. The material was distilled in bulk under reduced pressure on the vacuum line and a middle cut fraction retained for further use.

Before use, the olefin was tested for purity (as were all other components of kinetic mixtures) by Gas Chromatography. The column material was composed of a liquid phase of silicone D.C. 550 and a support of chromosorb W, acid washed, 60/80 meshed. This material was purchased prepacked with 5% liquid phase on the support. The column itself was a twelve foot by one quarter inch aluminium alloy tube, turned into a coil, some twelve inches in height by four inches in diameter. The lower end was partially blocked by a stainless steel sintered disc clamped into position.

The column coil was carefully filled by slowly pouring the column material into the top end, applying steady suction from a pump connected to the lower end and maintaining a steady tapping of the column to ensure tight packing. Once filled, the top of the column was sealed with another stainless steel sintered disc and then locked into position in a Perkin Elmer Vapour Fractometer (Model 154). "Baking" of the column in this position for twenty four hours at 135°C eliminated any primary "bleeding" of the column during subsequent operations.

Samples of Aldrich 1-octene were admitted to the column in five microlitre volumes from a Hamilton microlitre, gas tight syringe. The column temperature employed for analysis was 125°C with a hydrogen carrier gas pressure of five pounds per square inch. The resulting chromatograms showed an impurity content of approximately 0.4%.

(c) Benzene

Univar "Analar" Grade - Ajax Chemical Co.

This solvent was initially dried over sodium wire, degassed and distilled on the vacuum line with a middle cut fraction retained for further experiment. Because of the danger of a benzene-water azeotrope in accurate work (particularly with aluminium alkyls), the retained fraction was used as a solvent in the polymerisation of styrene by n-butyllithium. The benzene was distilled, when required, from the brilliant orange "living" polystyrene solution. The purity of this solvent was always maintained by the living ends of the polystyrene. These purge any impurities in the solution and, in turn, terminate their growing polymer ends. This purity was confirmed by g.c. analysis.

(d) Cyclohexane

Merck "Uvasol" spectroscopic grade.

This solvent was dried over calcium hydride for twenty four hours, degassed and distilled on the vacuum line onto more calcium hydride. The cyclohexane was stored under vacuum and used when required.

(e) Tetra-methyl Silane

Fluka "purissimum" grade.

The ampoule container was carefully cracked and the contents poured into a round-bottomed flask containing calcium hydride. The T.M.S. was degassed and distilled under vacuum onto more calcium hydride. The high vapour pressure at room temperature made it necessary to store the T.M.S. under vacuum and refrigeration.

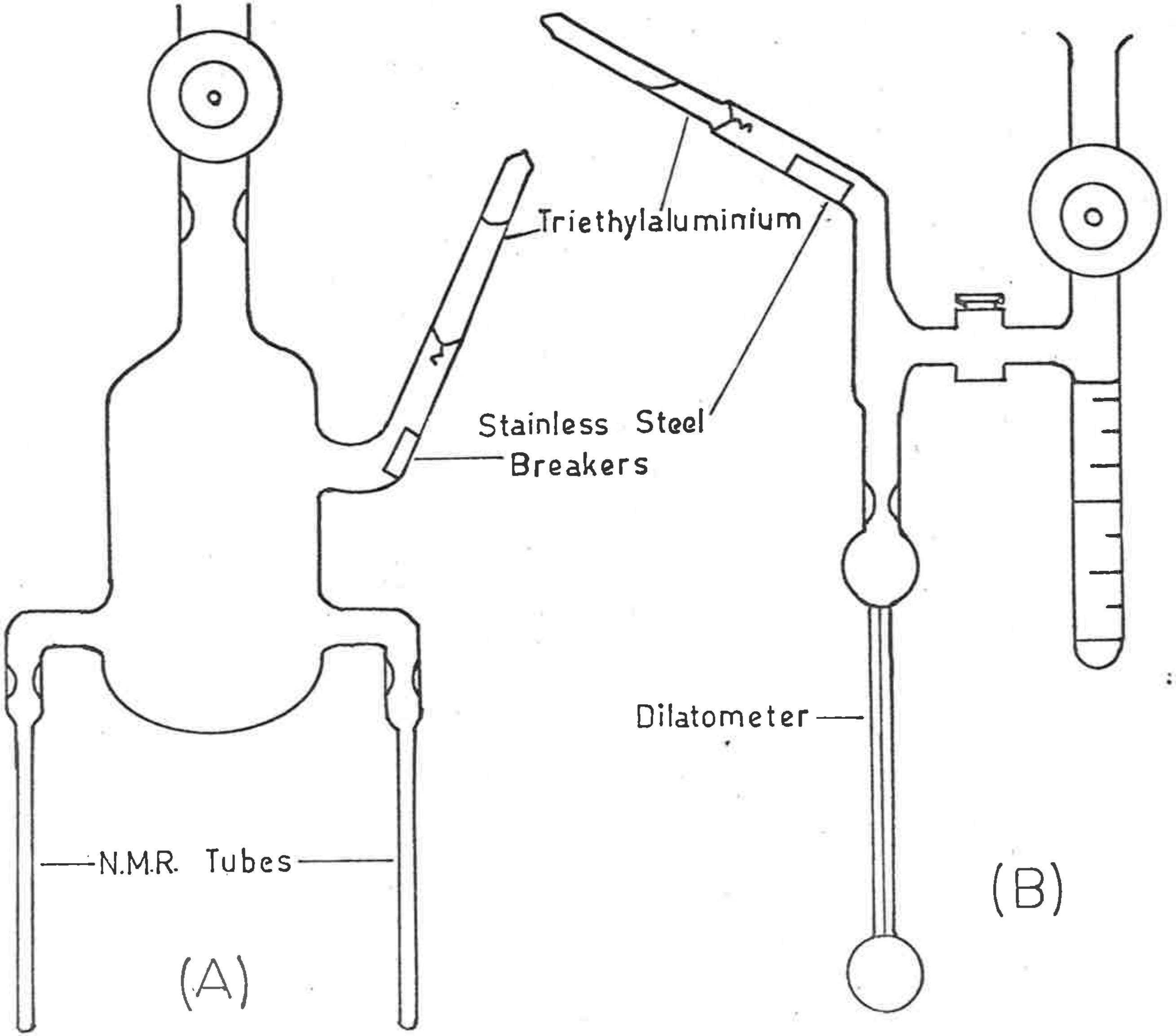
Preliminary Experiments

Several experiments were necessary before embarking on any accurate kinetic runs. A preliminary proton magnetic resonance experiment to check the predicted structural changes between reactant and product olefin; a dilatometric investigation of the reaction (rate data obtained by this technique could possibly be used to confirm p.m.r. results); some preliminary product analyses necessary to check the mechanism of the reaction, i.e. analysis of an hydrolysed reaction mixture, extraction of products and identification by gas chromatography and mass spectrometry; a justification that the number of moles of reactants in the vapour phase in a sealed n.m.r. tube is insignificant when compared with the number of moles in the liquid phase.

For the predicted structural change experiment, the apparatus used is shown in Fig. 4(A) and was pumped out on the vacuum line at a pressure of $< 10^{-3}$ torr for twenty four hours. A small amount of degassed tetramethylsilane (for use as an n.m.r. lock signal) was distilled into the base of each n.m.r. tube. Approximately equal volumes of 1-octene were distilled into each tube on top of the T.M.S. The respective volumes of 1-octene were calculated from cathetometer measured heights. When the contents of each tube were re-frozen with liquid N_2, the vessel was pumped out and sealed off from the manifold. The alkyl breakseal was smashed and the liquid allowed to flow into the vessel base. Aliquots of alkyl were carefully tipped into each tube in

APPARATUS FOR PRELIMINARY EXPERIMENTS

FIG 4

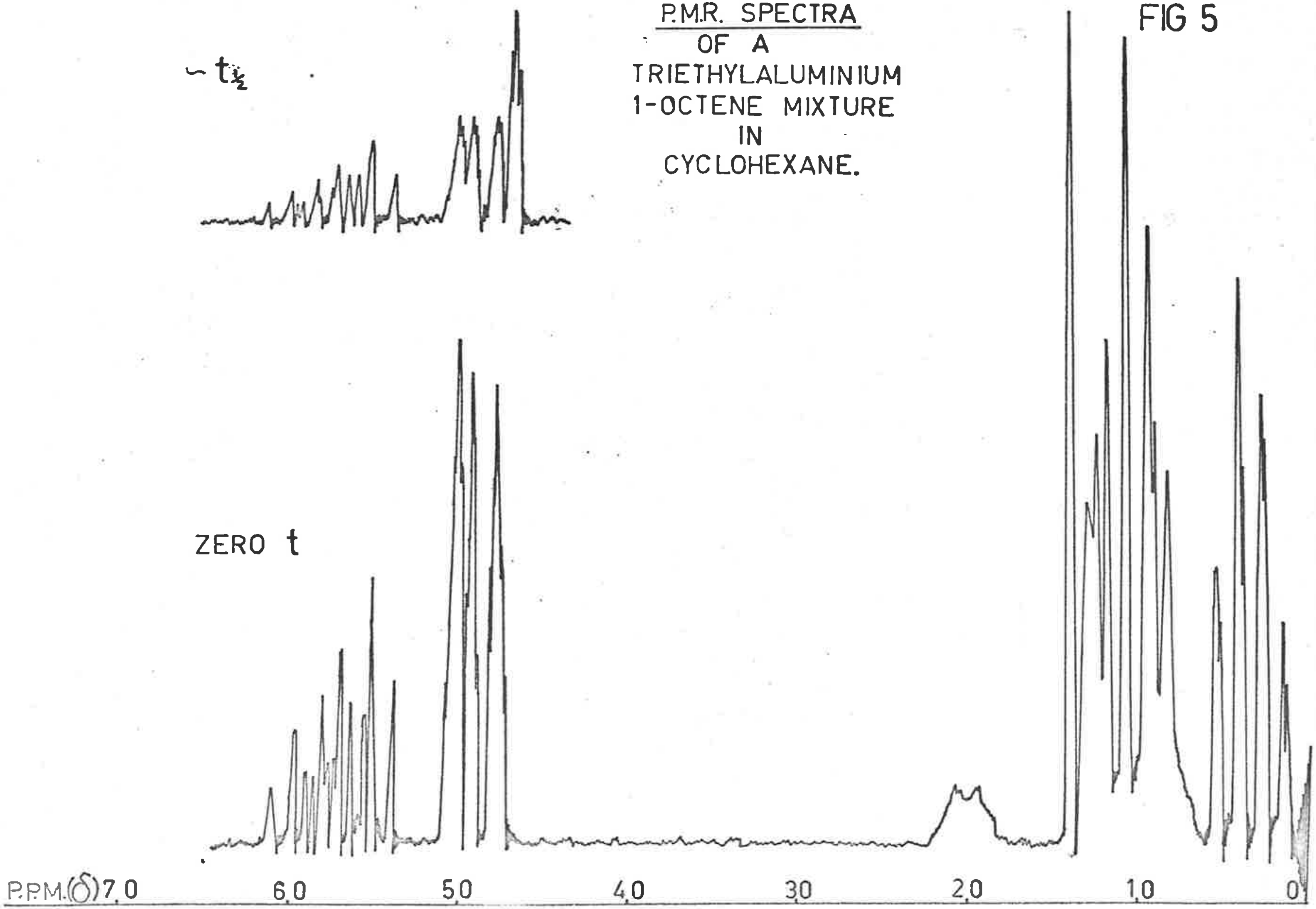


amounts to approximately form 1:1 and 3:1 molar ratios of 1-alkene and triethylaluminium. Both tubes were sealed off from the main vessel and the initial p.m.r. spectra recorded at the probe temperature of 29.0°C. The two samples were then placed in a tube furnace controlled by a variac at 100.0 ± 2.0°C for fifty hours. On re-measuring the spectra after this period there was a marked decrease in the absorption of the olefin vinyl protons and also present was a singlet peak growing on the up-field edge of the original reactant ($CH_2=$) triplet. This spectrum effect with time is shown in Fig. 5. No accurate measurements were intended here; only experimental confirmation of the predicted structural changes. Confirmation was evident from the spectra of Fig. 5 and the data for ensuing kinetic runs will be measured by the p.m.r. methods of reactant decay and product formation as outlined previously.

The technique of dilatometry was attempted to determine whether this method could provide results which would substantiate the p.m.r. measurements. There were, however, several disadvantages confronting such a technique and these have already been discussed in detail in Chapter I.

Experimentally, the heating medium was an oil bath (pyrex glass) filled with Ondina 33 oil and a de-oxidant 2:6-Di-tert-Butyl-para Cresol preventing the oil from colouring. Four 200 watt heating probes were immersed in the oil and regulated by a proportional

FIG 5

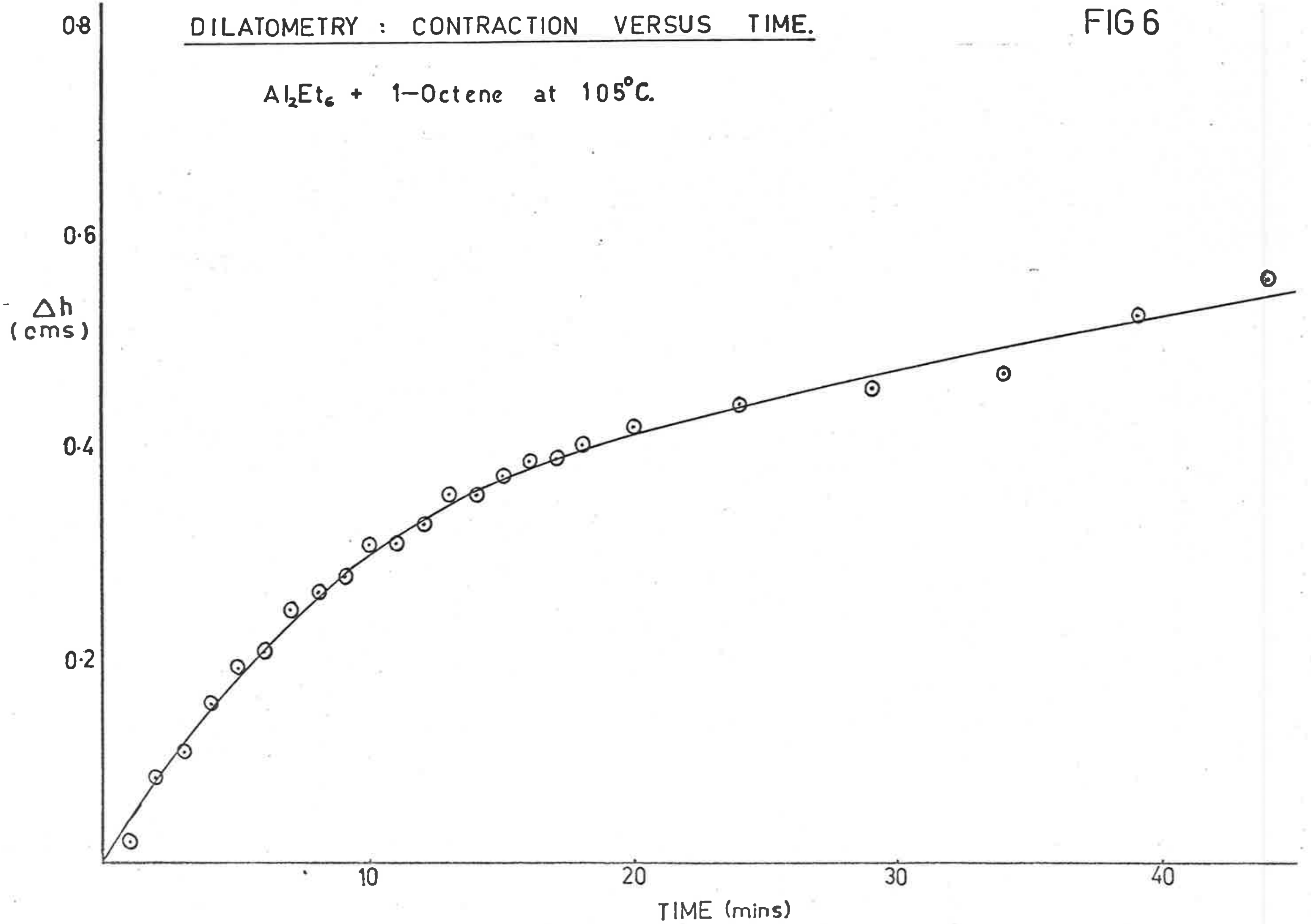


P.M.R. SPECTRA OF A TRIETHYLALUMINIUM 1-OCTENE MIXTURE IN CYCLOHEXANE.

control box, triggered by a Stantel F14, 10K ohm. thermistor, at the end of a metal probe immersed in the oil. The bath temperature is gained by "dialling" the temperature on the calibrated control box scale, and maintained by the sensing thermistor. Temperature control with this combination was T ± 0.05°C.

The dilatometer-filling apparatus (shown in Fig. 4(B)) was pumped out to $< 10^{-3}$ torr for ten hours. The Springham "greaseless" tap (2) was closed, the alkyl seal broken and the liquid drained into the base bulb of the dilatometer. This alkyl was frozen with liquid N_2 and the vessel pumped out to an acceptable vacuum. With tap (2) closed again, n-1-octene was distilled into the graduated tubing and finally tap (1) closed. The olefin was carefully distilled onto the alkyl in the dilatometer base and the mixture kept frozen. When the correctly calibrated volume of 1-octene had been distilled over and greaseless tap (2) closed, the dilatometer was sealed off at the constriction and the contents thawed. The dilatometer was clamped on a perspex frame and immersed in the heating medium. The contraction was initially measured every minute, and as the reaction progressed, in periods of several minutes. Contractions were measured as decrease in height increments Δh, with a cathetometer and plotted versus time (see Fig. 6). The resulting

FIG 6



DILATOMETRY : CONTRACTION VERSUS TIME.

Al_2Et_6 + 1-Octene at 105°C.

graph on conversion plot appears to show two kinetic phases. It is curved initially and then the reaction appears to reach a steady state with contraction occurring linearly with time.

Hay, Jones et al.[13] reported the contraction at 111-131°C, of 1-hexene, triethylaluminium mixtures, was linear with respect to time up to about 10% consumption of 1-hexene. This implies a zero internal order of reaction with respect to 1-hexene which is not consistent with either proposed mechanism. Fig. 6 shows a typical curve for a 1-octene, triethylaluminium mixture at 105.0°C. After an initial rapid rate the reaction settles down to a steady state which may be zero or first order. The initial rapid decay period appears to obey an internal second order equation rather than first order. It is possible that the initial phase arises from the consumption of a more reactive impurity in the triethylaluminium. Diethylaluminium hydride would most likely be the substance to account for this phase as the Al-H bond is more reactive than the Al-C bond towards addition reactions. However our purified and carefully handled triethylaluminium, when tested by product hydrolysis, showed no evidence of any hydride content. It seems more likely that the apparent change in order arises from the factors described in chapter I; in particular, it may be a reflection of volume changes due to the different states of association of aluminium compounds present as reaction intermediates in the earlier stages of reaction. Although it would perhaps be permissible to ignore the initial decay phase, which covers only a relatively slight extent of reaction and use the stationary state rates, it is far preferable to adopt a technique not open to this ambiguity.

Hydrolysis of the reaction mixtures was carried out in a polythene "Glove-bag". The bag was purged of all air with oxygen-free nitrogen for approximately fifteen minutes. While the nitrogen flush was in progress, two beakers, one containing distilled water and the other a polished stainless steel block, were placed in the bag together with the reaction tube. The glove-bag was sealed at the aperture, filled with more nitrogen and subsequent manipulations carried out via the "re-entrant" arms into the gas atmosphere. The reaction mixture was removed from the tube by forcibly cracking it with the stainless steel block. Controlled hydrolysis occurred because of the now wet nitrogen atmosphere. On completion of the hydrolysis (i.e. when all fuming had ceased) the aqueous solution was removed from the glove-bag and the organic products extracted with dry ether by conventional means. The bulk of the ether was then distilled from the etherate and the residue remaining was 1.0 ml. of "octene smelling" yellow oil.

The sample was analysed on a Perkin-Elmer Model 800 Gas

Chromatograph, with a column composition of 5% Apiezon supported on Chromosorb W. The "Model 800" chromatograph has dual columns, is temperature programmed and uses flame ionisation detection. Four products were present on the resulting trace plus the reactant 1-octene. The reactant's presence was proved by "spiking" the product sample with 1-octene, the result being an enlargement of the first peak (in order of retention time). However, the resolution was poor and a column material more specific for separating olefins was required.

It was convenient at this stage to examine the "product" mixture by mass spectrometry. The instrument was a Hitachi-Perkin-Elmer RMU-6D double focussing mass spectrometer using a Honeywell 1508 Visicorder for the recording of spectra. The visicorder trace peaks were replotted on the basis of relative abundance versus mass on charge ($\frac{m}{e}$) ratio. The most abundant peak, termed the base peak, is arbitrarily assigned a value of 100% abundance and all other peaks are plotted relative to the base peak. The mass spectrum of 1-octene alone compared favourably when plotted in the above manner with similar values listed in the literature.[18] The parent peak of approximately 12% abundance occurs at an $\frac{m}{e}$ ratio of 112.0.

However, the "product" spectrum, because of its composition of some five compounds exhibited a complex array of peaks. The only salient features were possible parent peaks at $\frac{m}{e}$ ratios of 224 and 140, corresponding to the mass numbers of 2-hexyl-1-decene and 2-ethyl-1-octene respectively. These products are to be expected by analogy with products found by previous workers. (See Chapter I) Our product analyses show nothing contrary to any previous work and we have no reason to suspect any deviation in the proposed addition mechanism.

The one doubt about kinetic p.m.r. spectroscopy under vacuum conditions is the precision of concentration determination. One source of error might arise from the volatility of reaction components. Molecules in the vapour phase would not be accounted for in the integrated peak readout from the spectrophotometer. To reduce such a possibility, the volumes of reaction mixtures in each tube were always kept as large as possible. However, a small vapour space always existed because of the tube seal off procedure. It was, therefore, necessary to prove the insignificance of the number of moles present in this space when compared with the number of moles in the liquid phase.

For a typical example the calibrated volume was 1.80 ml. and the estimated maximum vapour space equal to 0.30 ml.

Assuming that Raoult's Law is obeyed

$$p_A = \chi_A p_A^{\circ}$$

and

$$p_B = \chi_B p_B^{\circ}$$

where $p_A{}^o$ and $p_B{}^o$ are the vapour pressures of pure components, triethylaluminium and 1-octene respectively; p_A and p_B are the vapour pressures of these components above a solution of concentrations χ_A and χ_B (the mole fractions of components A and B).

Assuming ideal behaviour, then $P_{total} = p_A + p_B$. The vapour pressure of pure 1-octene at 100°C = 402.7 mm;[19] the vapour pressure of pure triethylaluminium at 100°C = 11.6 mm.[20]

For a typical sample mixture $\chi_A = 0.58$, $\therefore p_A = 0.58 \times 11.6 = 6.7$ mm

$\chi_B = 0.42$, $\therefore p_B = 0.42 \times 402.7 = 169.1$ mm.

Now the ideal gas equation is $pV = nRT$ or

$n_B = \frac{p_B V}{RT}$ where n_B is the amount of n-octane in the vapour phase, i.e. n_B moles.

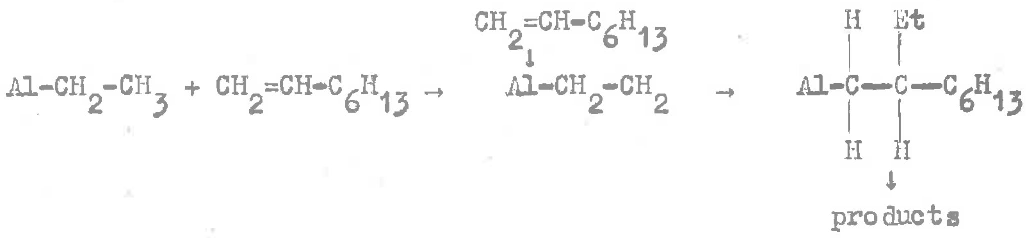
$$\therefore n_B = \frac{\frac{169.1}{760.0} \times 3.15 \times 10^{-4}}{0.082 \times 373.0} = \underline{2.3 \times 10^{-6} \text{ moles}},$$

and $n_a << n_B$.

The number of dispensed moles of octene is $\underline{1.90 \times 10^{-3}}$. Thus the number of moles in the vapour phase is considered insignificant.

Attempted Detection of 1-Alkene-Triethylaluminium Complexes

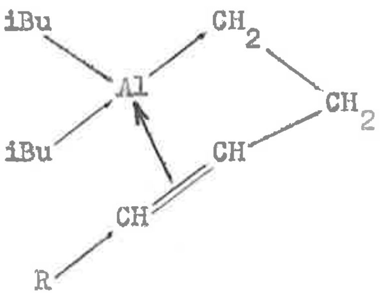
Ziegler's addition step in the original growth mechanism is often said to proceed via an intermediate π complex formation between the acceptor, or electron deficient aluminium atom and the donating π system of the olefin. This postulate is schematically represented,



$$Al\text{-}CH_2\text{-}CH_3 + CH_2{=}CH\text{-}C_6H_{13} \rightarrow \overset{CH_2=CH-C_6H_{13}}{\overset{\downarrow}{Al\text{-}CH_2\text{-}CH_2}} \rightarrow \underset{\substack{\downarrow \\ \text{products}}}{Al\text{-}\overset{H}{\underset{H}{C}}\text{—}\overset{Et}{\underset{H}{C}}\text{—}C_6H_{13}}$$

The evidence for this mechanism was kinetic. If it is correct that dimeric triethylaluminium is unreactive towards alkenes, then this could be explained on the basis that in the dimer, no site for coordination of 1-alkene π electrons is available. This has now been demonstrated spectroscopically in intramolecular 4-alkenylaluminium compounds.[21] The orientation of the groups in this compound brings the double bond into close proximity with the aluminium atom.

Structurally, this is represented in trans-hex-e-enyldiisobutylaluminium

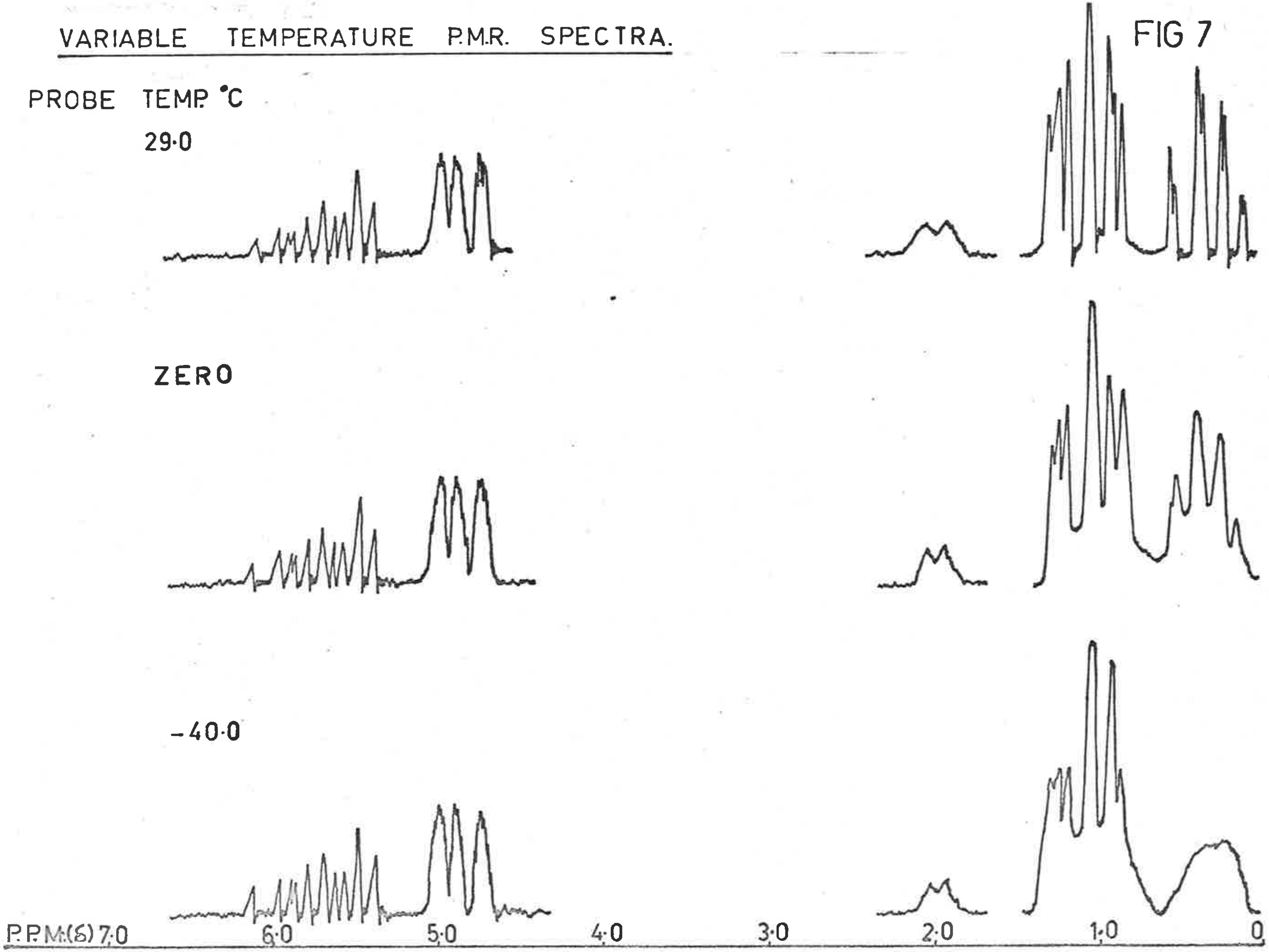


A π bond donation from the double bond to the electron deficient aluminium atom occurs. P.M.R. studies showed the olefinic protons to be less shielded and appear at lower fields than usual. The difference in chemical shift, when compared with a non-intramolecular complex forming alkyl, was 0.3 p.p.m. The explanation was in terms of a drainage of electron density from the vinyl region, which was responsible for the proton de-shielding. There was a corresponding upfield shift in the alkyl methylene protons for the converse reasoning, i.e. increase in electron density provides increased shielding and hence a peak will appear at higher fields.

We attempted to demonstrate such an effect in our system where the complexing would be intermolecular. The p.m.r. spectra of concentration mixtures (in particular 1:1 and 1:3 molar ratios) of triethylaluminium and 1-octene, at room temperature, showed no significant shift in any peak resonance position compared with that of pure reactant. The samples were then examined at temperatures of 0, -20, -30 and -40°C using variable temperature p.m.r. spectroscopy to observe if the complex was stable at low temperatures. Again no shift occurred in either olefin vinyl protons or triethylaluminium methylene protons. A series of spectra is shown in Fig. 7. The only effect observed was a broadening and eventual coalescence of the alkyl methylene quartet signal as the temperature was decreased; an equilibrium effect which is discussed in Chapter IV.

VARIABLE TEMPERATURE P.M.R. SPECTRA.

FIG 7



The experiments are thus inconclusive. Clearly, 1-alkenes form no strong complexes such as those at room temperatures between triethylaluminium and strongly electron donating compounds, e.g. methylmethacrylate.[22] Certainly any complex formed cannot attain sufficient concentration to give a detectable p.m.r. response.

There appears no gross chemical difference between the olefinic group in 4-alkenylaluminium compounds and in a free 1-alkene. The fact that no significant shift occurred in the vinyl hydrogen resonances in alkenylaluminiums, where the vinyl group was unfavourably placed for intramolecular coordination, confirms that an alkene group as remote as position 4 is not influenced by effects communicated from the aluminium atom along the chain. It would appear then that the special stability of the intramolecular coordination is derived purely from steric factors. The interaction between the π system and the aluminium atom is, in all probability, just as strong in the intermolecular case. However, in the absence of a favourable steric factor the stability of the complex is low. This, of course, in no way rules it out as a possible reaction intermediate.

Preliminary Data Summary

The predicted proton magnetic resonance changes during the course of the reaction are observed.

Dilatometry as a kinetic technique produces ambiguous results. From the gas chromatography, mass spectrometry and complex formation investigations, there is no reason to suggest that the rate determining addition step varies from that postulated.

Proton magnetic resonance spectroscopy is shown to be the best kinetic technique because of its ability to simultaneously measure reactant decay and product formation with time.

The conditions of the proposed p.m.r. kinetic experiments are shown to be satisfactory, particularly with respect to accurate concentration measurement.

CHAPTER III - KINETICS OF THE ADDITION REACTION

Introduction

Preliminary experiments have shown the advantage of p.m.r. spectroscopy as a kinetic method. The octene concentrations at various reaction times are calculated integrated peak areas and the reaction rate is measured from the decrease in integral peak height with time. The area underneath a particular p.m.r. signal is proportional, both to the concentration of the species providing that group and to the number of protons within the group.

Changes can occur in the external and internal spectrometer conditions from day to day, e.g. temperature, the magnetic and radiofrequency fields. For this reason it is fundamental to measure any changing integral relative to the integral of a reference substance which remains constant throughout the duration of the experiment. Ideally, this constant integral should be an inert solvent, of multiequivalent proton structure, which resonates close to the set of diminishing reactant peaks. Examples which are well suited for our purpose are cyclohexane, which has twelve equivalent protons at room temperature, resonating at δ = 1.4 p.p.m. and benzene, six equivalent protons at 7.2 p.p.m. (All shifts are measured relative to T.M.S. which is arbitrarily assigned zero p.p.m.) These two solvent peaks appear on either side of the 1-olefin vinyl region and for practical purposes it was convenient to use a mixture of the two. Cyclohexane was used as a lock signal and benzene as the constant integral.

Knowledge of the change in 1-octene concentration with time may be used to estimate:

the internal order of reaction with respect to triethylaluminium; following standard procedure, the reaction conversion parameter x, defined as

$$x = \frac{C_o - C_t}{\nu}$$

where C_o = 1-octene concentration at zero time

C_t = 1-octene concentration at t = t

ν = stoichiometric coefficient of 1-octene.

The differential rate equation can be assembled with a knowledge of ν, and the substitution of the assumed orders of reaction with respect to each reactant. The integration of the differential form leads to the final expression, the integrated rate equation. If the assumed orders of reaction are correct, plots of this function versus time should be straight lines, passing through the origin; the slope of the line being equal to the rate constant of reaction. The dependence of this rate coefficient on temperature may or may not obey the Arrhenius equation:

$$k = A\,e^{-E_A/RT} \quad \text{or} \quad \log k = -\frac{E_A}{2.303\,RT} + 2.303 \log A.$$

A linear relationship between logarithms of rate constants and the reciprocals of absolute temperature may be taken as an indication of the proof that the Arrhenius law is obeyed. The activation energy, E_A, for the reaction is proportional to the slope, and the pre-exponential factor A equal to the intercept at $1/T^{\circ}K = 0$. A non-Arrhenius dependence would imply that the reaction mechanism is complex, but an Arrhenius dependence does not necessarily imply that the reaction is simple. However, if the latter is the case, then the calculated activation energy, entropy and A factor may be of assistance in deciding this point.

Materials for Kinetic Run

(a) **Triethylaluminium**: type and purity, as described in preliminary section (Chapter II). Two large breakseals from the purified batch were sub-divided into eight varying calibrated volumes, in breakseals.

(b) **n-1-octene**: purified, type as before.

(c) **Solvents**: A solvent mixture was employed, consisting mainly of cyclohexane and a small amount of benzene. The mixture was chosen in preference to a one-component system for the following p.m.r. reasons.

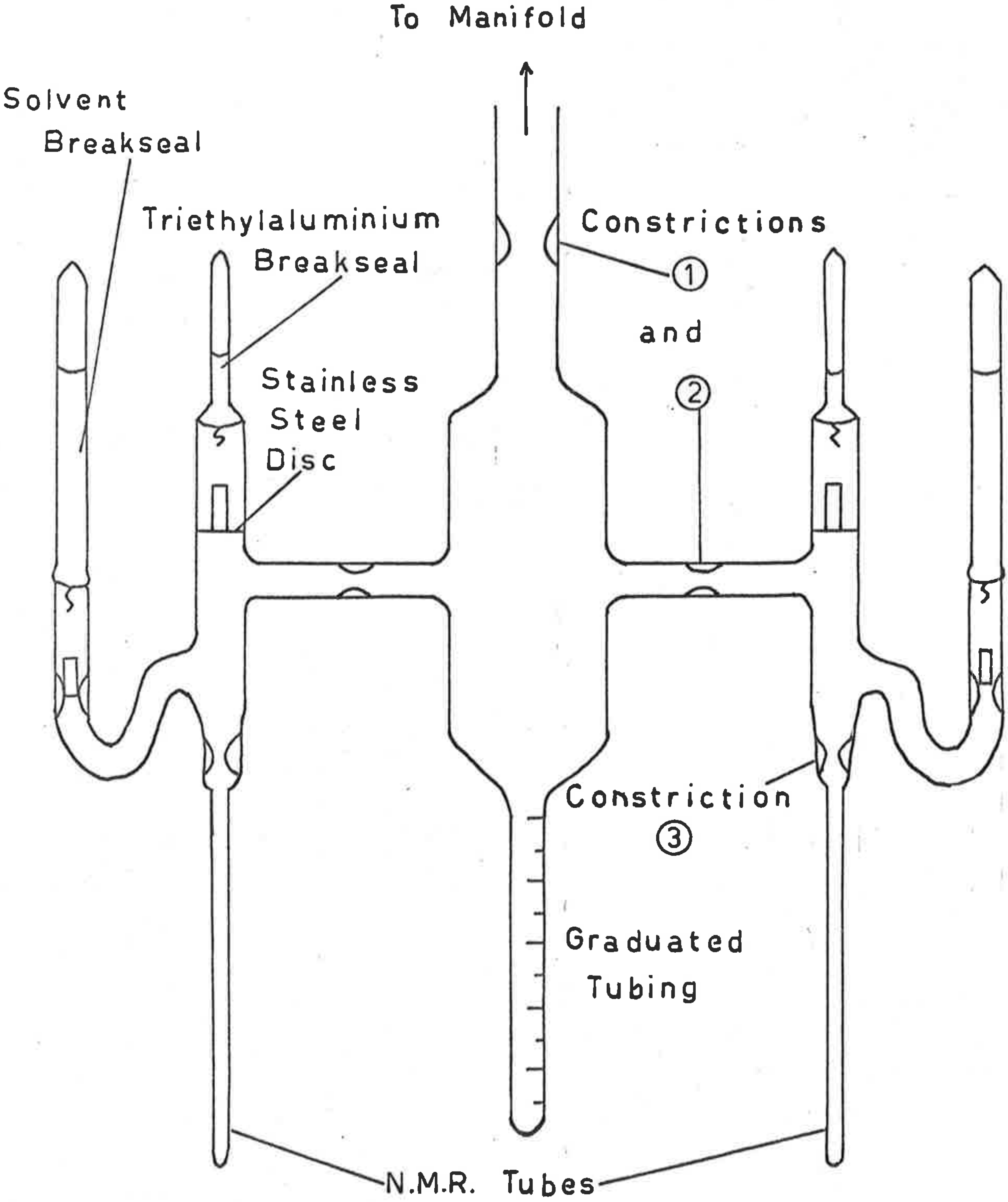
The constant reference peak is desirably benzene, because it is closer to the changing olefin vinyl region than cyclohexane, i.e. drift on phasing errors in the instrument will be less prominent. The concentration of benzene in the loaded n.m.r. tube is required to be about one third the initial concentration of the olefin. The benzene integral will be approximately the same as the vinyl $CH_2=$ triplet. By adjusting the sensitivity one can obtain large integrals and reduce the error in concentration estimation. The concentration of cyclohexane is made correspondingly large to provide a steady lock signal for the instrument.

Spectrograde cyclohexane was distilled on the vacuum line from a degassed external source into a receiving vessel. Surrounding this vessel were eight breakseals of 4 mm. internal diameter for convenience, as the internal diameter of an n.m.r. tube is 4.25 mm. The comparison allowed approximate volume estimations beforehand. Pure benzene was distilled from its degassed source into the same receiving vessel, on top of the cyclohexane. The frozen mixture was then sealed off while pumping. On thawing, and thoroughly shaking, the mixed solvent was poured into breakseals which were sealed off in turn and stored.

Apparatus, Procedure and Recording of Results

The apparatus used is shown in Fig. 8. In the initial kinetic run it was duplicated to provide eight n.m.r. samples for measurement. The method was basic in the requirement of constant 1-octene concentration, while varying the triethylaluminium concentration. For this purpose, the eight n.m.r. tubes were all pre-calibrated to a volume of 1.80 ml. Each breakseal of alkyl and solvent, with accompanying stainless steel breakers, was sealed into position and the whole apparatus pumped out at a pressure of $< 10^{-3}$ torr for twenty four hours. Normal 1-octene was distilled into the graduated base of the vessel. The olefin was frozen with liquid nitrogen and the apparatus sealed off at constriction (1), while pumping. A known volume of 1-octene (0.5 ml.) was distilled from the graduated tubing into one of the n.m.r. tubes and the sidearm sealed off at constriction (2). The same procedure occurred for the other three sidearms. The alkyl seals were broken in each and the liquid allowed to run down and mix with the olefin. A stainless steel sinter was used to prevent pieces of glass from the broken seal entering the n.m.r. tube. Small pieces would upset the homogeneity of the spinning sample during measurement, causing a loss in peak resolution, hence errors in concentration. The concentration of dispensed alkyl was later checked by burette

KINETIC RUN APPARATUS. FIG 8



calibration. The solvent breakseal was then smashed, the solvent tipped with the help of the U-tube, until the reactants were diluted to 1.80 ml. The tube was sealed off and refrigerated until measurement.

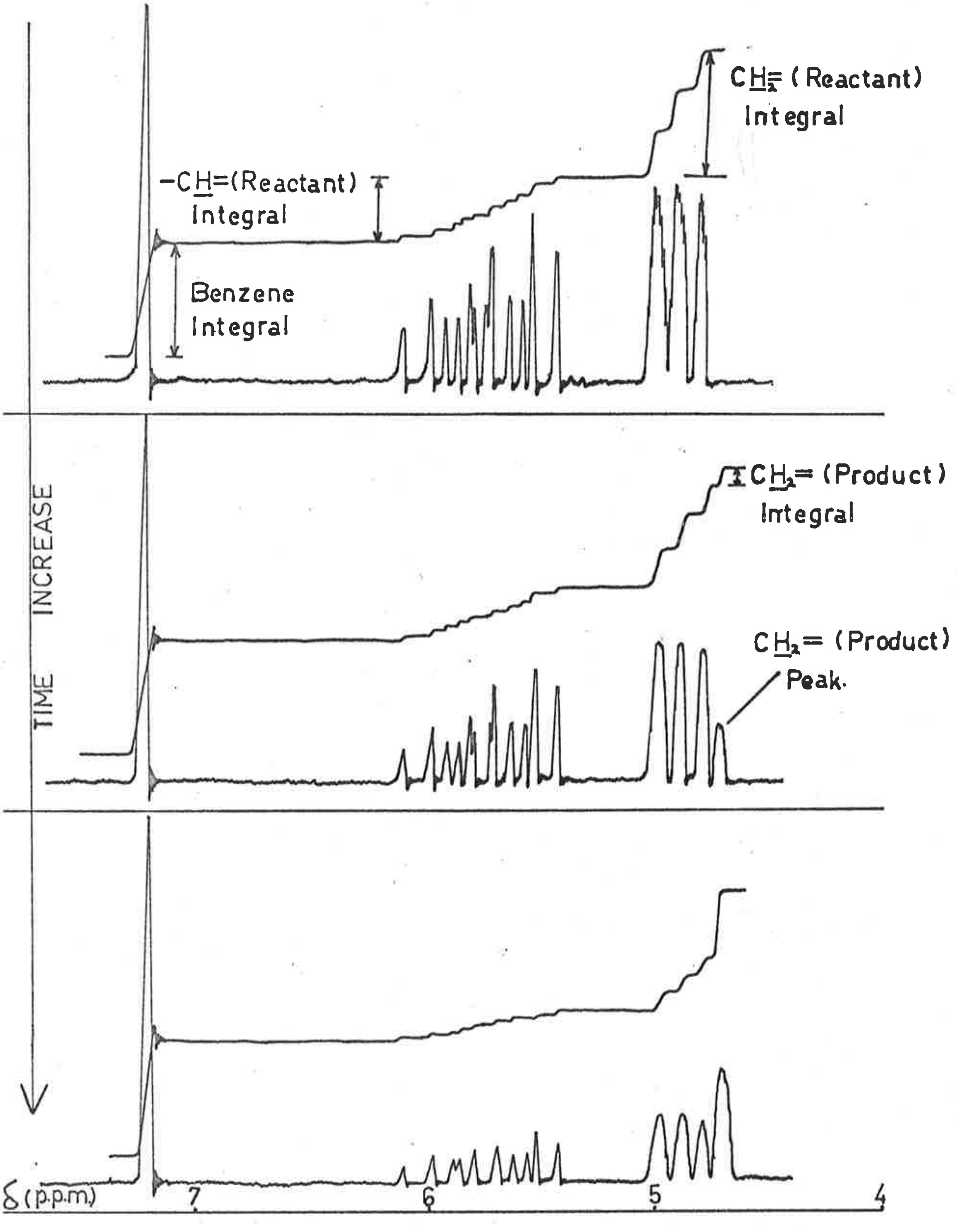
Initially, the spectrum of each tube was examined on a Varian Associates DA-IL 60 n.m.r. spectrometer at a probe temperature of 29.0°C. The internal lock signal used was cyclohexane. At any one time, the integrals of benzene and of the olefin vinyls were measured three times and an average value of the 1-octene vinyl $CH_2=$ to benzene ratio, in the same field sweep direction, used in concentration calculations.

The heating medium and its temperature control were the same as in the dilatometry investigation (see Chapter II). The samples were placed in clips on a perspex support and lowered into the oil bath controlled at the desired temperature. At the end of each heating period, the support rack was removed from the bath, each tube dried and refrigerated until measurement. This procedure was repeated until enough spectral data was available for a seven point plot of concentration versus time. Fig. 9 shows a decreasing series of reactant vinyl protons and their integrals as the reaction proceeds. The data was tabulated as concentrations of 1-octene and product "decene" with time; the product concentration estimated from the relation:

KINETIC RUNS

TYPICAL P.M.R. SPECTRA AND INTEGRALS.

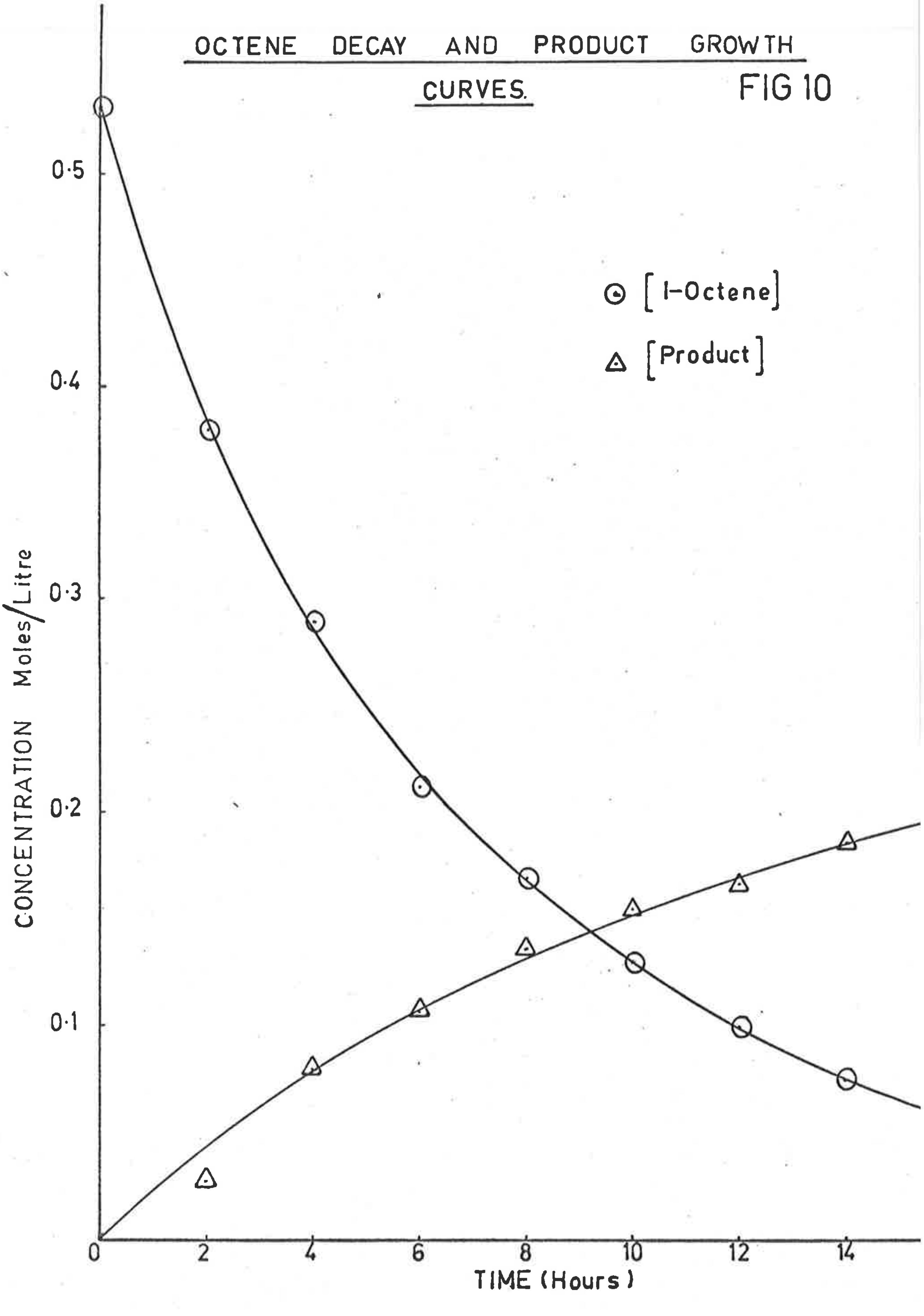
FIG 9



$$\text{product concentration} = \frac{\left\{\dfrac{I_{CH_2=}\,(Pr)}{I_{BENZ}}\right\}_{t=t}}{\left\{\dfrac{I_{CH_2=}}{I_{BENZ}}\right\}_{t=0}} \times [\text{1-octene}]_{t=0}$$

where $I_{CH_2=}$ (Pr) is the integral of the product vinyl $CH_2=$ singlet.

A representative plot of 1-octene decay and product decene growth with time is shown in Fig. 10. The results confirm the stoichiometry of 1-octene, (= two) as the amount of product decene formed, tends to a value of half the amount of 1-octene consumed, as the reaction proceeds. Whether the stoichiometry is maintained at all stages of the reaction, depends on the relative rates of the various reaction steps. In Fig. 10 and other run plots, there appears to be a lag in the product formation in the early stages, i.e. the amount of product decene formed is less than half the amount of octene consumed. If this is a real effect, it would mean that the rate of reaction measured by product yield would differ from that measured by reactant consumption, especially at initial conversions. The balance between the two rates would be made up of a term allowing for the concentrations of certain intermediates. This would be an interesting observation, in view of the discrepancies in kinetic equations derived from product yield and reactant consumption respectively. However, we are not



OCTENE DECAY AND PRODUCT GROWTH CURVES.

FIG 10

confident that the effect is real, because it is only apparent at low conversions, where the error in the product integral and the zero error in the initial 1-octene integral are at a maximum.

Thus stoichiometrically the reaction is confirmed as,

$$\frac{1}{2}\ Al_2Et_6 + 2\ CH_2{=}CH{-}C_6H_{18} \rightarrow Et_3AlC_8H_{17} + \text{2-Et-1-octene.}$$

If the reaction involves the associated form of triethylaluminium, the rate equation would be of the mixed second order type, viz.

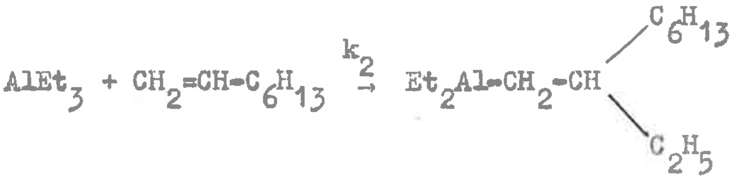
$$\frac{dx}{dt} = k[C_8H_{16}][Al_2Et_6]$$
$$\simeq k[C_8H_{16}]C_{Al_2}$$

where C_{Al_2} is the total alkyl concentration in terms of gram atoms of aluminium per mole dimer.

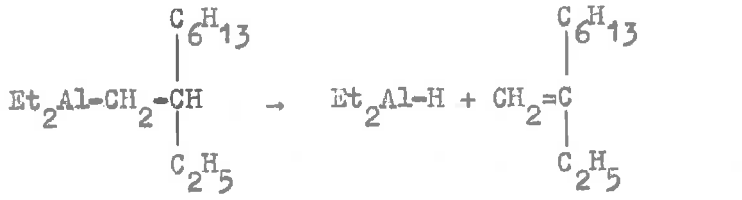
If however, the reactant is dissociated $AlEt_3$ then the mechanism becomes

$$Al_2Et_6 \overset{K_d}{\rightleftharpoons} 2\ AlEt_3 \qquad (1)$$

(where K_d is the dimer dissociation constant)



$$AlEt_3 + CH_2{=}CH{-}C_6H_{13} \xrightarrow{k_2} Et_2Al{-}CH_2{-}CH(C_6H_{13})(C_2H_5) \qquad (2)$$



$$Et_2Al\text{-}CH_2\text{-}CH(C_6H_{13})(C_2H_5) \rightarrow Et_2Al\text{-}H + CH_2{=}C(C_6H_{13})(C_2H_5) \qquad (3)$$

product decene

$$Et_2Al\text{-}H + CH_2{=}CH\text{-}C_6H_{13} \rightarrow Et_2AlCH_2 \cdot CH_2 \cdot C_6H_{13} \qquad (4)$$

There is no evidence for the state of association in the intermediate and product alkylaluminiums. At low conversion, they most likely form mixed associates with unreacted monomer $AlEt_3$. Under our experimental conditions, the formation of products beyond reaction (4) (as in the Perry and Ory mechanism) cannot be neglected. However, our conditions were less drastic than theirs.

Overall, reaction (2) is assumed to be rate controlling, with the other stages following rapidly. There is, in fact, no evidence that the diethylaluminium decyl adduct, in reaction (2), has anything other than a transient existence, and therefore it is more practical to regard reactions (2) and (3) as a single step. Reaction (4), the addition of 1-alkene to diethylaluminium hydride is considered rapid, as the addition of alkenes to Al-H bonds is significantly faster than the same addition to an Al-C bond. The only point of doubt about the assumption of reaction (2) being rate controlling, is the possible stoichiometric imbalance at small conversions. Again, if this is a real effect it soon disappears, presumably as the rate of reaction (2) begins to decrease.

The rate equation corresponding to this mechanism would be,

$$\frac{dx}{dt} = k_{APP}[AlEt_3][C_8H_{16}]$$
$$\simeq k_2 K_d^{\frac{1}{2}} [C_{Al_2}]^{\frac{1}{2}} [C_8H_{16}]$$

where k_{APP} = the apparent or observed rate constant.
To establish this rate equation we must initially estimate the order of reaction with respect to triethylaluminium by the method of van't Hoff.[23] The initial velocity of a reaction is related to the initial reactant concentration by

$$r_o = kc_o^n \text{ or } \log r_o = \log k + n \log c_o.$$

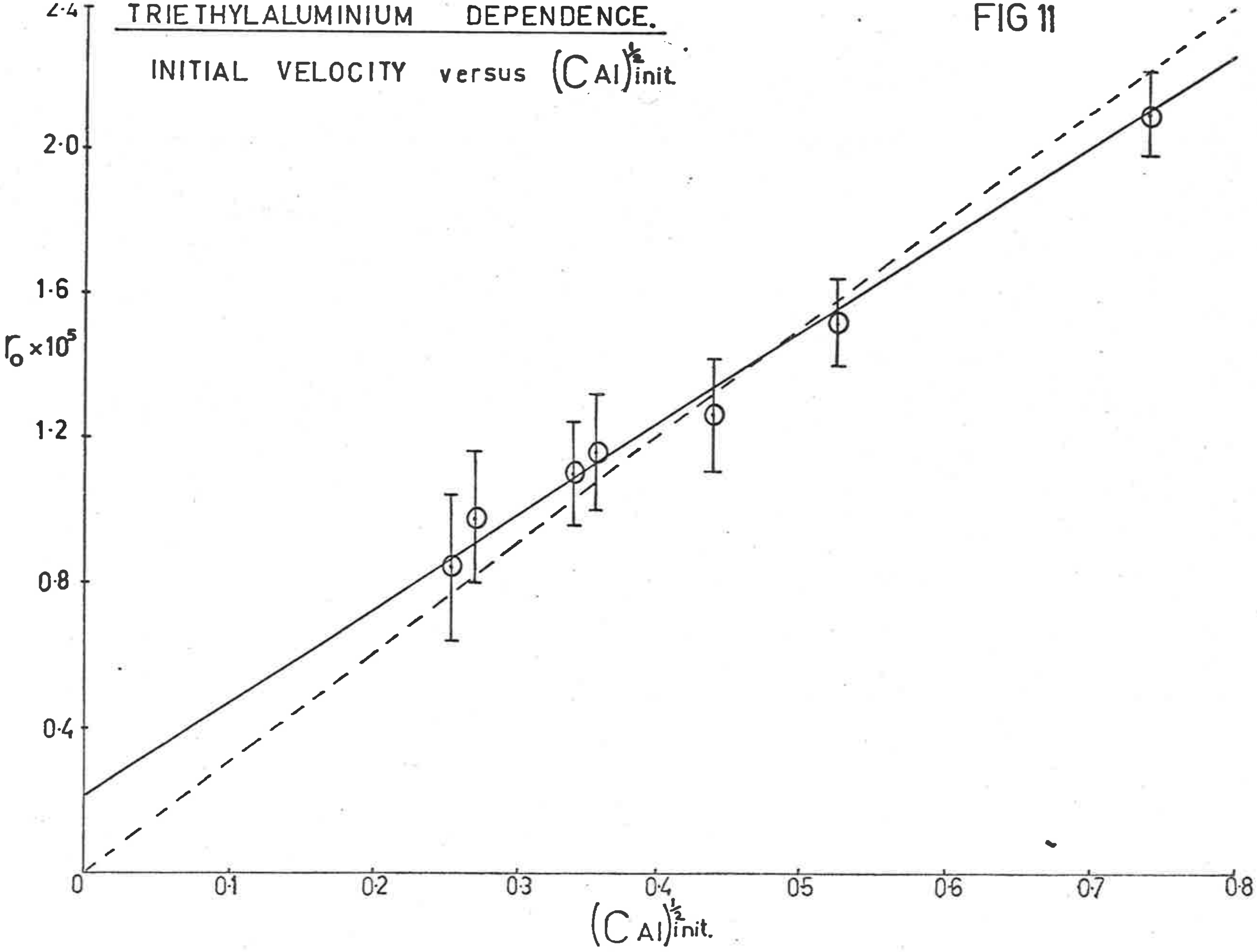
A log-log plot of initial reaction velocity versus initial concentration should be a straight line. The slope of this line is n, the external order of reaction with respect to the varying reactant. The log-log plot can give misleading results if taken over a limited concentration range, and should always be checked by a plot of r_o versus c_o^n; the confirmation being a straight line passing through the origin. In this manner, any doubt that the log-log value of n only refers to the instantaneous value of a variable order is eliminated. The distinction between the above mechanisms depends on the order being $\frac{1}{2}$ or 1, corresponding to monomer or dimer participation.

Table of Results

Sample	Initial Velocity r_o litre $mole^{-1} sec^{-1}$	Total $[alkyl]_{initial}$ as dimer (C_{Al_2}) moles/litre	Total $[alkyl]^{\frac{1}{2}}_{initial}$ as dimer (C_{Al_2})
1	1.52×10^{-5}	0.276	0.525
2	2.10×10^{-5}	0.546	0.739
3	1.26×10^{-5}	0.194	0.440
4	1.09×10^{-5}	0.116	0.341
5	1.16×10^{-5}	0.126	0.355
6	8.55×10^{-6}	0.065	0.255
7	9.80×10^{-6}	0.073	0.270

The initial velocity versus the square root of the initial alkyl concentration is shown in Fig. 11 and the log-log plot of these quantities in Fig. 12. The error bars for each initial velocity point are the maximum and minimum values of tangents drawn at zero time on the decay plots. The magnitude of the error bars indicates the difficulty in accurately drawing the exact tangent representative of the initial velocity (unless there are a large number of data points at small conversions) and the method must be

FIG 11

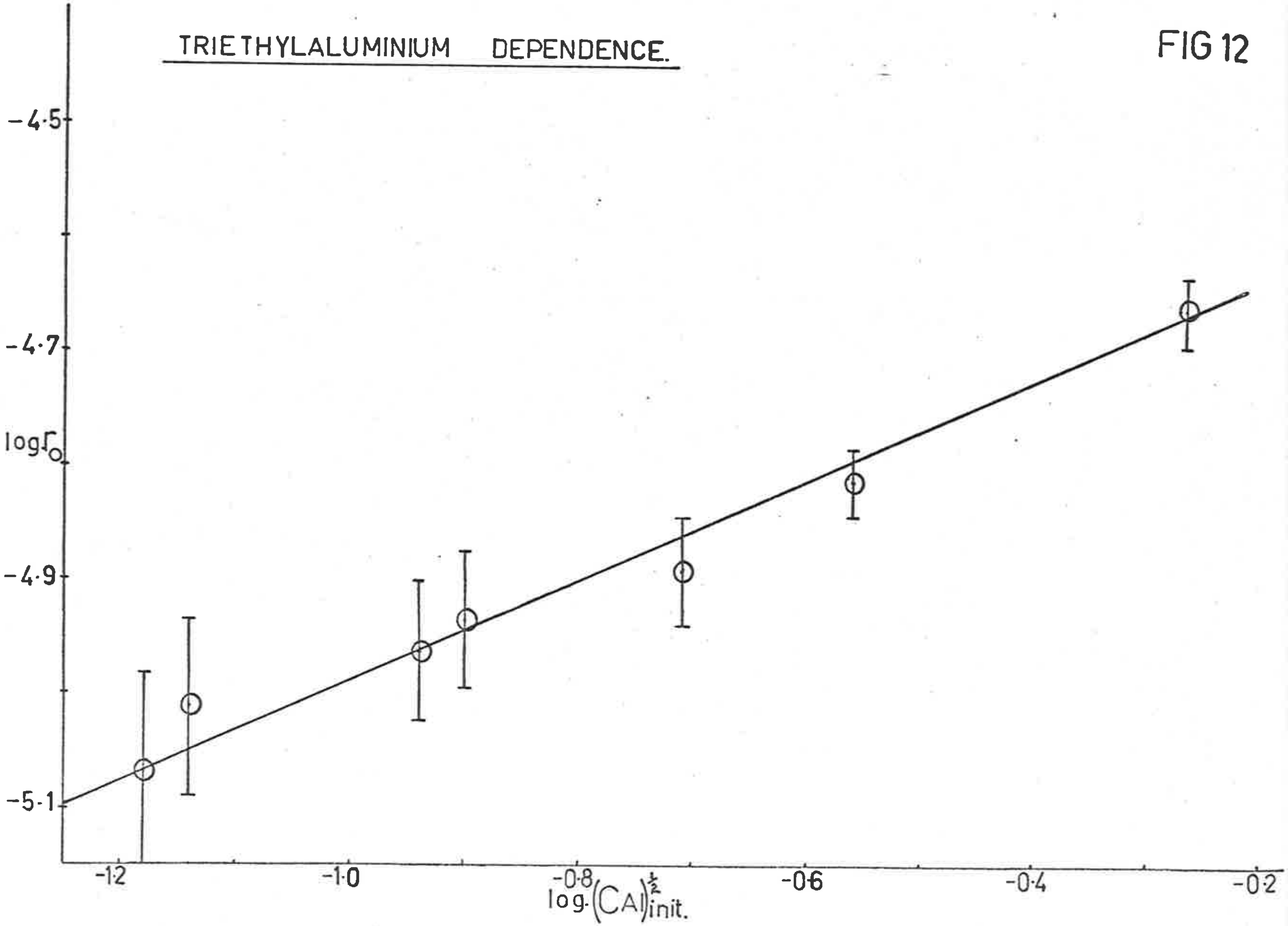


TRIETHYLALUMINIUM DEPENDENCE.

INITIAL VELOCITY versus $(C_{Al})^{\frac{1}{2}}_{init}$

FIG 12

TRIETHYLALUMINIUM DEPENDENCE.



regarded as suspect. However, random estimates of the initial velocity produced a straight line relationship when plotted in either manner described above. The least squares slope of the r_o versus $(C_{Al_2})^{\frac{1}{2}}$ plot has an intercept of 0.215×10^{-5} litre mole^{-1} sec^{-1} with a standard error of ± 0.075. The dotted line represents a line that can be drawn through the origin, yet still within the limiting error bars for each point. The graph shows the order with respect to triethylaluminium to be slightly less than one half. In addition, the least squares slope of the log-log plot is 0.43, however the errors involved allow us to approximate the order to one half.

Thus, from the graphs the relationship $r = k\ C_{Al_2}^{\frac{1}{2}}$ appears likely. The first order dependence with respect to 1-alkene is well established by previous workers.

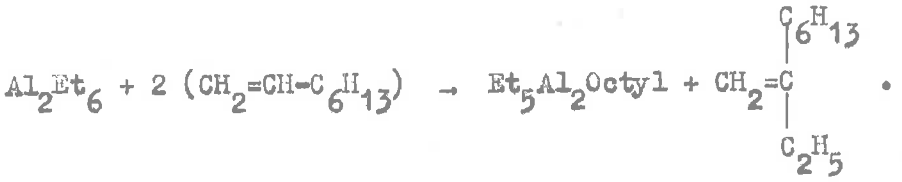
Thus the rate $= k_{APP}[C_8H_{16}][Al_2Et_6]^{\frac{1}{2}} \simeq k_2K_d^{\frac{1}{2}}[C_8H_{16}]C_{Al_2}^{\frac{1}{2}}$

i.e. consistent with the mechanisms of reactions (1), (2), (3) and (4) above.

Kinetic Results and Discussion

The method of integration provides a technique to show the assumed orders of reaction are correctly chosen. The data is applied to the integrated equation, usually by graphical means. Proof of the equation, when the function is plotted versus time, is a straight line passing through the origin, the slope of the line being equal to the rate constant (k_{APP} in this case).

The apparent or observed reaction has been defined as



$$Al_2Et_6 + 2\,(CH_2{=}CH{-}C_6H_{13}) \rightarrow Et_5Al_2Octyl + CH_2{=}\underset{\displaystyle C_2H_5}{\overset{\displaystyle C_6H_{13}}{C}} \;.$$

If the initial concentrations of alkyl and olefin are a and b and if x is the concentration of product formed after time t, then the concentrations of reactants are reduced to (a-x) and (b-2x) respectively.

Thus the apparent reaction rate $= k_{APP}(Al_2Et_6)^{\frac{1}{2}}(CH_2{=}CHC_6H_{13})$

$$= k_{APP}(a-x)^{\frac{1}{2}}(b-2x)$$

$$\therefore \frac{dx}{dt} = k_{APP}(a-x)^{\frac{1}{2}}(b-2x)$$

$$\text{or} \quad k_{APP}\,dt = \frac{dx}{(a-x)^{\frac{1}{2}}(b-2x)}$$

This is the differential form of the rate equation which now has to be integrated. The complete derivation of the integrated rate equation is included in Appendix I. Briefly, solutions of the integrated form are complicated by the fractional order present. Three solutions are possible depending on the relative magnitude of the initial reactant concentrations.

(a) when $a > \frac{b}{2}$ (when triethylaluminium is in stoichiometric excess)

$$k_{APP}t = \frac{1}{(a - \frac{b}{2})^{\frac{1}{2}}} \left[\ln\left\{ \frac{1 + \left(\frac{a - \frac{b}{2}}{a - x}\right)^{\frac{1}{2}}}{1 - \left(\frac{a - \frac{b}{2}}{a - x}\right)^{\frac{1}{2}}} \right\} - \ln\left\{ \frac{1 + \left(\frac{a - \frac{b}{2}}{a}\right)^{\frac{1}{2}}}{1 - \left(\frac{a - \frac{b}{2}}{a}\right)^{\frac{1}{2}}} \right\} \right]$$

(b) when $a = \frac{b}{2}$

$$k_{APP}t = 2\left\{ \frac{1}{(a)^{\frac{1}{2}}} - \frac{1}{(a-x)^{\frac{1}{2}}} \right\}$$

(c) when $a < \frac{b}{2}$ (1-octene in stoichiometric excess)

$$k_{APP}t = \frac{2}{(\frac{b}{2} - a)^{\frac{1}{2}}} \left\{ \arctan\left(\frac{a}{\frac{b}{2} - a}\right)^{\frac{1}{2}} - \arctan\left(\frac{a-x}{\frac{b}{2} - a}\right)^{\frac{1}{2}} \right\}$$

In practice, the graphs of the right hand sides of expressions (a) and (c) were plotted versus time and were reasonable straight lines passing through the origin. Values of the apparent rate constant were calculated from the least squares slopes of these graphs and tabulated below.

The degree of reliability one could place in these results was expressed in the form of confidence limits. The development of confidence limits is included in Appendix III. The "best and worst fit" sets of data from the total population of rate constant measurements included in the table are shown in Fig. 13

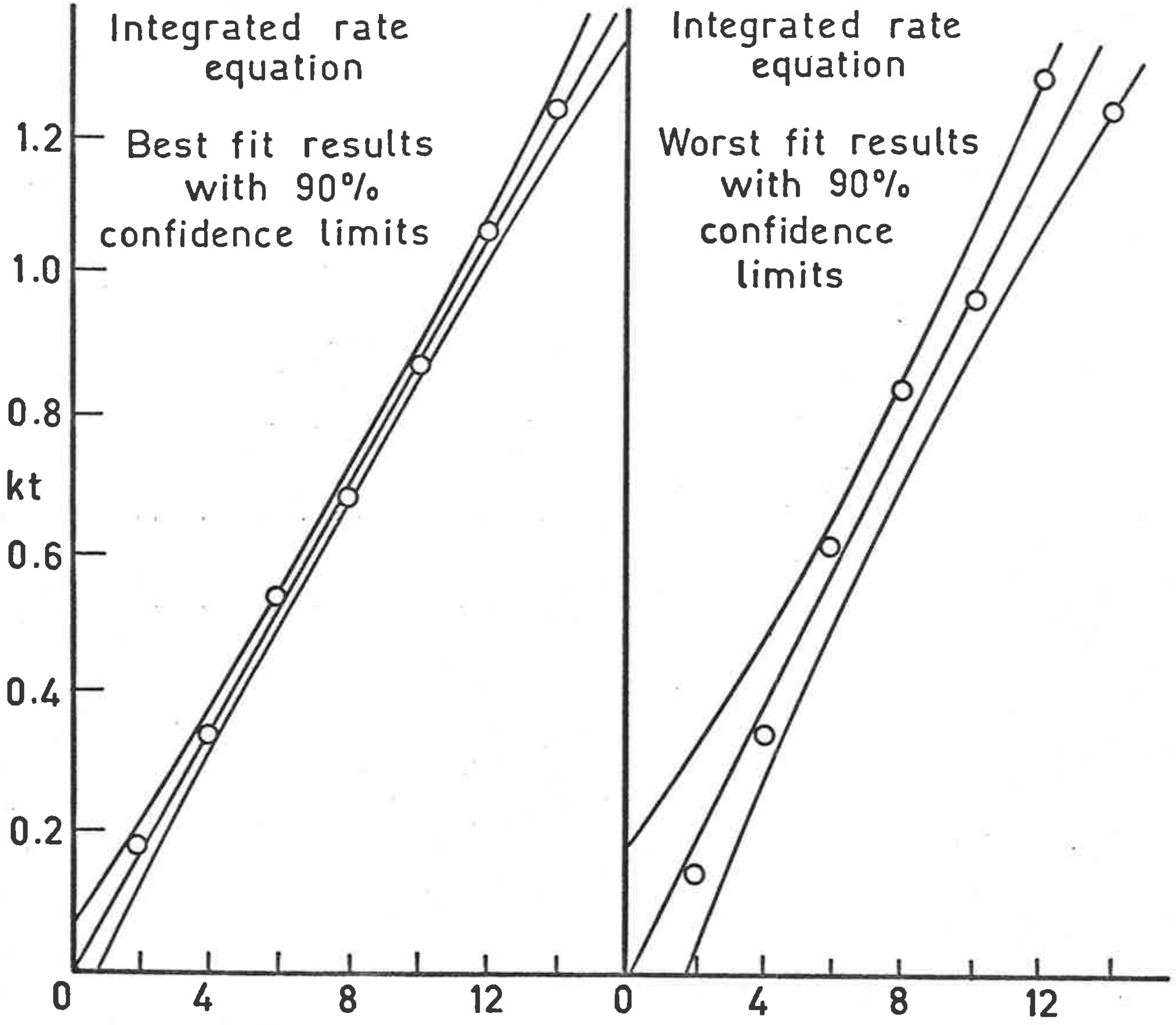


FIG. 13. TIME (hours)

with their 90% confidence limit hyperbolas.

Statistically, we are comparing the least squares straight line represented by our data with the "true" line representing the defined integrated rate equation, which passes through the origin and with a slope equal to the true rate constant.

We have arbitrarily selected a 5% level of probability, or tolerance limit. This corresponds to symmetrical 90% confidence limits on our fitted line, and we assert a priori that the true value of kt at any t is contained in these limits, then we are making the correct statement 90% of the time. In other words, we have placed 100 α % (where α is the probability) or symmetrical 10% tolerance limits on the fitted data with 100 $(1 - \alpha)$% or 90% confidence.

Even in the "worst fit" case, the intercept on the least squares straight line is most obviously less than the standard deviation. In statistical terms, the correlation of the data to the integrated rate equations (a) and (c) above is significant. These equations are specific to the mechanism involving reactions (2) to (4) above. The alternative mechanism implies mixed second order kinetics. The integrated rate equation for this mechanism was tested by a number of data sets, and distinct curvature was observed in plots of second order kt versus time.

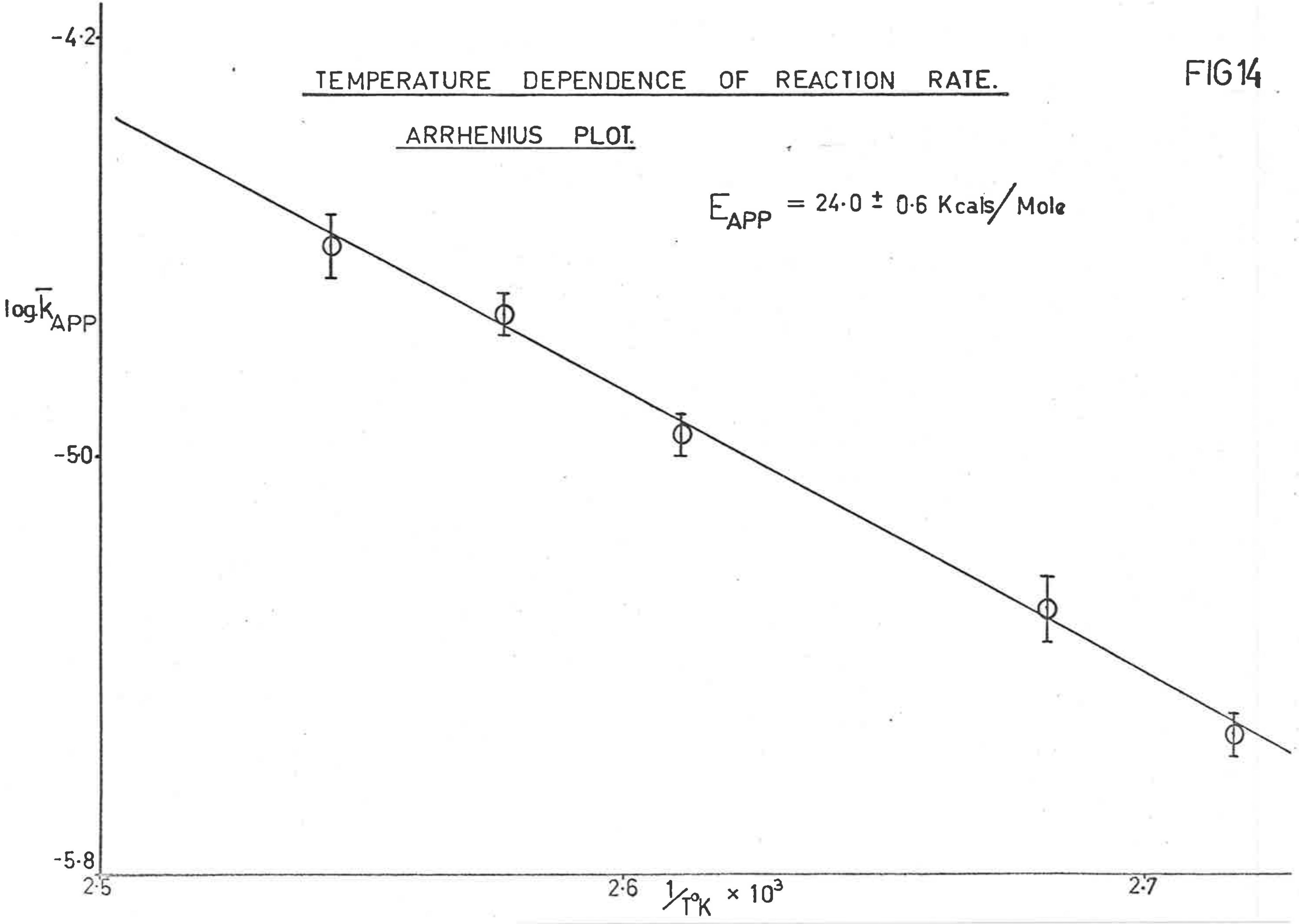
It is clear therefore that the method of integration confirms the order of reaction estimated from the van't Hoff method. The internal and external orders are identical at $\frac{1}{2}$ and 1 (1-octene).

Each population of rate constants at a particular temperature exhibited a randomness about a mean value $\bar{k}_{APP}$, which was tabulated as representative of that population. A standard deviation in $\bar{k}_{APP}$ is governed by the population variance from this mean value. Since the standard deviations at each temperature are reasonably constant, there was no reason to tabulate a weighted $\bar{k}_{APP}$.

The temperature dependence of the reaction was tested by the Arrhenius law in the form $\log \bar{k}_{APP} = \frac{-E_A}{2.303\ RT} + \log A$. When $\log k_{APP}$ was plotted against the reciprocal of temperature in degrees absolute, a straight line was obtained (see Fig. 14). The least squares slope of the Arrhenius plot gave an activation energy $E_A = 24.0$ kcal/mole with an S.E. $(E_A) = 0.6$ kcal/mole. The intercept at $1/T\ \text{Å} =$ zero produced a pre-exponential factor of $A = 10^{9.0}$ litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ sec^{-1} with an S.E. $(\log A = 0.3)$.

The superiority of the integrated rate function, with the half order term over the completely second order integrated rate equation, confirms the assumed external order with respect to triethylaluminium of one half. Again, the correct integrated rate plots confirm the mechanism which stands as follows:

FIG 14



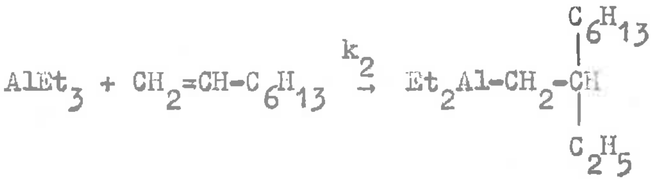
TEMPERATURE DEPENDENCE OF REACTION RATE.

ARRHENIUS PLOT.

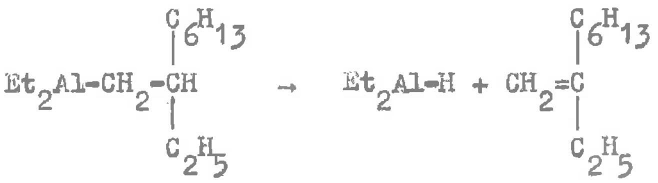
Table of Rate Data

Run Temperature		Concentrations (moles/litre)		k_{APP}	$\bar{k}_{APP} \pm$ S.D.$(\bar{k}_{APP})$
^{o}C	$\frac{1}{T^{o}K}$	1-octene	Al_2Et_6	(litre$^{\frac{1}{2}}$/mole$^{\frac{1}{2}}$ sec)	
120.0	2.544×10^{-3}	1.33	0.34-0.99	2.15×10^{-5}	$2.50 \times 10^{-5} \pm 0$
				2.46×10^{-5}	
				2.76×10^{-5}	
				2.99×10^{-5}	
				2.98×10^{-5}	
				2.01×10^{-5}	
				2.03×10^{-5}	
				2.64×10^{-5}	
115.0	2.577×10^{-3}	1.59	0.31-1.12	1.70×10^{-5}	$1.86 \times 10^{-5} \pm 0$
				1.94×10^{-5}	
				2.21×10^{-5}	
				1.60×10^{-5}	
110.0	2.611×10^{-3}	1.60	0.46-0.98	1.19×10^{-5}	$1.08 \times 10^{-5} \pm 0.14$
				1.23×10^{-5}	
				1.00×10^{-5}	
				8.99×10^{-6}	
100.0	2.681×10^{-3}	1.62	0.29-0.95	5.55×10^{-6}	$5.13 \times 10^{-6} \pm 0$
				5.31×10^{-6}	
				4.78×10^{-6}	
				4.87×10^{-6}	
95.0	2.717×10^{-3}	1.63	0.48-1.44	3.30×10^{-6}	$2.94 \times 10^{-6} \pm 0.25$
				2.59×10^{-6}	
				2.86×10^{-6}	
				2.99×10^{-6}	

$$Al_2Et_6 \overset{K_d}{\rightleftharpoons} 2\,AlEt_3 \qquad (1)$$



$$AlEt_3 + CH_2{=}CH{-}C_6H_{13} \xrightarrow{k_2} Et_2Al{-}CH_2{-}\overset{C_6H_{13}}{\underset{C_2H_5}{CH}} \qquad (2)$$



$$Et_2Al{-}CH_2{-}\overset{C_6H_{13}}{\underset{C_2H_5}{CH}} \rightarrow Et_2Al{-}H + CH_2{=}\overset{C_6H_{13}}{\underset{C_2H_5}{C}} \qquad (3)$$

$$Et_2Al{-}H + CH_2{=}CH{-}C_6H_{13} \rightarrow Et_2AlCH_2.CH_2.C_6H_{13} \qquad (4)$$

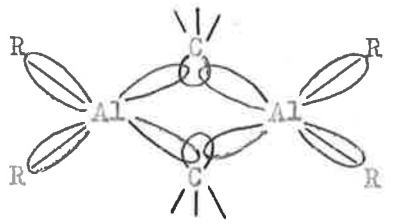
We infer that the degree of dimer dissociation is not excessive, hence the overall or observed rate constant $k_{APP} = K_d^{\frac{1}{2}}k_2$. The rate constant k_2 of the addition or rate determining step is the required quantity and to obtain it we need an estimate of the liquid phase dimer dissociation constant within our kinetic temperature range.

CHAPTER IV - ASSOCIATION IN TRIALKYLALUMINIUMS

Introduction

The ability of trialkylaluminiums to associate and achieve greater stability is a function of the unique bonding properties of these compounds. The basic bonding configurations of the electron deficient bridge bonds, which cause the stability, have been explained in Chapter I. Briefly, a three-centre bond exists between the two aluminiums and the carbon atom of the bridging group. Two electrons are shared in an overlap of the two aluminium atom sp^3 orbitals with the carbon atom sp^3 orbital.

Hence, the equilibrium $2\ AlR_3 \rightleftharpoons Al_2R_6$ exists and the dimer bonding structure is schematically represented as



The size and shape of the alkyl group R restricts the ability of the monomeric trialkyl to dimerise. Steric hindrance prevents the approach of two monomers into an orientation close enough for molecular orbital overlap.

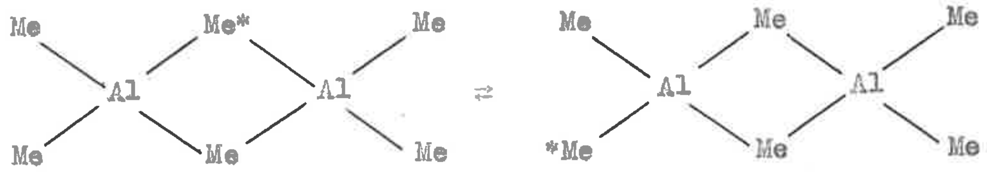
Tri-n-alkylaluminiums, where the alkyl group ranges from methyl to n-butyl, are known to be associated at room temperature. Alkylaluminiums with R containing a secondary carbon atom attached to the Al atom are essentially monomeric.

Two direct techniques utilised to establish the association experimentally are X-ray crystallography and p.m.r. spectroscopy. Association was predicted from I.R.[24] and Raman spectroscopy.[25] Additional evidence was forwarded by molecular weight measurements from various methods (ebulliometry,[26] cryoscopy,[27,28] vapour pressure measurement[29,30]).

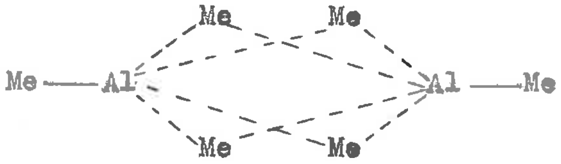
Lewis and Rundle,[31] in an X-ray crystallographic analysis of trimethylaluminium, measured the bridging bond angle (Al-C-Al, 70°) and the Al-C bond lengths for both bridged (2.24 Å) and terminal (2.00 Å) bonds. A similar study was made some years later by Vranka and Amma.[32] They agreed with Lewis and Rundle on the shape of the dimer molecule, but with slight differences in the bridging bond angle (75°) and in the bridge bond length (2.14 Å). It is interesting to note that the distance between Al atoms is within the accepted theory of metal-metal bond lengths, which may also increase the dimer stability.

The presence of dimer formation has been demonstrated, equally as effectively, by proton magnetic resonance. Muller and Pritchard[33] showed the room temperature p.m.r. spectrum of trimethylaluminium to contain only one peak. The inference from this spectrum was two-fold; all of the protons present were magnetically equivalent, i.e. they all resonate at the same p.m.r. chemical shift; if there are two types of methyl groups present (bridging and terminal) they must be involved in a rapid exchange process.

Schematically the exchange equilibrium occurs possibly by way of dissociation.



When the temperature of a sample of Al_2Me_6 in cyclopentane was lowered to -75°C and the p.m.r. spectrum measured, two signals with an integrated peak area ratio of 2:1 are now present. The appearance of two resonances confirmed the presence of two types of methyl groups and the single resonance at room temperature was due to the rapid exchange process. At the lower temperature, the dimeric structure was "frozen" and the individual terminal and bridging methyls become apparent, i.e. the exchange rate was drastically reduced. The authors concluded that at room temperature, the monomer was probably not formed as an intermediate, but that the exchange process was intramolecular by two possible mechanisms:- the breaking of an Al-C bond or the deformation of the molecule into four methyl bridge bonds in the conformation of a square.



The estimated activation energy for this process was between 6-14 kcal/mole.

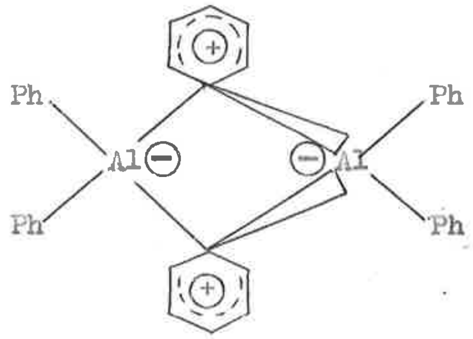
Ramey et al.[34] investigated the low temperature p.m.r. spectrum of triethylaluminium. The normal room temperature methylene quartet signal broadens as the temperature is lowered and finally (at -60°C) emerges as two groups of quartet signals at 0.08 and 1.08 p.p.m. These quartet signals correspond to the terminal and bridging methylenes respectively. An exact 2:1 integral ratio was not observed in this case as the lowest field methylene signal overlapped into the methyl signal. The effective decrease in electron density about the protons of the bridging methylene causes a shift (paramagnetic) in this group's resonance, to appear at lower fields.

A similar investigation[35] of triethylaluminium in toluene at low temperatures confirmed the dimeric structure of this compound.

We observed the beginning of methylene group broadening in a low temperature investigation of possible complexing between triethylaluminium at 1-octene (see Chapter II and Fig. 7). The temperature on this occasion was not low enough to observe two distinct resonances.

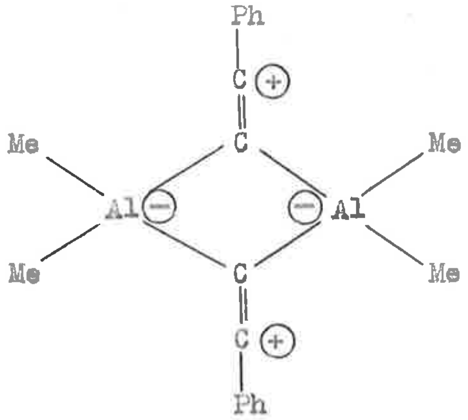
Additional evidence for the dimeric character of the tri-n-alkylaluminium series has been obtained from infra-red spectroscopy and various molecular weight and vapour pressure measurements. Ziegler[36] and Coates[37] et al. have thoroughly reviewed the I.R. spectroscopic properties of organoaluminium compounds. Vapour pressure measurements[12,29] have yielded heats of dissociation for the trimethylaluminium dimer, the values being 20.2[13] and 20.4[29] kcal/mole of dimer.

Triphenylaluminium was reported to be largely (80%) associated by ebulliometry,[25] however cryoscopic measurements[38] did not support such an association. An X-ray crystallographic analysis[39] of triphenylaluminium shows the bridging phenyl groups to be inclined at an angle to the plane of the Al_2C_2 ring. The distortion of the phenyl ring introduces the concept of π bond donation to the electron deficient bonds which increases the stability of the molecule even further. Schematically this is shown



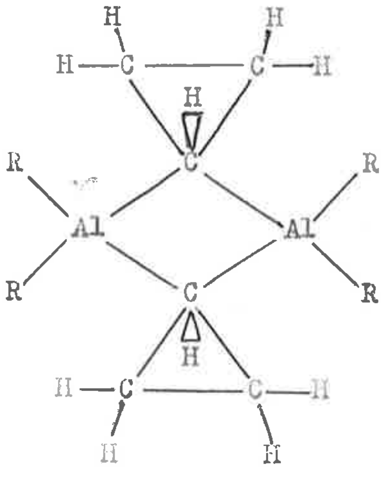
This idea is contradicted by the Al-C bridge bond length which is longer by 0.04 Å than the corresponding bond length in trimethylaluminium where no such donation can occur. The bridge bond lengths of trimethylaluminium are longer than the terminal bond lengths, due to the decreased electron density within the bridge bond. In the case of triphenylaluminium, one might have expected the bridge bond length to approach the terminal bond length and be significantly less than the trimethyl bridge bond. Apparently this is not the case.

The π bond donation effect has been observed in p.m.r. measurements on alkenyl-diisobutylaluminium compounds[21] and dimethyl(phenylethynyl)aluminium compounds.[40] Here, the spectrum contains a signal due to aryl protons and only one other peak, regardless of temperature, showing that bridging occurs via the phenylethynyl group. This is a result of the enhanced stability offered to the three centre bond by the π orbital system of the ethynyl group.



The structure could be represented as shown above, although the presence of the conjugated system could localise the positive charge within each phenyl ring. More recently,[41] p.m.r. studies have shown the tricyclopropylaluminium dimer to be an interesting example of bridge bonding with enhanced stability. In fact, the authors claim this molecule to be the most stable of the trialkylaluminium dimers. A room temperature spectrum shows two types of cyclopropyl groups in the integrated peak area ratio of 2:1 corresponding to the usual terminal to bridging group ratio.

The structure is represented



It is claimed that the formation of the bridge bond occurs by the overlap of an sp^2 orbital from the cyclopropyl carbon with the aluminium sp^3 orbitals to give a σ type three-centre bonding molecular orbital (the accepted electron deficient bond formation), assisted by the overlap of a pπ type orbital from the cyclopropyl group with this σ molecular orbital.

On raising the temperature and recording the p.m.r. spectra, the exchange between terminal and bridging positions does not commence until 70°C, implying that the activation energy for this process is larger than any other studied. However, in the absence of the determination of a value for the activation energy, the author's conclusion that the enhanced stability at lower temperature arises from energy rather than entropy factors is premature.

Although sterically hindered trialkylaluminiums do not associate to form dimers, if they are mixed with dimeric trialkylaluminiums then mixed dimeric trialkylaluminium species are formed. This effect has been demonstrated by E.G. Hoffman[42] using mixtures of triisobutylaluminium and trimethylaluminium and is discussed in more detail later in this chapter.

The only reported molecular weight studies on triethylaluminium are Laubengayer and Gilliam's vapour density and pressure studies at high temperatures, and Hoffman's "adiabatic cryometry" used to establish the molecular weight at low temperatures.

This lack of molecular weight data, particularly in the temperature range 80-125°C prompted our investigations, which follow.

The Measurement of Equilibrium Parameters for the Triethylaluminium Monomer-Dimer Equilibrium

Introduction and Choice of Method

In 1941, vapour density and pressure measurements were used to establish the apparent molecular weight of triethylaluminium in the vapour phase at several high temperatures.[12] This data is the only molecular weight investigation available (apart from a low temperature cryoscopic determination[28]). The authors conceded doubt in their highest temperature measurement, because of sample decomposition at that temperature. A previous paper[43] outlined the type of vapour density and pressure measurements used. No attempt was made to calculate an equilibrium constant from these measurements. Unfortunately in the triethylaluminium case, the pressure at which each vapour density measurement was carried out, was not reported. If equilibrium parameters are to be calculated from this data, it is necessary to make some assumption about the manner in which these experiments were carried out. Two such attempts have been made and in each case a different assumption was made concerning the pressure. Allison et al.[11] considered that the Laubengayer and Gilliam experiments were performed at the vapour pressure, whereas Hay et al.[13] assumed a pressure of 100 mm. The former assumption is almost certainly incorrect. An alternative approach to a pure and simple guess, is to examine the experimental procedure reported in the previous paper.[43] Here, vapour density and pressure measurements were performed in the same apparatus on gallium halides and the relevant experimental factors were all properly recorded. Even if the triethylaluminium measurements were carried out in the same way, there are no grounds whatsoever for assuming each experiment was carried out at the same pressure. In addition, the pressure prevailing in the gallium halide series varied from experiment to experiment determined apparently by the vicissitudes of individual sampling. Thus, no dependence can be placed on any of the attempted estimations of K_d(gas) from Laubengayer and Gilliam's data. Their results are summarised in the following table.

Temperature °C	Apparent Molecular Weight	The Antoine equation
150.6	128.5	$\log_{10} p\ (\text{mm.}) = -\dfrac{A}{T^{\circ}K} + B$
165.5	125.3	
185.5	123.5	where A = 3625 and B = 10.784
200.0	124.5	

The 200°C reading was believed to be in error because of irreversible dissociation of the compound.

Hay et al.[14], using a more modern vapour pressure measurement technique and triethylaluminium preparation, have fully examined the monomer ⇌ dimer equilibrium in the temperature range 60–120°C. The tabulated vapour pressures are slightly higher than those obtained by Laubengayer and Gilliam and a comparison is shown by their respective Antoine equations.

Laubengayer and Gilliam: $$\log_{10} p = \frac{-3625}{T^{\circ}K} + 10.784$$

Hay et al.: $$\log_{10} p = \frac{-3613}{T^{\circ}K} + 10.85$$

The dissociation constants for the equilibrium <u>in the gas phase</u> have been determined and are tabulated below.

Temperature °C	K_d (moles/litre) x 10^3
100	4.34
90	2.87
80	1.94
70	1.31
60	0.973
50	0.542

The calculated dissociation constants K_d were small and showed that the monomer was only present at high dilution. Under normal experimental concentration conditions ($>$ 0.2 moles/litre of Al_2Et_6) the dimer was the dominant species.

Hoffman[28] established the apparent molecular weight of triethylaluminium in benzene by the principle of adiabatic cryometry. The method relies on the determination of freezing point depression of solutions relative to solvent over a wide concentration range. It is a colligative property method which determines the number of solute molecules. The molecular weight range of 229-196 was established for a concentration range of 0.2-0.005M. Hoffman queried the lowest concentration molecular weight (196) because of the significance of oxygen and water impurities at such concentrations. The results were expressed as the "degree of polymerisation" or "the association number" and the author attempted to compare this plot (association number versus concentration) with a similar curve for the benzoic acid system. However, the scatter in the triethylaluminium results did not permit the drawing of a smooth curve, even though there was an obvious resemblance to the benzoic acid calibration curve. Unfortunately, the individual molecular weights used to calculate the degree of polymerisation were not tabulated. We have estimated these molecular weights from the graph by photographic means, and discussed them later in this chapter. As discussed in the previous chapter, the complete kinetic characterisation of the reaction between triethylaluminium and 1-octene depends on a knowledge of the value of K_d. The relevant parameter is the equilibrium constant (in concentration units) for the equilibrium in hydrocarbon solution over the temperature of our kinetic experiments. The difficulties in estimating even K_d in the gas phase at Laubengayer et al. experimental temperatures have already been discussed. Although Hay et al. results are good confirmation of the earlier vapour pressure study, we considered it essential to our system to establish the equilibrium dissociation constant in the liquid phase; the phase of the kinetic experiments and data we wish to correct. The gas phase dissociation constant is not relevant to the solution equilibrium where there is a nett charge in the number of molecules in the stoichiometric process.

In practice, the apparent molecular weight, which is the number average molecular weight of the species of compound, is estimated. The degree of dimer dissociation can then be calculated and from this value, the dissociation constant, K_d, as follows.

K_d is defined for the equilibrium equation

$$Al_2Et_6 \rightleftharpoons 2\ AlEt_3$$

Number of moles of species	$(1 - \alpha)n$	$2\alpha.n$
Concentration of each species	$(1 - \alpha)c$	$2\alpha.c$

where $c = C_{Al_2}$ = the total concentration of compound, in all forms, estimated as dimer = $[Al_2Et_6] + \frac{1}{2}[AlEt_3]$. The square brackets define the actual molar concentration of the molecular species enclosed. The mole fractions of each species are

$$\frac{1 - \alpha}{1 + \alpha} \quad \text{and} \quad \frac{2\alpha}{1 + \alpha}$$

$\therefore$ M.W. app (apparent molecular weight) $= \frac{1 - \alpha}{1 + \alpha} \cdot 228.2 + \frac{2\alpha}{1 + \alpha} \cdot 114.1$

$$= \frac{228.2}{(1 + \alpha)}$$

$$\therefore \alpha = (\frac{228.2}{\text{M.W. app}} - 1)$$

The molar concentrations of dimer and monomer are

$$\frac{(1 - \alpha)c}{1 + \alpha} \quad \text{and} \quad \frac{2\alpha c}{1 + \alpha}$$

respectively.

The dissociation constant for the equilibrium is

$$K_d = \frac{[AlEt_3]^2}{[Al_2Et_6]} = \frac{4\alpha^2 d}{1 - \alpha}$$

A table of K_d with temperature can be constructed and the linear relationship between these two parameters tested.

$$\text{Now} \quad \frac{d \ln K_d}{dT} = \frac{\Delta H_d}{RT^2} \quad \text{or} \quad \frac{d \ln K_d}{d(1/T)} = - \frac{\Delta H_d}{R}$$

The slope of a graph of $\log_{10} K_d$ plotted against the reciprocal of temperature in degrees absolute should be a straight line of slope $-\Delta H_d/2.303\,R$. Thus this method provides a ready calculation of the heat of dissociation per mole dimer.

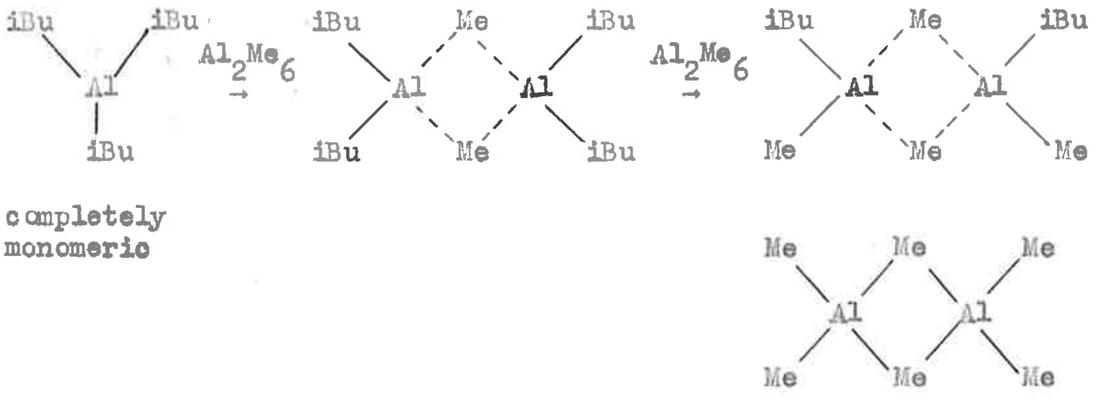
The choice of experimental methods to calculate the molecular weight of triethylaluminium is limited by: the nature of the compound itself, an extremely reactive liquid; the necessity of establishing the liquid phase K_d within our kinetic temperature range, and the reported vapour pressure of triethylaluminium.[12,14]

Initially, the three molecular weight estimation methods chosen were the isopiestic method, a proposed method using p.m.r. spectroscopy and by boiling point elevation (ebulliometry).

The isopiestic method depends on a non-volatile solute, as the attainment of equilibrium partial pressures is fundamental. This method was rejected because of the reported volatility of triethylaluminium.

The idea of proton magnetic resonance, as a molecular weight method, was developed from a paper by E.G. Hoffman.[42] Here, the non-associating monomeric triisobutylaluminium and the strongly associating almost exclusively dimeric trimethylaluminium were mixed. A mixed dimeric species forms, its structure determined by the relative concentrations of initial reagent.

Schematically,



completely
monomeric

dimeric

As explained previously, the rapid rate of exchange at room temperature prevents the bridging and terminal methyl groups of trimethylaluminium from showing separate resonances and a single peak is observed in an intermediate field position. The relative intensity and position of this signal depends on the ratio of bridged to terminal methyls at any one time. The above scheme shows this ratio to increase as the trimethylaluminium concentration in the mixture decreases. The nett effect observed is a shift down-field of the α methyl signal and its eventual disappearance.

A similar situation might occur with triethylaluminium. The dimer contains six p.m.r. equivalent groups, four terminal and two bridging. Again the p.m.r. equivalence is due to the rapid rate of alkyl group exchange.

The extent of dimer dissociation increases with temperature, with corresponding increase in monomer concentration, until at some hypothetical temperature, only monomer is present in the sample. The concentration of terminal ethyls will thus increase at the expense of bridging ethyls. This removal of bridging ethyls will produce a reduction in electron density at the aluminium and will in turn cause a decrease in electron density about the protons of the α methylene group. This electronic de-shielding should be evident in p.m.r. spectra as a shift downfield of the α-CH_2 quartet, towards the methyl triplet, i.e. a decrease in the internal chemical shift of triethylaluminium. The internal chemical shift ($-\delta$) is defined as the difference in chemical shifts of the methyl and methylene group resonances. The chemical shift of the methyl triplet is the centre signal, and for the methylene the calculated centre of the quartet group of signals (see Fig. 21).

In theory, the temperature may be raised to a position where no further reduction in $-\delta$ occurs. This would correspond to complete dissociation and the integrated peak area equivalent to the monomer concentration. The graph of internal chemical shift ($-\delta$) with temperature should be sinusoidal and on extrapolation one should obtain a value representing the monomer $-\delta$. This value could be compared with $-\delta$ obtained at low temperatures ($-70^{\circ}C$) corresponding to terminal and bridging ethyl resonances in the ratio 2:1.[34,35] It is highly unlikely that the complete dissociation limit could be attained in practice because of intervention of irreversible decomposition of the Al-C_2H_5 bonds. However, some extrapolation procedure might be applied.

Alternatively, the equilibrium is concentration dependent and enhanced monomer concentration will occur in dilute solutions. Again a plot of $-\delta$ versus alkyl concentration should also be sinusoidal. It may be possible to extrapolate to a position where no further reduction in $-\delta$ occurs with decrease in dimer concentration. This extrapolated concentration should correspond to monomer alone.

Summarising, a value of K_d for the equilibrium might be derived in simple terms by the following: the fraction of dimer molecules p (in dilute solution) is given by

$$p = \frac{(-\delta) - (-\delta_M)}{(-\delta_D) - (-\delta_M)}$$

where $(-\delta)$ is the observed internal chemical shift of the alkyl species present at a particular temperature or concentration; $(-\delta_M)$ is the internal chemical shift of the alkyl species at infinite temperature or dilution, i.e. monomer; $(-\delta_D)$ is the internal chemical shift of the alkyl species at lower temperatures, i.e. dimer.

The equilibrium constant at any temperature is then:

$$K = \frac{p}{1 - p}$$

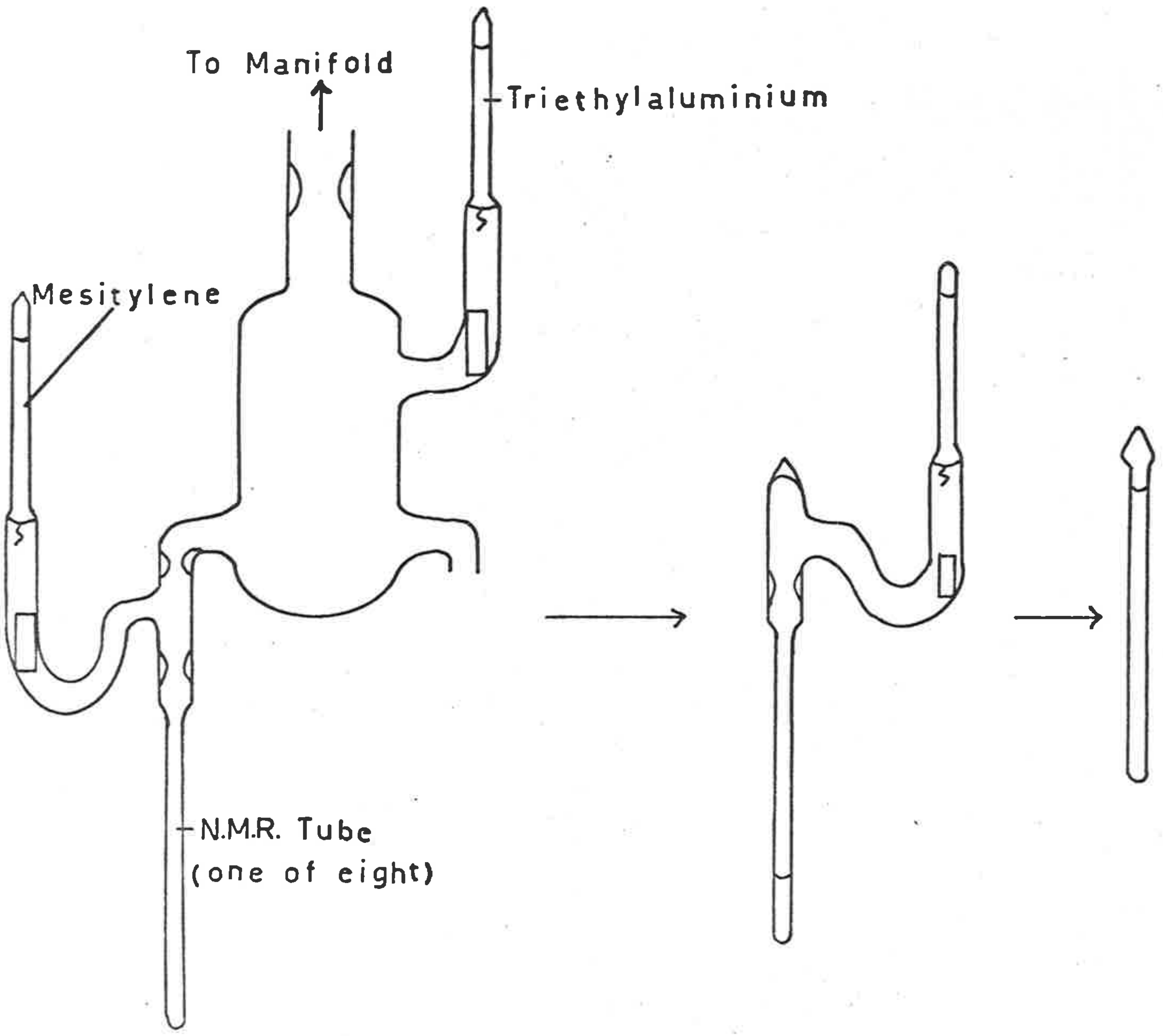
Although considerable approximations, including extrapolation to high temperature or dilution, would be involved in an experiment of this type, it was considered worth trying because it was by far the most convenient method of attempting to measure K_d. The equilibrium could be measured under conditions of high purity and minimum handling.

The experimental apparatus designed to test the above ideas is shown in Fig. 15 and was evacuated to $< 10^{-3}$ torr for twenty four hours. The attached solvent breakseals had been loaded previously by distilling dry "living end" purged mesitylene into a dispensing vessel. This vessel was sealed from the manifold while pumping, each calibrated breakseal filled to the mark and then sealed off from the main vessel. The apparatus was sealed off at the constriction, the triethylaluminium breakseal ruptured and the alkyl allowed to flow into the base of the vessel. Varying amounts were poured into each n.m.r. tube and the volumes present calculated from cathetometer measured heights. Each n.m.r. tube, with its accompanying solvent breakseal, was sealed off, the solvent breakseal ruptured, and the alkyl in the n.m.r. tube diluted to a pre-calibrated mark. After dilution each n.m.r. tube was sealed off and the p.m.r. spectra recorded as follows.

The spectrum of the most dilute sample of Al_2Et_6 was recorded at 10°C intervals from 60°C to 140°C inclusive. No apparent change in internal chemical shift occurred at any stage.

APPARATUS FOR ATTEMPTED Kd DETERMINATION BY P.M.R. SPECTROSCOPY.

FIG 15



Each of the eight concentrations of triethylaluminium was measured at 110°C. Again, no significant change in the interval chemical shift resulted.

The conclusion is that the method is insensitive to the possible small change in electronegativity or a "dilution" effect. The number of aluminium-carbon bonds is reduced from eight to six if complete dissociation occurs. The small change in electronegativity at the aluminium atom on monomer formation is "diluted" even further by its distribution amongst three equivalent ethyl groups. Thus the change in electron density about the methylene group protons appears insignificant and no apparent change in internal chemical shift is the result.

The equilibrium might best be studied by variable temperature Al^{27} broad-line n.m.r. where one would be measuring the change in electronegativity where it should be most marked, i.e. at the aluminium nucleus. However, sensitivity problems could also be encountered and in addition we had no facility for broad-line studies.

Description of Selected Method

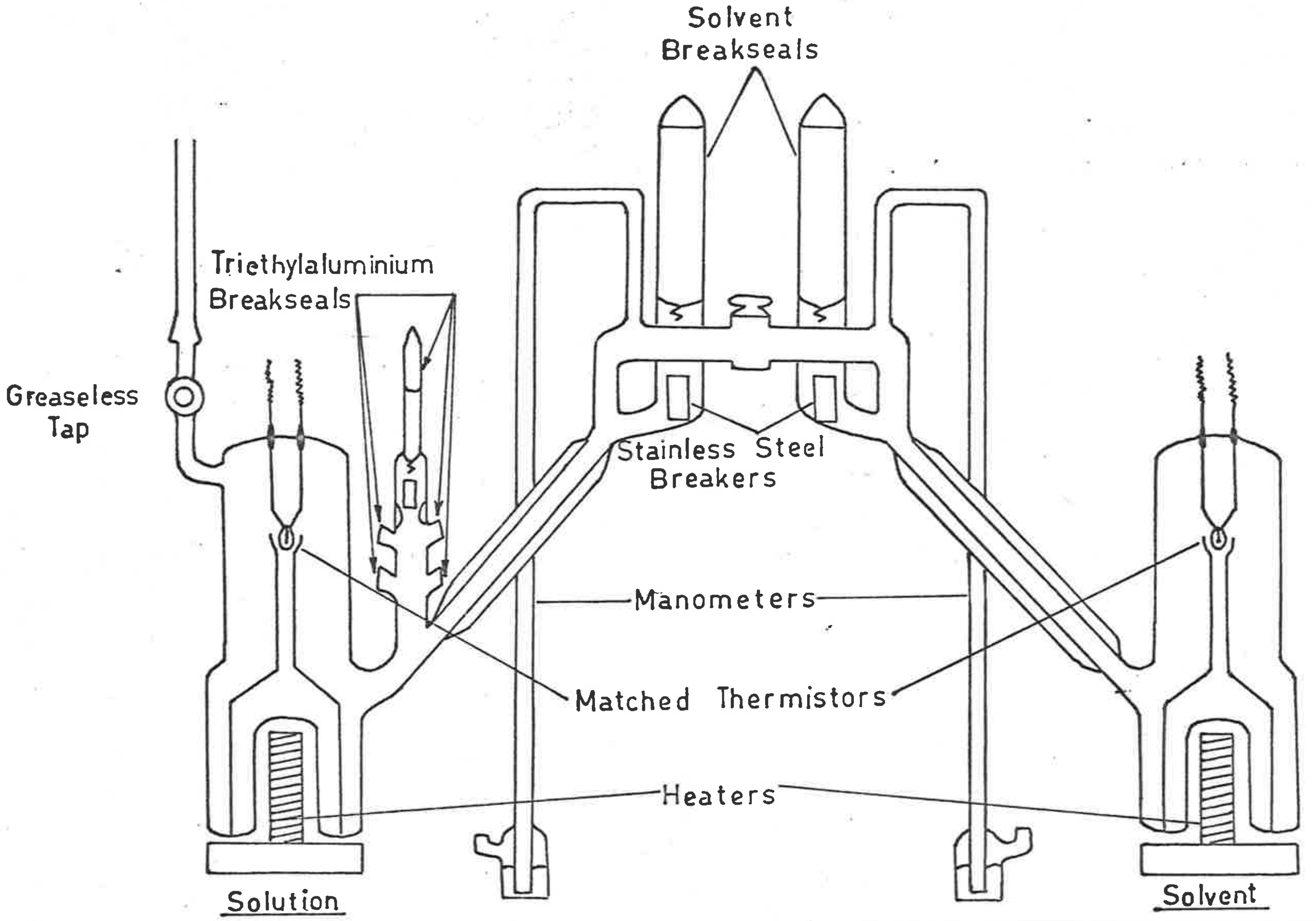
The technique remaining is that of ebulliometry, the advantage here still being the possibility of determining K_d directly and in the desired temperature range. However, there were two disadvantages. Triethylaluminium is a difficult solute to handle in this type of experiment because of its pyrophoric nature. Any experiment would have to be carried out in a closed system under an inert atmosphere of dry oxygen-free nitrogen. Secondly, the reported vapour pressure of triethylaluminium is high enough to necessitate correction, as an experiment of this type requires a non-volatile solute. Normal ebulliometry is performed in an open system and a knowledge of the barometric pressure is required. Any deviation from atmospheric pressure can be accounted for with the boiling point correction for each solvent.

A twin ebulliometer system (the ebullioscope) (see Fig. 16) with resistance matched thermistors as the two detecting, opposed arms of a D.C. Wheatstone bridge was assembled. When used with suitable components, this apparatus was calculated to provide enough sensitivity to measure temperature differences to greater than 0.01°C. The designs of ebulliometers are many and varied,[44-47] however ours had to be modified to eliminate the above disadvantages.

Each ebulliometer consists of a boiler of about 40.0 ml. capacity with a heating finger coated with powdered glass to provide boiling nuclei and reduce super heating effects. Heat is supplied by two identically resistance wound heaters which project up into the re-entrant finger. A Cottrell pump sprays

THE EBULLIOSCOPIC APPARATUS.

FIG 16



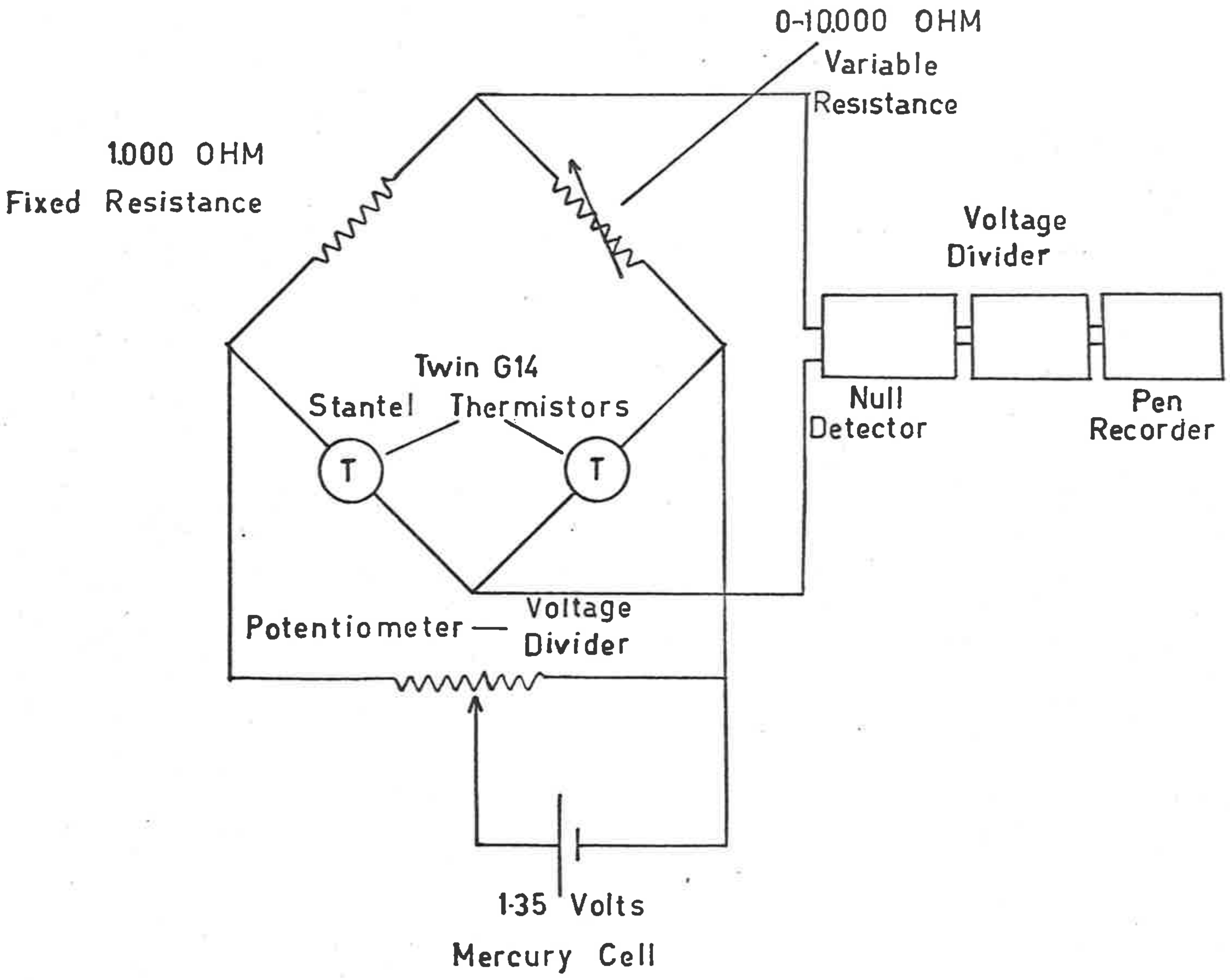
the boiling liquid-vapour mixture over a thermistor (Stantel G14 "bead" type), the vapour filling the dead space above the liquid level and condensing in the sidearm condenser. The thermistors are connected to the D.C. bridge via tungsten-glass seals making the apparatus an all-glass system. A mercury manometer is connected to each ebulliometer and the solute ebulliometer connected to a two-stage "Dynavac" rotary oil diffusion pumpvia liquid N_2 cooled traps. The insulation for each ebulliometer comprises an aluminium box, packed with rockwool, with a glass viewing port cut into the front. Small apertures for the thermistor and heater leads are also present.

The D.C. bridge circuit (see Fig. 17) consists of a 1000 ohm. fixed resistance, a Cambridge Instruments 0-11,000 ohm. decade resistor and the two matched thermistors. Current to the circuit is supplied by a 1.35 volt mercury Mallory cell (RM-42R) with a "Spectrol" precision potentiometer (2 Kohm.) as a voltage breaker for increased sensitivity. The circuit was designed to eliminate any self-heating effects in the thermistors.[48] This is a function of the current flowing through the thermistor (wattage = i^2R) which is kept at a minimum and the thermistor resistance which is kept small compared with the other bridge components.

The galvanometer is a Leeds Northrup Electronic Null Detector (Model 9834). The output signal is chart recorded via a voltage

BRIDGE CIRCUIT.

FIG.17



breaker, by a Philips PR 2500 pen recorder. The relation between resistance and temperature is given, to an appropriate level of approximation, by the relation:

$$R = Ae^{B/T}$$

where R = the resistance value at an absolute temperature T. A and B are constants for a given thermistor and e is the base of the natural logarithm (e = 2.718). The matching of thermistors requires that their B constants be approximately the same over the measured temperature range. The value of B may be found in the following way. The resistance value is measured at two temperatures, T_1 and T_2.

$$\therefore R_1 = Ae^{B/T_1} \qquad \text{and } R_2 = Ae^{B/T_2}$$

Dividing $\dfrac{R_1}{R_2} = e^{(B/T_1 - B/T_2)}$

or $\log R_1 - \log R_2 = B(\frac{1}{T_1} - \frac{1}{T_2}) \log e$

which gives

$$B = \frac{1}{\log e} \cdot \frac{(\log R_1 - \log R_2)}{(\frac{1}{T_1} - \frac{1}{T_2})}$$

The thermistors were individually calibrated at each of the boiling solvent temperatures using the bridge with a fixed 1000 ohm. resistance substituted for the thermistor not being measured. The resistance values R_1 and R_2 were substituted into the above relation and a reasonable agreement was obtained with the B value quoted[49] for the G.14 thermistor of 3.4×10^3 °K.

Again, the relationship between the ratio of thermistor resistances and temperature is:

$$\ln \frac{R}{R_o} = B\left(\frac{1}{T_o} - \frac{1}{T}\right)$$

where R = ratio of solvent thermistor resistance to that of solution thermistor; R_o the same ratio as R, but with both thermistors measuring boiling solvent only; T_o = the boiling point of pure solvent in degrees K; T = the elevated boiling point of solution in degrees K.

Now the activity of the solvent (i) in solution is equal to

$$\ln a_i = \frac{\Delta H_{v_i}}{R_G}\left(\frac{1}{T} - \frac{1}{T_o}\right)$$

This relation applies in the case of a non-volatile solute. ΔH_{v_i} is the molar latent heat of vapourisation of the solvent and is assumed independent of temperature over the small range of boiling point elevation. R_G is the gas constant.

Thus

$$\ln a_i = -\frac{\Delta H_{v_i}}{R_G B} \ln \frac{R}{R_o}$$

Thermodynamically, one has to assume the solutions are ideal and dilute. The $R = R_o + \Delta R$ and expanding logarithms, an expression for the molecular weight of solute (j) is obtained.

$$M_j = \frac{R_G B\ M_i R_o m_j}{\Delta H_{v_i}\ m_i\ \Delta R}$$

where m_i is the solvent mass; m_j is the solute mass; M_i is the solvent molecular weight.

Stokes and Pugh[50] were responsible for this derivation which shows a direct relationship between resistance change and solute molecular weight. It is necessary to test both the relationship and the efficiency of our apparatus in a preliminary experiment before attempting any triethylaluminium molecular weight studies.

Preliminary Experiment

The twin ebulliometer apparatus was initially used as an open system (open to the atmosphere) in an attempt to measure the molecular weight of para-toluidine.

The materials used were n-heptane "Unilab" reagent grade, p-toluidine BDH "analar" grade. Earlier experiments had shown that solvent boiling was most efficient when a volume of 35.0 ml. of solvent was present in the boiler. By efficient, we infer that a steady liquid vapour stream was passing over the thermistor head and the vapour was condensing only in the sidearm condenser.

Thus 35 ml. of solvent was pipetted into the boiler of each ebulliometer via the condenser and the heaters turned on. The problem of solvent super heating was reduced by the small pieces of ground glass attached to the boiler finger; these providing boiling nuclei. Once a steady bridge resistance balance was obtained after approximately an hour at the correct heater input voltage, a known weight of para-toluidine was admitted to the solute ebulliometer through the condenser. Some thirty minutes was allowed to elapse (to ensure renewed equilibrium conditions) before a new bridge null was established. The resistance increment attributed to the mass of solute admitted was then tabulated. Repeated additions were performed until a four-point graph of resistance increments versus solute weights could be drawn. The plot was found to be approximately linear and the data accepted and substituted into the molecular weight equation as total resistance charge with total mass of solute added.

Data Summary

Initial bridge null resistance = R_0 = 981.2 ohm. After addition of 0.51 gm. of p-toluidine, a new bridge null was obtained at R_1 = 996.6 ohm.

Addition of 0.41 gm. $R_2 = 1010.8$ ohm.
Addition of 0.46 gm. $R_3 = 1026.7$ ohm.
Addition of 0.37 gm. $R_4 = 1040.6$ ohm.

By definition $\Delta R = R_4 - R_o = 59.4$ ohm. and $M_2 = 1.75$ gm.

$$\therefore \text{ Molecular weight apparent} = \frac{1.987 \times 3{,}400 \times 100.21 \times 981.2 \times 1.75}{7575 \times 23.8 \times 59.4}$$

$$= 110.0$$

There are several corrections to be made to this value and are outlined as follows.

A boiling point correction must be applied to the total resistance change ΔR (proportional to temperature). For n-heptane, the correction is 0.0007°C[51] for each milliametre variation in the barometric pressure from 760.0 mm. The precision we required for this experiment deemed the correction negligible. A more important correction is that for solvent-holdup in the vapour space above the boiling liquid. Calibration of each ebulliometer showed this vapour space to be approximately 100 ml. By assuming ideal conditions and hence one mole occupies 22.4 litres, one can calculate the mass of solvent hold-up and subtract it from the mass of solvent dispensed. The holdup mass was calculated as 0.3 gm. and the corrected molecular weight of p-toluidine is 111.4.

Under the conditions employed, this value compared favourably with the theoretical molecular weight of 107.12. Errors are to be expected from the method of transferring the solute from the weighing balance into the ebulliometer, i.e. errors from the dispensed solute mass compared with measured solute mass.

However, the preliminary experiment showed that the assembly of ebullioscope and bridge circuit and detection worked satisfactorily.

Molecular Weight Determinations of Triethylaluminium

The preliminary experiment with p-toluidine showed that, with care, molecular weights could be obtained using our method and apparatus. However, in addition to the two molecular weight corrections outlined previously, the vapour pressure of triethylaluminium has to be accounted for. Hay et al.[14] have quoted the A and B constants for the Antoine equation which relates vapour pressure to temperature.

$$\log_{10} p = -\frac{3613}{T^{\circ}K} + 10.85$$

Hence the vapour pressures of triethylaluminium at our intended reaction temperature are tabulated below.

Temperature °C	Vapour pressure (mm.)
125.6	61.60
110.6	25.70
98.4	12.70
81.0	4.15

A correction factor must be applied to the observed molecular weight to allow for the solute volatility.

The pressure difference between solvent and solution is

$$\Delta P = p_1^o - P_{solution}$$

where p_1^o = the vapour pressure of pure solvent.

If Raoult's law is obeyed, for an involatile solute, the total pressure over the solution is

$$P_{solution} = p_1 = x_1 p_1^o \quad (x_1 = \text{mole fraction of solvent})$$

$$\therefore \quad \Delta P_{inv} = p_1^o - x_1 p_1^o = p_1^o (1 - x_1) = x_2 p_1^o$$

where ΔP_{inv} = the involatile pressure change and x_2 = mole fraction of solute. However, for a volatile solute $P_{solution}$ $= p_1 + p_2$.

$$\therefore \quad P_{solution} = (1 - x_2) p_1^o + x_2 p_2^o \, .$$

Again, from above $\Delta P_{vol} = p_1^o - P_{solution}$

where ΔP_{vol} = the volatile pressure change

$$\therefore \quad \Delta P_{vol} = p_1^o - \left\{(1 - x_2) p_1^o + x_2 p_2^o\right\}$$

$$= x_2 (p_1^o - p_2^o) .$$

$$\therefore \qquad \frac{\Delta P_{inv}}{x_2 p_1^o} = \frac{\Delta P_{vol}}{x_2(p_1^o - p_2^o)}$$

$$\therefore \qquad \Delta P_{inv} = \left(\frac{p_1^o}{p_1^o - p_2^o}\right) \Delta P_{vol} \text{ or } \Delta P_{vol} = \left(\frac{p_1^o - p_2^o}{p_2^o}\right) \Delta P_{inv}$$

The observed molecular weights will all be decreased by the factor $\left(\frac{p_1^o - p_2^o}{p_1^o}\right)$. The equilibrium vapour pressure of solvent at its boiling point is 760 mm. Hence, the following correction factors for the molecular weight determined in a particular solvent will have to be employed.

Solvent	Boiling temperature (°C)	Correction Factor
n-octane	125.6	0.919
toluene	110.6	0.966
n-heptane	98.4	0.983
cyclohexane	81.0	0.990

Materials

Triethylaluminium, obtained and purified as described in Chapter II, was reduced into calibrated breakseals in approximate volumes of 0.25 ml. Five breakseals were sealed into position on the solute ebulliometer as shown in Fig. 16.

Solvents

(a) cyclohexane, Merck "UVASOL" grade
(b) n-heptane, " " "
(c) toluene, Univar "Analar" grade
(d) n-octane, Merck "UVASOL" "

Each of the solvents was predried over calcium hydride, degassed and distilled into a receiving vessel with two large breakseals precalibrated to 35.0 ml., attached as sidearms. This vessel was sealed off while pumping, the solvent tipped to the mark and each breakseal removed. Once the two solvent breakseals and breakers were sealed into position, the whole apparatus and insulation was assembled and evacuated for ten hours. With the main tap to the pump closed, dry oxygen-free nitrogen was allowed to flow in (via the inlet tap) at a pressure to cause it to bubble out through the manometers. This nitrogen was purified in the same manner as described in Chapter II. After several minutes, the inlet tap was closed and the gas removed by the diffusion pump until a reasonable vacuum was obtained again. Repetition of this purging procedure occurred several times until the final situation was the apparatus filled with a nitrogen atmosphere. The solvent breakseals were then ruptured and the liquid allowed to run into the boilers, with a reasonable time lapse allowed for drainage.

The heater voltage was turned (slowly) to the precalibrated boiling point value and after allowing some time for equilibrium conditions to be obtained, the null detector and pen recorder were turned on. A pressure of approximately one atmosphere was always maintained, as the expanding nitrogen escaped via the manometer blowout. The pressure in each vessel was always equalised by turning the connecting tap before any resistance readings were recorded.

A bridge null position was determined by turning the decade box to the balancing resistance as indicated by the null detector and pen recorder. This resistance ratio is designated R_o. An adjusted working sensitivity was a combination of null detector sensitivity, potentiometer controlled bridge current and the millivolt range of the pen recorder. Once the null resistance was recorded, the first breakseal of triethylaluminium was shattered and the alkyl allowed to run down into the condensing solvent. A large time lapse of one hour was allowed before measuring the new bridge null resistance R_1. Approximately a half hour was allowed for solute drainage and an additional half hour for equilibrium conditions to be established before adjusting the galvanometer assembly to the balancing resistance. The resistance change was attributed to the amount of solute in the breakseal. This amount was estimated on completion of the experiment by volume calibration of the breakseal to the original filled level. Usually, four further admissions of solute occurred, with the above measurement procedure repeated in each case, until a five-point plot of resistance increment versus solute mass could be constructed. In each experiment, for a particular solvent used, this plot was reasonably linear.

The apparent molecular weight of the species present ($M.W._{APP}$) was calculated from the previously described equation, hence α, K_d and an estimation of the heat of dimer dissociation ΔH_d.

Table of Results

Temp. °C	$\frac{1}{T^oA} \times 10^3$	$M.W._{APP}$ *	$M.W._{APP}$ **	α	C_{Al_2} (moles/litre)	$K_d \times 10^2$ ** (moles/litre)
81.0	2.82	187.3	196.4	0.224	0.142	3.52
98.4	2.69	181.6	178.5	0.278	0.152	6.60
110.6	2.61	177.5	170.3	0.339	0.204	14.30
125.6	2.51	176.8	162.5	0.402	0.205	21.90

* corrected for solvent holdup

** corrected for solvent holdup and solute volatility

The relationship between the equilibrium dissociation constant and temperature is expressed by the relation

$$\log_{10} K_d = - \frac{\Delta H_d}{2.303\, R} \cdot \frac{1}{T^o A} + \text{const.}$$

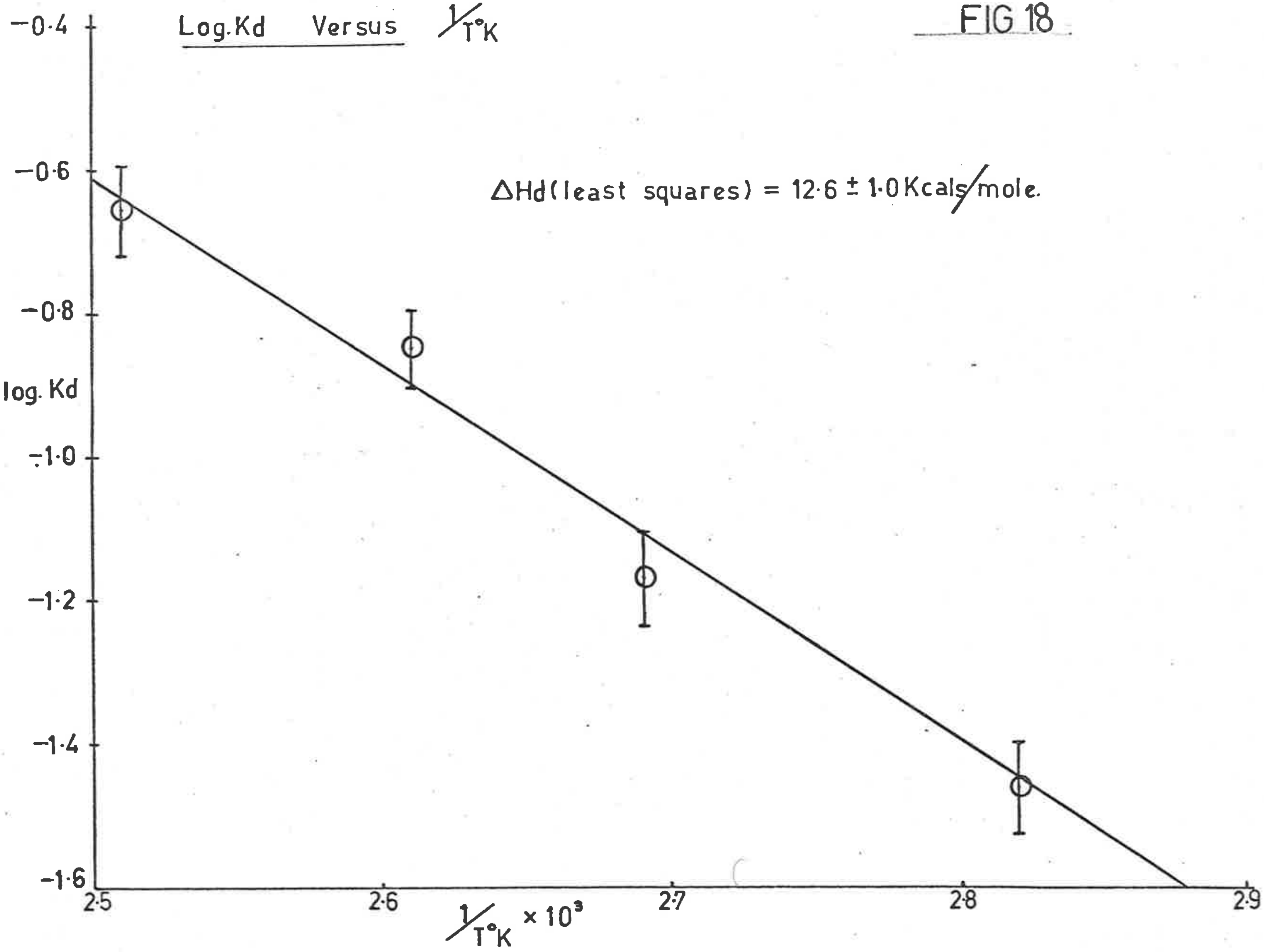
A graph of $\log_{10} K_d$ versus the reciprocal of temperature in degrees absolute should be a straight line with a slope $= -\frac{\Delta H_d}{2.303\ R}$. The least squares slope of this line produced a heat of dimer dissociation = -12.6 kcal/mole with a standard error of ± 1.0 kcal/mole. The temperature dependence plot is shown in Fig. 18.

Discussion of Results

Before the publication of Hay's recent paper, there appeared to be some doubt on the validity of Laubengayer and Gilliam's results, with particular reference to errors in technique and errors in assumptions made using their data. However, confirmation of these original vapour density and pressure results is apparent. There seems no doubt that triethylaluminium is volatile, although the extent claimed is still questionable on the grounds of a large difference in boiling point estimation between the above authors (186°C) and Texas Alkyls (207°C), who prepare bulk samples of triethylaluminium. We have corrected our results for solute volatility using Hay's data.

At a given temperature, there is a large difference between the K_d (gas) calculated from vapour density measurements and our K_d (solution) calculated from ebulliometry. It is interesting to note that if we calculate the apparent molecular weight we can expect from their K_d estimate at our maximum concentration of

FIG 18



Log.Kd Versus $1/T°K$

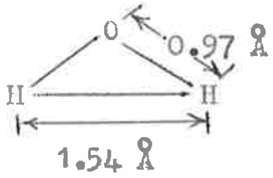
ΔHd(least squares) = 12·6 ± 1·0 Kcals/mole.

triethylaluminium, then a result little different than the dimer formal molecular weight arises. If we assume K_d (solution) to be 10^{-3} moles/litre at our concentration of 0.205 moles/litre, then since $K_d = \frac{4\alpha^2 c}{1-\alpha}$, the substitution of the above values into this relation yields a degree of dimer dissociation of 3.49×10^{-2} and an apparent molecular weight of 220.5. Our initial calibration results with p-toluidine leave us confident that such a value lies well outside the likely error of our determination.

It is as well at this stage to consider the possible errors in the two methods.

Hay's method and his assumptions as described appear solid. A minor consideration which should be taken into account when examining the results is the possible adsorption of a mono-molecular layer of water on the inner surface of their experimental vessel. This would consume a small amount of triethylaluminium which is calculated as follows.

We assume their vessel to be a sphere of capacity 100 ml. In addition we assume a water molecule to occupy a discrete area of surface of 0.454 square Angstroms, this area calculated assuming the water molecule is a triangle of the dimensions,



Knowing the total surface area and Avogadro's number, we can calculate the weight of a mono-molecular water layer and hence the weight of triethylaluminium consumed, which is 4.12×10^{-4} gram. This might significantly affect their lower temperature data .

The total errors in our method are quoted as an error of ± 1 kcal/mole in ΔH_d. These are described as follows:

(a) An error of ± 0.1 ohms. in all resistance readings; the limitation here is the extreme sensitivity exhibited by the galvanometer and the smallest resistance increment of the decade resistor being 0.1 ohms.

(b) An error of ± 0.02 ml. in the burette calibration of the alkyl concentrations.

There seems no doubt, unless there is a concealed systematic error and we have checked for this, that we have no alternative but to accept our results.

It is possible to make an approximate comparison of our molecular weight date with Hoffman's,[28] the only other condensed phase data available. By choosing the lowest molecular weight of his range (196) and plotting the corresponding equilibrium constant on a graph of our log K_c versus $1/T^{\circ}K$, we find the Hoffman point lies below our extrapolated least squares straight line. Again,

$$K_c = \frac{4\alpha^2 c}{1-\alpha^2} \qquad \therefore 4\alpha^2 c + K_c \alpha^2 = K_c$$

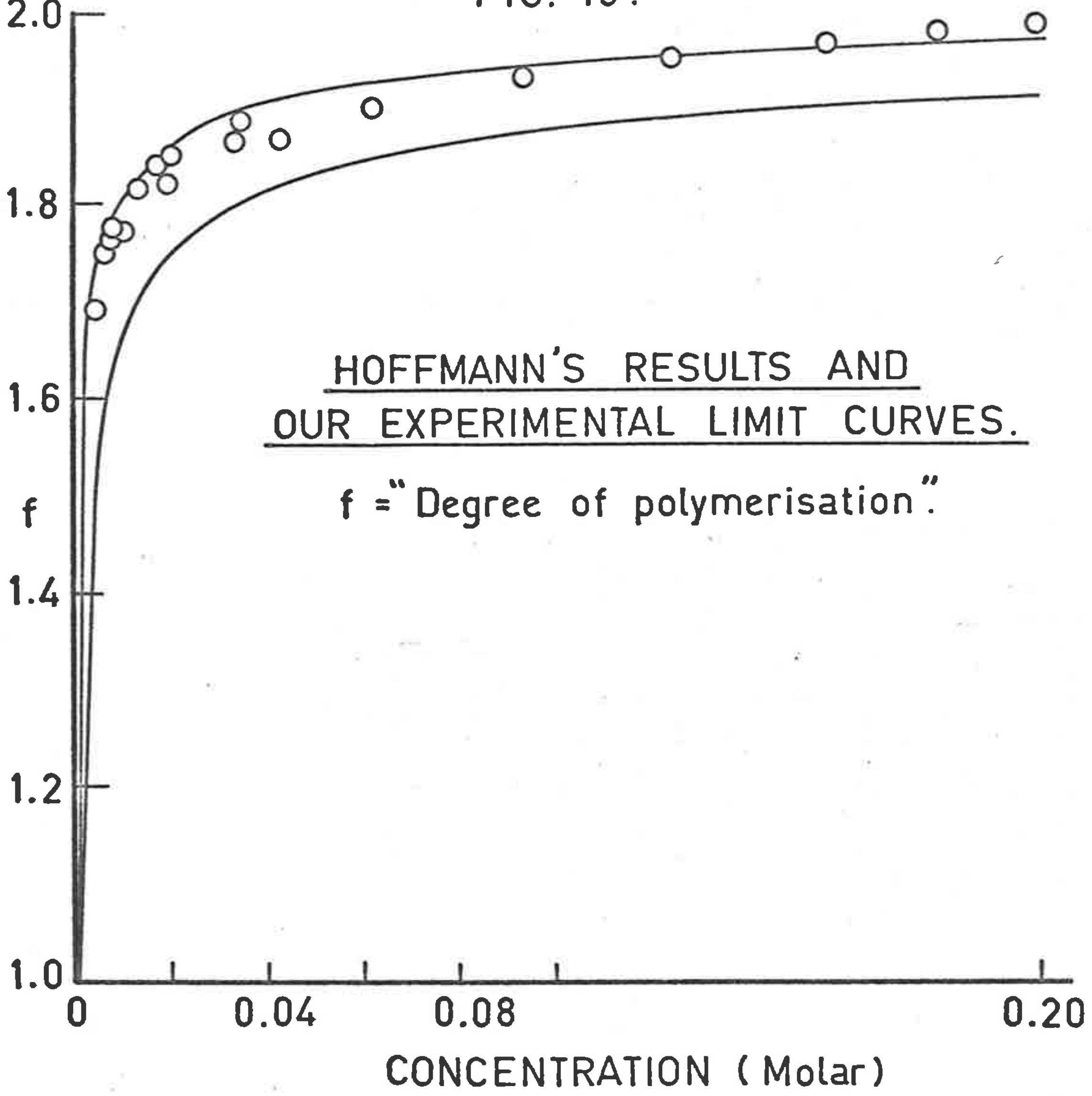
$$\therefore \alpha^2 = \frac{K_c}{4c + K_c} \quad \text{or} \quad \alpha = \left(\frac{K_c}{4c + K_c}\right)^{\frac{1}{2}}$$

Now Hoffman's "Degree of Polymerisation" or "Association Number" is equal to

$$\frac{\text{molecular weight observed}}{\text{molecular weight monomer}} = \frac{2}{1 + \left(\frac{K_c}{4c + K_c}\right)^{\frac{1}{2}}} .$$

We define the variance in our results to be ± the difference in our extrapolated K_c from Hoffman's K_c. By substituting both $\pm \Delta K_c$ into the above relation we obtain two limiting curves of "Degree of Polymerisation" versus concentration. An estimate of Hoffman's points was then obtained by photographically enlarging the published graph and using a travelling microscope to obtain the relative position of each point to scale. A combined plot of Hoffman "Degrees of Polymerisation" and our limiting curves is shown in Fig. 19. It can be seen that our limits are slightly incorrect, especially at high concentrations. A small alteration in the numerical value of $\pm \Delta K_c$ would include all of the Hoffman data, however, the graph suffices to show the agreement between the two molecular weight determinations.

FIG. 19.



HOFFMANN'S RESULTS AND OUR EXPERIMENTAL LIMIT CURVES.

f = "Degree of polymerisation".

When comparing Hay's results and our own, there is a fundamental difference in the experimental conditions used, i.e. gas phase versus liquid phase estimations of K_d. The irrelevance of K_d (gas) when applied to our kinetic results must be emphasised. The ratio of solution and gas phase equilibrium constants K_S/K_G can be shown[51a] to be directly proportional to an entropy term, actually a volume ratio (V_o/V_f). V_o is the volume per mole of solution; V_f is presumably the molar volume less the volume occupied by the molecules themselves.

Summarising, our kinetic experiments (Chapter III) were performed in the liquid phase and hence we require K_d (solution) to correct for the dimer dissociation postulated by the mechanism. When comparing dissociation constant estimates from gas and liquid phases, one must consider entropy effects in solution. We have no reason to doubt our results at this stage. The ebulliometric determination was performed "illegally" in a thermodynamic sense, with respect to solute volatility, but corrected to ideal behaviour of components.

The only course of action open is another independent investigation of K_d (solution) by a different technique if possible, which may or may not confirm our efforts.

CHAPTER V - A KINETIC INVESTIGATION OF THE REACTIONS OF TRIALKYLALUMINIUM ETHERATES WITH n-1-OCTENE

Introduction

Over the last few years, Ziegler Natta catalysts have become the most widely applied catalyst in industrial polymerisation. Although many patents have been issued, the catalyst structure retains the basic combination of organometallic-transition metal halide. The organometallic has usually been one of the trialkylaluminium series and often triethylaluminium. These catalysts are remarkable for their efficiency and the stereoregularity of the product polymer. However, the mechanism of the polymer formation is not yet fully understood, and because of industrial and academic interest, many investigations on the mode of action of Ziegler-Natta catalysts are in progress. At least four mechanisms, each with their supporting experimental evidence, have been put forward. The common unknown involves the identity of the active site or the position from which the polymer grows. Excellent reviews[52,53] on the present Ziegler-Natta catalyst mechanims are available.

One particular theory, the bimetallic theory, favours the formation of a bimetallic complex between aluminium and titanium, joined by bridging carbon bonds. There are two electron deficient Al-C-Ti bonds, and the metal-carbon bond is postulated as the active site.

Another theory with outstanding electron micrograph evidence favours the titanium atom in the titanium halide lattice as the active site.

Because of the number of theoretical and experimental variables involved in a rate study of such a system, it appeared logical to us for a preliminary investigation to choose a simpler system, yet similar in composition to the Ziegler-Natta catalyst. By similar, we assume the catalyst to be a complexed trialkylaluminium and postulate that rate data from this combination may throw some light on the mechanism of Ziegler-Natta polymerisation. The Arrhenius parameters themselves could be a useful comparison.

Aluminium alkyl etherates are known to be stable complexes and were the catalyst combination chosen. The bonding is a direct result of the electron deficiency of the aluminium atom which attracts electrons from the oxygen in an attempt to gain the desired octet configuration. Brownstein et al.[54] demonstrated this complexing by p.m.r. studies on the triethylaluminium-diethylether system. They concluded that the electron withdrawing power of aluminium in pure aluminium alkyls is decreased when coordinated to the ether. The electron donation increases the electron density about the metal and decreases its tendency to share electrons of the metal-carbon bond. Takashi,[55] in a study of the roles of electron donor compounds in three component

Ziegler type catalysts, used p.m.r. measurement to investigate the complex formation between triethylaluminium and various donors. Each donor produced only one type of complex within which the electronegativity of the aluminium atom was lowered. The electrical conductivity of these complexes indicated ionic structures.

Hatada and Tuki[56] in a similar investigation developed a "basicity" constant for each donor; the numerically more positive the basicity constant, the stronger the complex formed.

Due to the efforts of the above workers it is apparent that the ease of complexing is due to the following factors.

(a) The electron donating ability of the donor, e.g. the presence of lone pairs of electrons or the ease of charge localisation at a particular vulnerable position in the donor.

(b) Steric hindrance, or the ease of orientation of both donor and an acceptor into a position in which complexing is feasible.

Such factors are illustrated in the heats of formation of these complexes.[57] Tetrahydrofuran readily complexes because of the presence of an exposed oxygen atom and its lone pairs. The complex between triethylaluminium and anisole is weaker because of the bulky phenyl and methyl groups surrounding the donor atom which restrict close approach of the oxygen and aluminium atoms. Welch[58] observed the addition of small amounts of such powerful solvating agents as tetrahydrofuran on tertiary amines accelerates polymerisation catalysed by n-butyllithium. Several authors[59] reported the addition of electron donating compounds to Ziegler type mixed catalysts, increased the rate of polymerisation and improved the stereospecificity in the polymerisation of α olefins and dienes.

As previously argued, because of the complex series of reactions in Ziegler-Natta catalysts, it is necessary to obtain kinetic information of the reactions between trialkylaluminiums and electron donors as well as transition metal halides and electron donors. We chose to attempt the former of these two possibilities. Allison,[60] investigated the reaction system triethylaluminium/tetrahydrofuran/1-hexene, with T.H.F. as the coordinating solvent ether. Kinetic data was calculated from results of product analysis by gas chromatography. Briefly, the reaction mixtures of known reactant concentrations were heated for periods of time, hydrolysed and the products V.P.C. analysed. Low product octene conversion exaggerated any measurement errors. Experimental conditions and particularly the measurement technique dictated the choice of T.H.F. as the coordinand. The author admitted some difficulty in obtaining an alkyl-ether adduct of true 1:1 mole ratio. To ensure all the triethylaluminium was complexed, an approximate 2:1 excess of donor was employed in reaction mixtures. Allison concluded that some revision in experimental technique was imperative in order to further the accuracy of the measurement.

We considered proton magnetic resonance spectroscopy to be an accurate technique from previous work and chose to kinetically investigate coordinated alkyl/1-octene system by this method.

Preliminary Experiments

Introduction

Initially, we decided to reinvestigate Allison's system as closely as possible, if only for the sake of comparison. However, p-dioxan was used instead of tetrahydrofuran as the coordinand, the former being a more easily handled liquid by our intended method.

The calculated electronegativity of the aluminium atom,[55] by the Narashimham method[61] is the same in both complexes (1.33 units). There was a marked difference in the specific conductance, the T.H.F. complex being 13.3 $\mu\Omega$/cm. and the dioxan complex 0.1 $\mu\Omega$/cm.[62] This difference in electrical conductivity indicates the dioxan complex is certainly less ionic. P.M.R. measurements[55] showed a 2:1 mole ratio complex forms between triethylaluminium and p-dioxan compared with a 1:1 ratio for T.H.F. complexes. In addition, the heat of complex formation is -10.7 kcal/-mole compared with the T.H.F. complex formation value of -14.0 kcal/mole.[57] If we compare the structure of the dioxan complex with that of free triethylaluminium, the steric hindrance of the dioxan on the all-important Al-C bond may not be as large as first thought. A crystal structure of the trimethylaluminium p-dioxan complex[63] shows the Al-O bond length to be longer (2.02 Å) than the Al-C bond (1.96 Å). Also, the hybridisation about the Al atom appears to show more trigonal character than tetrahedral. The C-Al-C bond angles have been increased beyond tetrahedral to 117.0°.

Summarising, from the above comparisons, it would appear that our system should exhibit a rate faster than Allison's and a rate not too removed from the pure system.

Materials

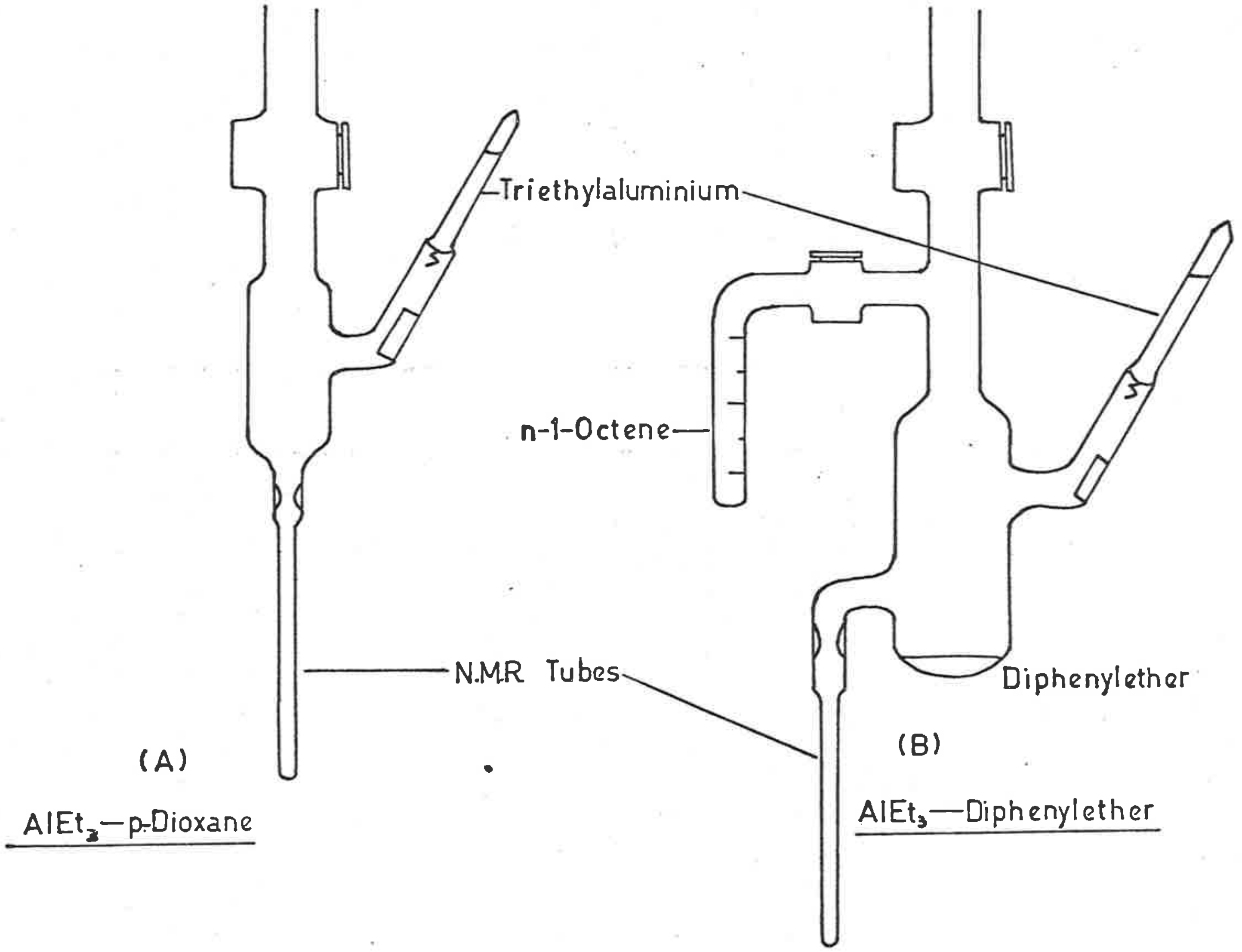
(a) Triethylaluminium, 1-octene and benzene were obtained and purified as previously described.

(b) p-Dioxan: Univar "Analar" grade dioxan was initially dried over calcium hydride and distilled on the vacuum line into a receiving vessel containing sodium wire and some fluorenone. The solution adopted a deep yellow colour due to the formation of the ion pair species Na^+ $(\text{fluorenone})^-$ by charge transfer. The ion pair is solvated by the dioxan and the presence of the colour indicated that the solvent purity was maintained. A more detailed account of this purification is by T.E. Hogen-Esch and J. Smid.[64]

Preparation of the Triethylaluminium Dioxan Complex

P.M.R. measurements[55] had shown the acceptor-donor ratio of the complex to be 2:1. For a preliminary experiment it was decided to prepare a complex of this stoichiometry within an n.m.r. tube and then distil in the 1-olefin and relevant p.m.r. marker. The n.m.r. tube was initially calibrated to a volume of 1.80 ml. as a concentration check. The apparatus shown in Fig. 20A was pumped out at $< 10^{-3}$ torr for ten hours. With the greaseless tap to the manifold closed, the alkyl breakseal was smashed and the liquid allowed to run into the base of the n.m.r. tube. The initial concentration of triethylaluminium was known because of the use of precalibrated breakseals. The dispensed alkyl concentration was re-checked from the height in the precision bore n.m.r. tube. The correct volume of dioxan was distilled into the tube to a calculated height. Because of the difficulty of distilling accurately, a very slight excess of donor was allowed to ensure all the alkyl was complexed. Thawing of the mixture was slowly controlled because of the reported heat of complexing. A clear solution resulted with no sign of any crystal formation. (Atwood et al.[63] had observed crystal formation in their preparation of the trimethylaluminium dioxan complex.) Amounts of n-1-octene and benzene as an n.m.r. marker were distilled in, diluting the mixture to the calibrated volume of 1.8 ml. The tube was sealed

APPARATUS FOR PRELIMINARY COMPLEXING EXPERIMENTS. FIG 20



(A)

AlEt$_3$—p-Dioxane

(B)

AlEt$_3$—Diphenylether

off at the constriction and the initial time p.m.r. spectrum recorded (Fig. 21). The important features of the spectrum are:

(a) The lock signal was the benzene singlet - offset to 8.33 p.p.m. (500 c.p.s.).

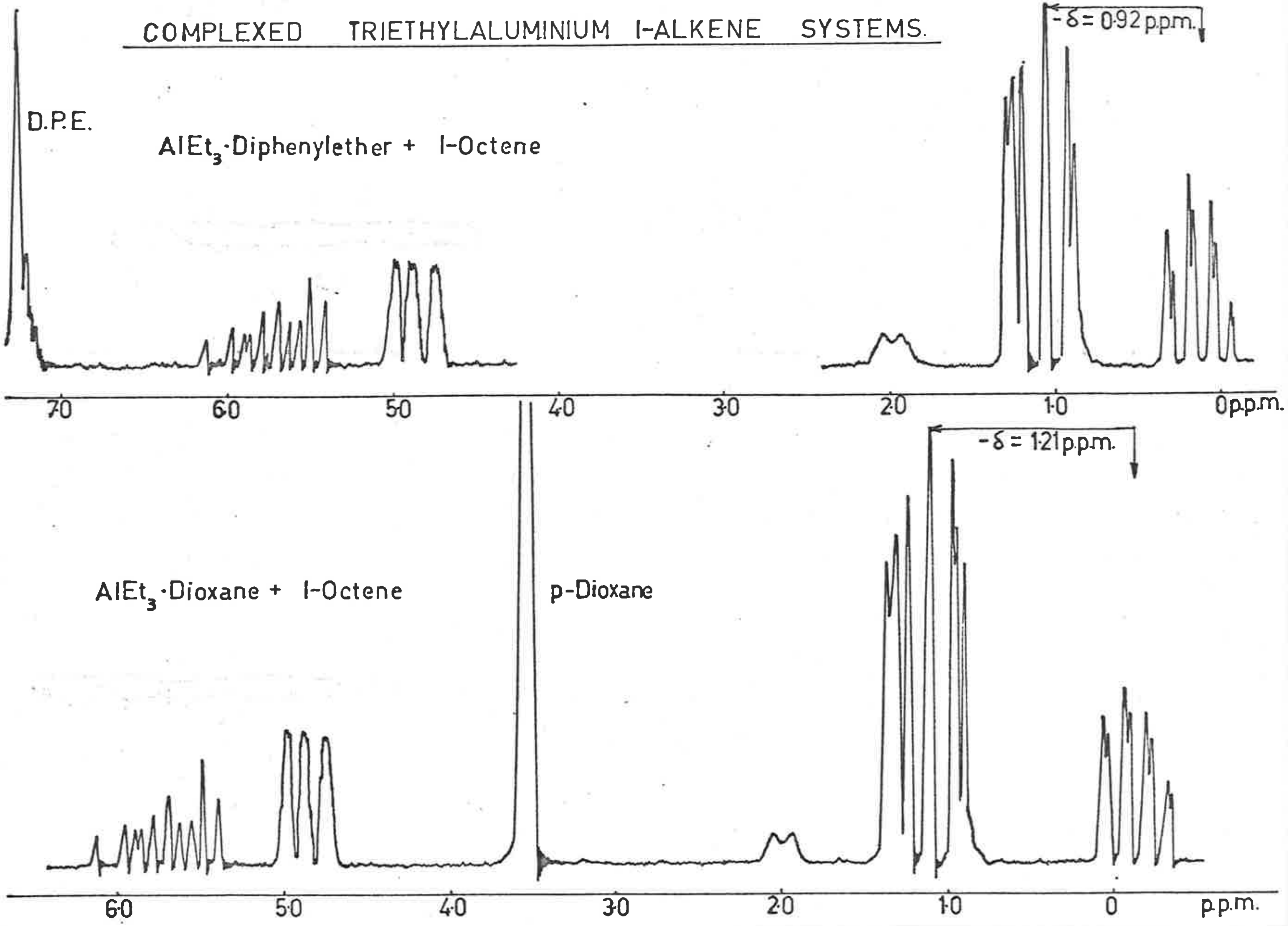
(b) The olefin vinyl region was clearly recorded with all peaks in their normal resonance positions.

(c) The large dioxan peak at 3.7 p.p.m. was devoid of any fine structure, which might have indicated the presence of both free and complexed forms of dioxan. This is unlikely however, as Takashi had shown the ligand exchange between free and complexed forms as rapid. Only one type of signal should be observed, corresponding to the weighted mean of $\delta_{complex}$ and δ_{free}. (The chemical shifts of free and complexed dioxan.)

(d) The internal chemical shift ($-\delta$) between the triethylaluminium methyl and methylene signals was increased to 1.20 p.p.m. compared with pure alkyl in benzene ($-\delta = 0.77$ p.p.m.). This complexed shift compared favourably with values obtained by other workers (Takashi[55] -1.23 p.p.m.; Hatada et al.[56] -1.21 p.p.m.).

The sample tube was heated for a total of fifty hours in a thermostatted oil bath at 105°C. Spectra were recorded at the probe temperature (29.0°C) on several occasions. However, no change occurred in the appearance of the spectrum and the olefin vinyl integral was numerically comparable with its initial time value.

P.M.R. SPECTRA OF COMPLEXED TRIETHYLALUMINIUM 1-ALKENE SYSTEMS.



The conclusion of no observable reaction is contrary to Allison's results, where a measurable rate for the T.H.F. system was recorded. On this basis, we did expect some reaction. For the olefin to approach close enough to the Al-C bond (one mechanism) to allow addition, it may be necessary to overcome the energy associated with the heat of complex formation before an addition reaction can occur. The fact that no reaction occurred with dioxan whereas an observable rate was reported for T.H.F. is surprising as the dioxan example should be more favoured thermochemically than T.H.F. The inhibiting factor here could be steric, but this seems unlikely and in fact the dioxan complex appears sterically more vulnerable to the approach of an octene molecule than the T.H.F. complex.

In other words, if the complexed addition mechanism requires the replacement of coordinand by the olefin (ligand exchange), a considerable increase in the activation energy should result. It may be, in our case, that the complex is strong enough to resist the experimental conditions, i.e. the reaction fails to clear the kinetic hurdle. On this assumption, it was decided to select a coordinating ether with a considerably lower heat of complex formation with triethylaluminium.

Preparation of the Triethylaluminiumdiphenylether Complex

Diphenylether appears suitable, with a ΔH complexing of -2.7 kcal/mole.[57] Diphenylether, B.D.H. analar grade, a solid with a melting point of 28.0°C was purified by distillation under reduced pressure, the vapour condensing as glassy needle-like crystals. Most ethers are prone to the formation of dangerous peroxide impurities. The organic mechanism of peroxide formation requires the presence of a hydrogen on the carbon atom α to the oxygen. With diphenylether, no such hydrogen exists. The purified sample was stored in vacuo over silica gel.

Stoichiometrically, this complex was assumed to have a donor-acceptor ratio of 1:1, this ratio being proved later in the chapter. The apparatus used in this preparation is shown in Fig. 20B and contains as a sidearm a calibrated breakseal of triethylaluminium. Initially, a calculated mass of diphenylether that would result in a slight equimolar excess to the alkyl concentration, was weighed into the vessel base. On sealing the vessel back onto the manifold, it was pumped out to a pressure of $< 10^{-3}$ torr, while simultaneously degassing the ether. The alkyl breakseal was ruptured and the solid ether in the base slowly dissolved. Degassed 1-octene was distilled from an external source into the graduated sidearm. With the main tap to the manifold closed, 0.5 ml. of olefin was distilled onto the complex. The sidearm tap was closed, the contents of the vessel base frozen with liquid nitrogen and the apparatus again pumped out to a reasonable vacuum. A small amount of cyclohexane, as n.m.r. marker, was distilled into the mixture and the vessel finally sealed off while pumping. On thawing, the contents were thoroughly mixed and tipped into the n.m.r. tube, which was, in turn, sealed off at the constriction.

The zero-time p.m.r. spectrum was recorded with cyclohexane as the lock signal at 1.40 p.p.m. (Fig. 21). The method of recording the spectrum was to scan in both up and down-field directions from cyclohexane. Downfield were the usual 1-olefin vinyl peaks with a complex diphenylether signal at 7.20 p.p.m. Upfield, the triethylaluminium internal chemical shift ($-\delta$) was found to have increased from 0.77 p.p.m. (pure alkyl) to 0.93 p.p.m. Again, this value was in agreement with the literature reported value[56] for the same complex.

The sample tube was heated in an oil bath controlled at 100.0°C for thirty hours and the p.m.r. spectrum re-measured on cooling. The presence of the familiar "product olefin" singlet peak growing alongside the decreased reactant 1-octene triplet, indicated immediately that some reaction had occurred. By comparing the integral ratios

$$\frac{\mathrm{Int}_{CH_2=}}{\mathrm{Int}_{D.P.E.}}$$

at zero-time and thirty hours it was apparent that about 30% of the 1-octene had been consumed. The p.m.r. changes agreed in every way with the structural changes accounted for in the reaction in hydrocarbon solution alone (Chapter III).

Summarising the preliminary experiments, diphenylether appeals as a "workable" coordinand. The reaction, either by direct ligand substitution of the coordinand by 1-alkene, or prior dissociation of the complex is by no means so thermochemically unfavourable as in the case of dioxan and T.H.F. In addition, the lowest kinetic run temperature should be 100.0°C.

Establishment of the Complex Stoichiometry

Introduction

The reported stoichiometry of complexes of trialkylaluminiums with monofunctional ethers is 1:1,[55] except p-dioxan (a difunctional ether) which forms 2:1 complexes. It was felt necessary to establish the stoichiometry of the triethylaluminium-diphenylether complex before proceeding with any kinetic work. The novel p.m.r. spectroscopic method developed involves the internal chemical shift ($-\delta$) which is used as a convenient parameter for the identification of complex formation. In the reaction of triethylaluminium with various donating ethers, the internal chemical shift decreases as the molar ratio

$$\frac{[\text{Donor}]}{[\text{AlEt}_3]}$$

increases. By decrease, we infer a numerical decrease, as δ is always negative in this sense. The negativity is explained in terms of the Narashimham relation[61]

$$\text{Electronegativity} = 0.62\,\delta + 2.07 \,.$$

In trialkylaluminiums, the electronegativity of the aluminium atom is always < 2.07 and hence δ is negative. This explains the inverse order of methyl and methylene group resonances in triethylaluminium. That is, the methylene protons are more shielded than the methyl protons and therefore they resonate at higher fields. The decrease in δ will cease and become constant at the molar ratio which corresponds to the complex ratio. In all examples, the constancy of $-\delta$ after an initial decrease, indicates the quantitative formation of only one type of complex. An interesting situation arises when methylmethacrylate is used as the donating species. Workers[65] have found evidence for the presence of both 1:1 and 2:1 alkyl to donor complexes present, depending on the molar ratio.

Experimental

The method was designed to obtain a varying donor acceptor mole ratio by keeping the alkyl concentration approximately constant and altering the diphenylether concentration above and below equimolar. The desired ratio range was from 0.1 to something in excess of 2.

The apparatus contains takeoffs to eight n.m.r. tubes, each with their accompanying solvent breakseals as U-tube sidearms. Each n.m.r. tube was calibrated to 1.80 ml. and a known, but varying, weight of diphenylether added to each tube. After sealing each tube back into its respective takeoff, the apparatus was pumped out and the ether samples degassed several times. Once a reasonable vacuum was attained, the apparatus was sealed off from the manifold. The alkyl breakseal was ruptured in the usual manner and the liquid allowed to pour into the vessel base. By carefully tipping the calculated volume into each tube, one could obtain the desired donor-acceptor ratio. To clarify the term "calculated volume", an estimate of the height of diphenylether in each tube was obtained during the degassing operation. Knowing the bore of the n.m.r. tube, one can calculate the volume of alkyl required for a particular ratio. Naturally, the tipping operation was not always correct, but mixtures were obtained near enough to those desired. An estimate of the final stoichiometry was made from the integral ratios of the alkyl and ether.

After sealing each tube and solvent breakseal off from the main vessel, the tube mixture was diluted to 1.80 ml. by admission of cyclohexane from the ruptured breakseal. Each filled n.m.r. tube was sealed off and the relative p.m.r. spectra recorded at the probe temperature.

In general, the spectra of samples with a donor-acceptor ratio < 1 were complicated, however a reasonable estimate of $(-\delta)$ could still be made. The error in $-\delta$ was accepted as ± 0.01 p.p.m.

Table of Results

Sample No.	Mole Ratio D.P.E./$AlEt_3$	$-\delta$ internal (c.p.s.)	δ internal (p.p.m.)
1	0.14	47.0	-0.78
2	0.23	48.0	-0.80
3	0.45	50.5	-0.84
4	0.65	52.0	-0.87
5	0.75	53.0	-0.88
7	1.44	57.0	-0.95
8	1.75	57.5	-0.96
pure Al_2Et_6		46.0	-0.77

The spectra of several of the above ratios are shown in Fig. 22. The graph of internal chemical shift (in p.p.m.) versus D.P.E./$AlEt_3$ molar ratio is shown in Fig. 23. The graph changes slope markedly at about a mole ratio of 1.0. In fact, the two intersecting dotted

FIG 22

P.M.R. SPECTRA OF COMPLEX FORMATION.

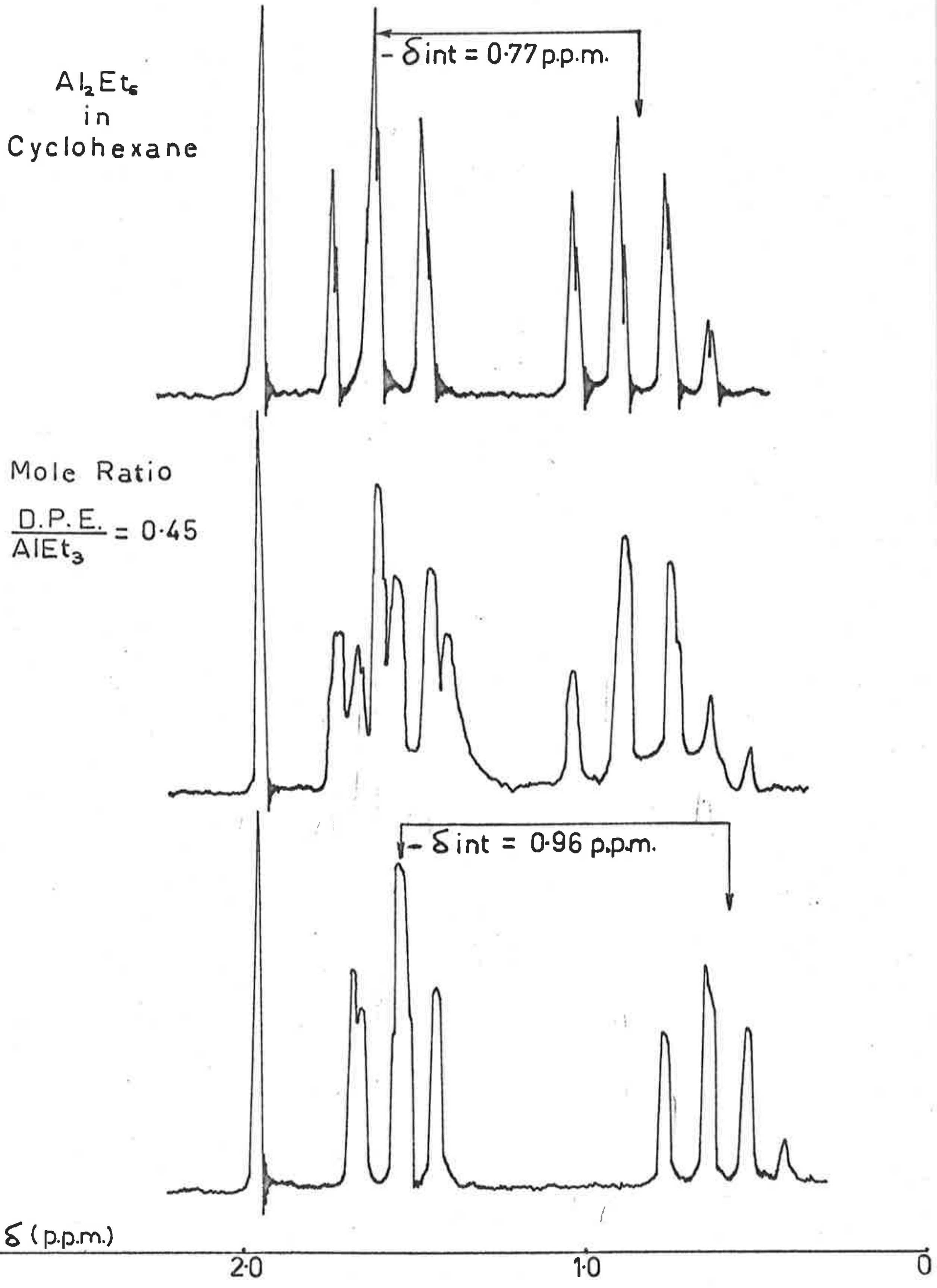
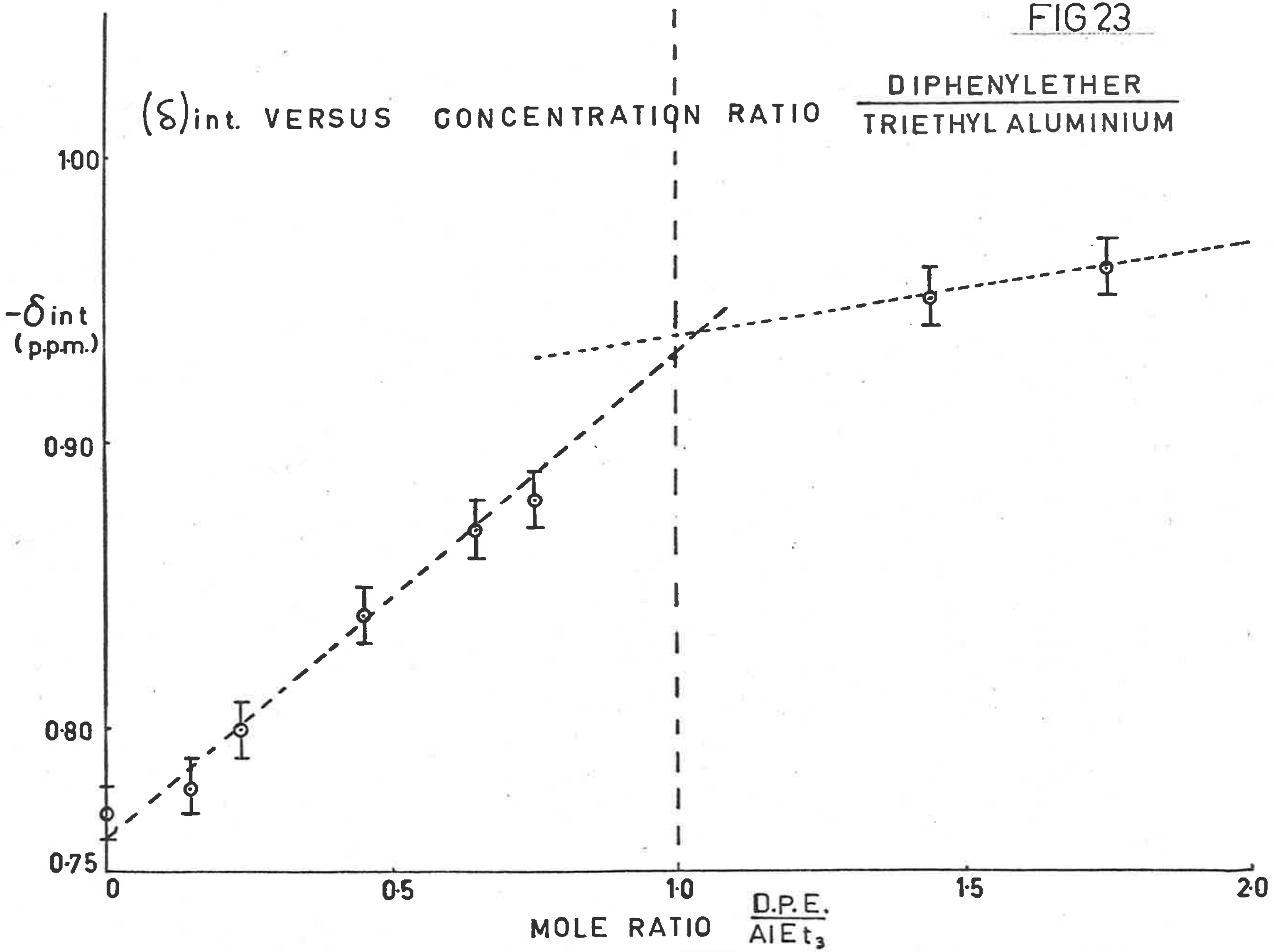


FIG 23



(δ)int. VERSUS CONCENTRATION RATIO $\frac{\text{DIPHENYLETHER}}{\text{TRIETHYL ALUMINIUM}}$

lines show the approximate theoretical curve for the formation of a 1:1 complex with a limiting high stability constant K_c. In addition, our value of $(-\delta)$ at the equimolar ratio agrees almost exactly with the value obtained by Hatada and Yuki (-0.92 p.p.m.).

In conclusion, the stoichiometry of the complex is undoubtedly 1:1 over this donor-acceptor ratio, although K_c is obviously not very large.

The Estimation of the Equilibrium Constant for the Complex Formation (K_c)

Introduction

Proton magnetic resonance spectroscopy and the subsequent treatment of results has often been used to evaluate equilibrium constants of complex formation. The prerequisite for the successful implementation of the technique is that some spectral parameter of one of the reactant species should be modified as a direct result of complex formation. The most successful application has been in studies of hydrogen bonding or very weak complexing. However, each individual mathematical derivation of K_c is a function of the conditions of the experiment. That is, most derivations assume equilibrium ideal dilute solutions usually with the donor present in large excess.

Hence for a donor-acceptor equilibrium

$$A + D \rightleftharpoons A...D$$

where $K_c = \frac{[A...D]}{[A][D]}$ - however $[D] \gg [A]$

hence $K_c = \frac{[AD]}{[A]}$ and so on.

Unfortunately, our experimental conditions were such that no excess donor assumption would be valid. Hence, both donor and acceptor equilibrium concentrations had to be taken into account. Stoichiometrically, the complex formation model is

$$Al_2Et_6 + 2\ Ph_2O \rightleftharpoons 2\ AlEt_3.Ph_2O$$

initial concentrations are $[A] = a$ $[E] = e$ $[C] = c$

equilibrium concentrations are $(a-x)$ $(e-2x)$ $2x$

$\therefore K_c$ is defined as $\frac{4x^2}{(a-x)(e-2x)^2} = \frac{[C]^2}{([A]-\frac{1}{2}[C])([E]-[C])^2}$

Now the observed chemical shift of the alkyl ethyl group is a function of the protons of that group present either as free alkyl or complexed alkyl,

i.e. $-\delta_{obs}$ = f(free alkyl protons + complexed alkyl protons)

or $$-\delta_{obs} = \frac{n_a}{n_a+n_c} - \frac{\delta_e}{a} \rightarrow 0 + \frac{n_c}{n_a+n_c} - \frac{\delta_e}{a} \rightarrow \infty$$

where $-\delta_{obs}$ = the observed internal chemical shift of a particular sample

n_a = the number of protons present as Al_2Et_6 ethyl protons

n_c = the number of protons present as complex ethyl protons

$-\frac{\delta_e}{a} \rightarrow 0$ = the internal chemical shift of the pure Al_2Et_6 ethyl group

$-\frac{\delta_e}{a} \rightarrow \infty$ = the extrapolated internal chemical shift of the complex ethyl group.

Again, the number of protons of a particular ethyl group species will be equivalent to the concentration of that species.

Hence,

$$\delta_{obs} = \frac{6[A]}{6[A] + 3[C]} \cdot \delta_{pure} + \frac{3[C]}{6[A] + 3[C]} \cdot \delta_{complex}$$

(δ_{pure} and $\delta_{complex}$ are equivalent to $-\frac{\delta_e}{a} \rightarrow 0$ and $-\frac{\delta_e}{a} \rightarrow \infty$ respectively)

$$\therefore \quad \delta_{obs} = \frac{2[A]\,\delta_{pure} + [C]\,\delta_{complex}}{2[A] + [C]}$$

$$\text{or } 2[A]\,\delta_{obs} + [C]\,\delta_{obs} = 2[A]\,\delta_{pure} + [C]\,\delta_{complex}$$

$$\therefore \quad 2[A](\delta_{obs} - \delta_{pure}) = [C](\delta_{complex} - \delta_{obs})$$

$$\therefore \quad \frac{[C]}{2[A]} = \left\{\frac{\delta_{obs} - \delta_{pure}}{\delta_{complex} - \delta_{obs}}\right\} = \Delta$$

In terms of equilibrium concentrations

$$\Delta = \frac{2x}{2(a-x)}$$

$$\therefore \quad \Delta a - \Delta x = x \quad \text{or} \quad x = \frac{\Delta a}{1+\Delta}$$

The complex concentration is now a function of internal chemical shift ratio and initial alkyl concentration.

At the equimolar concentrations of diphenylether and triethylaluminium as monomer, i.e. when e = 2a

$$K_c = \frac{4x^2}{(a-x)(2a-2x)^2} = \frac{x^2}{(a-x)^3}$$

now from above $x = \frac{\Delta a}{(1+\Delta)}$

$$\therefore \quad K_c = \frac{\left\{\frac{\Delta a}{1+\Delta}\right\}^2}{\left\{a - \frac{\Delta a}{1+\Delta}\right\}^3}$$

$$\text{i.e.} \quad K_c = \frac{\Delta^2(1+\Delta)}{a}$$

When $e \neq 2a$ let $\frac{e}{2a} = \frac{[Ph_2O]_o}{[AlEt_3]_o} = r$

$$\therefore \quad K_c = \frac{4x^2}{(a-x)(e-2x)^2} = \frac{x^2}{(a-x)(ar-x)^2} \quad \text{and again } x = \frac{\Delta a}{1+\Delta}$$

$$= \frac{\Delta^2 a^2}{(1+\Delta)^2} / (1 - \frac{\Delta a}{1+\Delta})(ar - \frac{\Delta a}{1+\Delta})^2$$

$$= \frac{\Delta^2 a^2}{(1+\Delta)^2} / a^3(\frac{1}{1+\Delta})(\frac{r + (r-1)\Delta}{1+\Delta})^2$$

$$\therefore K_c = \frac{\Delta^2(\Delta+1)}{a(a + (r-1)\Delta)^2}$$

Again Δ is defined as a ratio incorporating an extrapolated value of the complex internal chemical shift. The calculated value of $\delta_{complex}$ is -0.972 p.p.m. Substitution of the corresponding values for Δ, a and r for each $(-\delta)_{obs}$ recorded in the above relation for K_c produced a mean value $\bar{K}_c = 32.7 \pm 12.0$ litre mole^{-1}. The rather large standard error was attributed to two data points out of a total of seven. If one considers a less variant population of five points, the new $\bar{K}_c = 33.9 \pm 6.0$ litre mole^{-1}.

The significant variance can be further reduced by the inclusion of more data. However, one is limited by the total change in $(-\delta)$ of 0.15 p.p.m. from free alkyl to totally complexed alkyl. A systematic error is possibly present in the estimation of the limiting value of $(-\delta)$ complex, this value being fundamental to the estimation of K_c.

Kinetic Runs

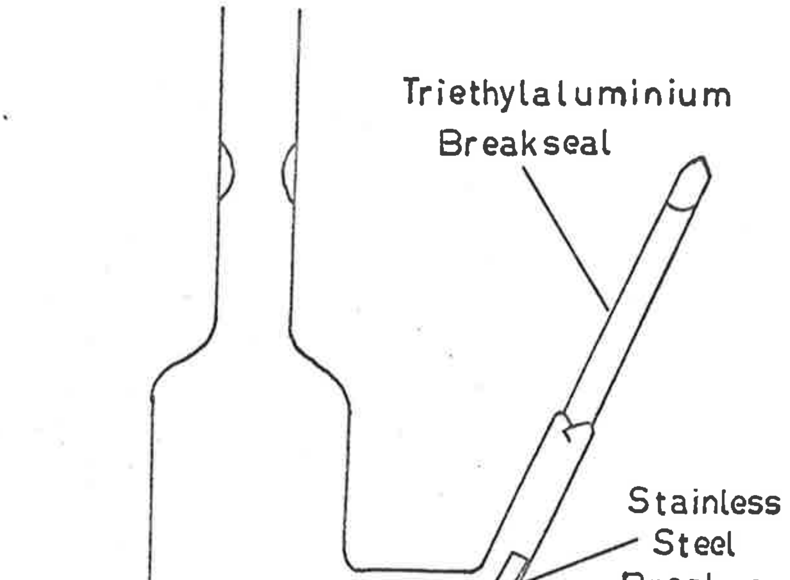
The kinetic run apparatus used in Chapter III (Fig. 8) provided a convenient and accurate method of filling the n.m.r. tubes with reactants. This apparatus was again used in the complex run series, the only difference being the use of breakseals of triethylaluminium-diphenylether complex in place of pure triethylaluminium.

Batches of complex were prepared in the apparatus of Fig. 23A. The vessel has two calibrated breakseals of triethylaluminium as sidearms. A calculated weight of diphenylether (for an equimolar complex concentration) was weighed into the vessel base, the vessel then sealed onto the manifold. After initially degassing the ether, the apparatus was sealed off from the line while pumping. The two alkyl breakseals were ruptured, the complex formed, mixed and varying amounts tipped into each of the eight breakseals. Each breakseal was sealed off in turn and stored until use.

With each of its attached n.m.r. tubes pre-calibrated to 1.80 ml., the kinetic run apparatus was pumped out on the line at a pressure of $< 10^{-3}$ torr for twenty four hours. Degassed n-1-octene was distilled from an external source into the graduated tubing attached to the base. The olefin was frozen with liquid nitrogen and the vessel sealed off while pumping.

FIG 23A

VESSEL FOR PREPARATION OF $AlEt_3 \cdot$ D.P.E. COMPLEX.



Carefully, 0.5 ml. of the olefin was distilled into one of the n.m.r. tubes which was then removed, together with its accompanying breakseals, by sealing off at the sidearm constriction. The complex breakseal was ruptured and the viscous liquid allowed to mix with the olefin in the n.m.r. tube base. This mixture was diluted to 1.80 ml. with cyclohexane from the solvent breakseal and finally, the n.m.r. tube and contents sealed off and refrigerated until use. This procedure was repeated until all four tubes were filled with a constant 1-octene concentration but varying complex concentration.

In the kinetic runs of Chapter III, the concentration of triethylaluminium as dimer was calculated from a post-calibration of the alkyl breakseal. Because of the possibility of two conflicting mechanisms here, it was necessary to know the initial concentration of triethylaluminium, estimated as monomer C_{Al}, in the complex series samples. However, once the complex mixture is formed, it is impossible to measure the alkyl concentration by any direct burette calibration. There are two possible methods for the determination of the initial triethylaluminium concentration.

(a) Spectrophotometric analysis.

Several methods[65,66,67] utilise the formation of highly coloured complexes of triethylaluminium with nitrogen bases such as isoquinoline, phenazine and pyrazine. With the phenazine complex, if it is titrated with pyridine, the triethylaluminium is displaced and there are several colour changes as each molecule of alkyl is removed from its coordination site.[66] It would be possible to determine the triethylaluminium concentration present as monomer by this method.

(b) A more convenient method for our purposes is to determine the alkyl concentration directly from the initial time p.m.r. spectrum of the reaction mixture.

The concentration of 1-octene is known accurately in each sample. The integral of the vinyl $CH_2=$ triplet peak can be directly equated to the triethylaluminium methylene quartet (both having the same proton number) and the concentration as total alkyl determined as monomer (C_{Al}),

$$\text{i.e.} \quad [AlEt_3]_{\text{init.}} = C_{Al} = \frac{\text{INT}(CH_2)\text{alkyl}}{\text{INT}(CH_2=)\text{octene}} \times \frac{[\text{1-octene}]_{\text{init.}}}{3}$$

The alkyl CH_2 integral has to be divided by 3 because of the presence of three equivalent methylene groups that contribute. Any error in the concentration estimation is a function of an instrument or integration error as well as a dispensing error (of 1-octene). The former could be kept at a minimum by adjusting the spectrometer conditions to provide large integrals and therefore more accurate readings.

The sequence of recording the initial time spectra was as follows. Diphenylether was first used as the p.m.r. lock signal (offset to 500 c.p.s. or 8.33 p.p.m.) and the spectrum scanned upfield recording both the spectrum and integrals of the 1-alkene vinyl region. As the intense cyclohexane peak was approached on scanning further, the power was reduced by a factor of 100 to avoid "throwing" the lock signal. On passing through the cyclohexane peak, the normal power level was reinstated in time to record both the spectrum and integral of the triethylaluminium methylene quartet resonance.

The lock signal was changed to cyclohexane at 1.37 p.p.m. and by scanning downfield, the spectra and integrals of the 1-alkene vinyl region and the phenylic proton signal (of diphenylether) were recorded. The zero-time concentration of 1-octene was checked by equating the integral ratio of the vinyl $CH_2=$ triplet to the total diphenylether integral. As the concentration of diphenylether remains constant throughout the reaction, the concentration of 1-octene at any time can be determined from a ratio of integral ratios, viz.

$$[\text{1-octene}]_{t=t} = \frac{\left[\frac{\text{INT}(\text{CH}_2=)}{\text{INT D.P.E.}}\right]_{t=t}}{\left[\frac{\text{INT }(\text{CH}_2=)}{\text{INT D.P.E.}}\right]_{t=0}} \times [\text{1-octene}]_{t=0}$$

Each sample n.m.r. tube was heated in a thermostatted oil bath for a prescribed time period. The temperatures designated for the five series were 100, 105, 110, 115 and 120°C. Upon removal of the samples from the bath and temperature quenching the reaction, the p.m.r. spectra were again recorded with cyclohexane as the lock signal and measuring the integral ratio of vinyl $CH_2=$ protons to total diphenylether protons. The product olefin with time was also recorded in a similar fashion to the method employed in Chapter III, viz.

$$[\text{product olefin}]_{t=t} = \frac{\left[\dfrac{\text{INT } CH_2= \text{(pr)}}{\text{INT D.P.E.}}\right]_{t=t}}{\left[\dfrac{\text{INT } CH_2=}{\text{INT D.P.E.}}\right]_{t=0}} \times [\text{1-octene}]_{t=0}$$

where INT $CH_2=$ (pr) = the integral of the product olefin singlet peak.

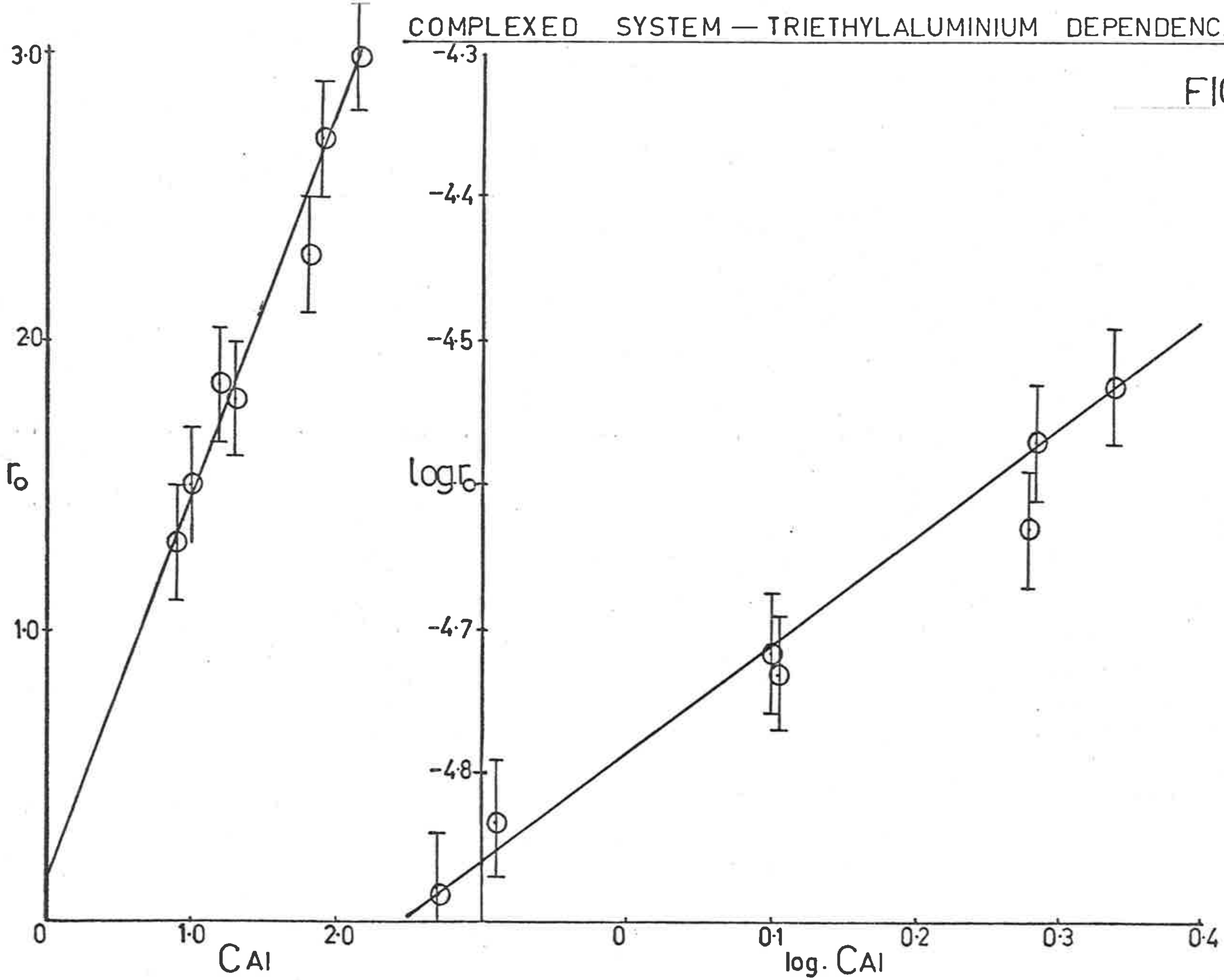
The kinetic run results were recorded and tabulated in a similar manner to those of Chapter III. Raw data was collected until at least a seven-point plot was available. Typical reactant decay and product growth curves were plotted, the result being similar to those of Fig. 10. From these plots it was apparent that the amount of reactant 1-octene consumed was approximately twice the amount of product formed at any time. This indicated a stoichiometric factor of two which will have to be accounted for in the mechanism and in any integrated rate equations.

The order with respect to triethylaluminium was attempted by the two methods previously described, i.e. the relationship between the initial velocity r_o and the initial concentration of triethylaluminium as monomer, and the log-log plot of this relationship. A large amount of error was encountered in estimating the limiting slope of the decay plot at $t = 0$. This error is reflected in the error bars of each particular initial velocity estimation. The log-log plot produced an approximate straight line of least squares slope = 0.82. The graph of r_o versus C_{Al} is a straight line passing through the origin, both results indicating a first order dependence in triethylaluminium concentration. The graphs are shown in Fig. 24 and the initial velocities tabulated below with their corresponding initial triethylaluminium concentrations.

Sample	Initial Reaction Velocity (litre/mole sec) $\times 10^5$	C_{Al} (as monomer) (moles/litre)
1	2.30	1.92
2	2.96	2.18
4	2.67	1.94
5	1.84	1.26
6	1.74	1.30
7	1.30	0.89
8	1.47	1.02

COMPLEXED SYSTEM — TRIETHYLALUMINIUM DEPENDENCE.

FIG 24



Again, the preliminary results appear to indicate a first order dependence in triethylaluminium concentration calculated as monomer. The order with respect to 1-octene is assumed to be one from a comparison with the decay curves of the kinetic runs of Chapter III, i.e. for the same reasons offered in Chapter III.

We assume the overall reaction to be simply

$$AlEt_3.D.P.E. + CH_2{=}CH{-}C_6H_{13} \xrightarrow{k_n} \text{products.}$$

Thus the reaction rate = $k_n[AlEt_3.D.P.E.][CH_2{=}CH{-}C_6H_{13}]$.
Now we can assume that the complex concentration is approximately equal to C_{Al}, the concentration of triethylaluminium estimated as monomer.

$$\therefore \text{Rate} = k_n\ C_{Al}[CH_2{=}CH{-}C_6H_{13}]$$

Now if the initial concentrations of triethylaluminium and 1-octene are a and b and x is the amount of kinetic product formed in time t, then the reduced reactant concentrations according to the stoichiometry will be (a-x) and (b-2x). Thus the rate of reaction $\frac{dx}{dt} = k_n(a-x)(b-2x)$ or $k_n dt = \frac{dx}{(a-x)(b-2x)}$. Integration of this differential rate equation leads to two solutions of the integrated rate equation, depending on which of the reactants is in stoichiometric excess.

When $a > \frac{b}{2}$

$$k_n t = \frac{2.303}{(2a-b)} \log \frac{b(a-x)}{a(b-2x)}$$

When $\frac{b}{2} > a$

$$k_n t = \frac{2.303}{(b-2a)} \log \frac{a(b-2x)}{b(a-x)}$$

The kinetic product is again determined from the relation

$$x = \frac{[\text{1-octene}]_{t=0} - [\text{1-octene}]_{t=t}}{\nu}$$

where ν is the stoichiometric coefficient. Substitution of a, b and x into the right-hand side of the above two integrated rate equations produced straight lines passing approximately through the origin. The "best and worst" fit data were selected from the total set measured and are shown in Fig. 25 with their confidence limit hyperbolas, the limit of confidence being arbitrarily selected as 90%. The straight lines shown are the least squares lines, the slopes of which are the apparent rate constants of reaction k_n. Each population of k_n, at a particular temperature, exhibited a randomness about a mean value $\bar{k}_n$, which was considered representative of that data set. A complete table of rate constants obtained at five different temperatures is shown as follows.

Table of Complexed System Rate Data

Run No.	Concentrations		$T^{o}C$	k_n x 10^6	$\bar{k}_n$ x 10^6	S.D. in $\bar{k}_n$
	$AlEt_3$	1-octene				
3C	1.16→1.92	1.58	120.0	14.3	14.4	± 0.21
				17.6		
				13.2		
				11.6		
1C	0.899→2.18	1.75	115.0	9.31	8.16	± 0.82
				6.57		
				7.72		
				8.42		
				7.53		
				8.43		
				9.09		
2C	0.781→3.14	1.60	110.0	7.59	6.21	± 1.80
				3.61		
				8.17		
				5.48		
4C	0.648→1.60	1.61	105.0	5.36	4.80	± 0.59
				5.13		
				3.91		
				4.90		
5C	0.747→1.59	1.62	100.0	2.98	2.59	± 0.36
				3.06		
				2.38		
				2.94		

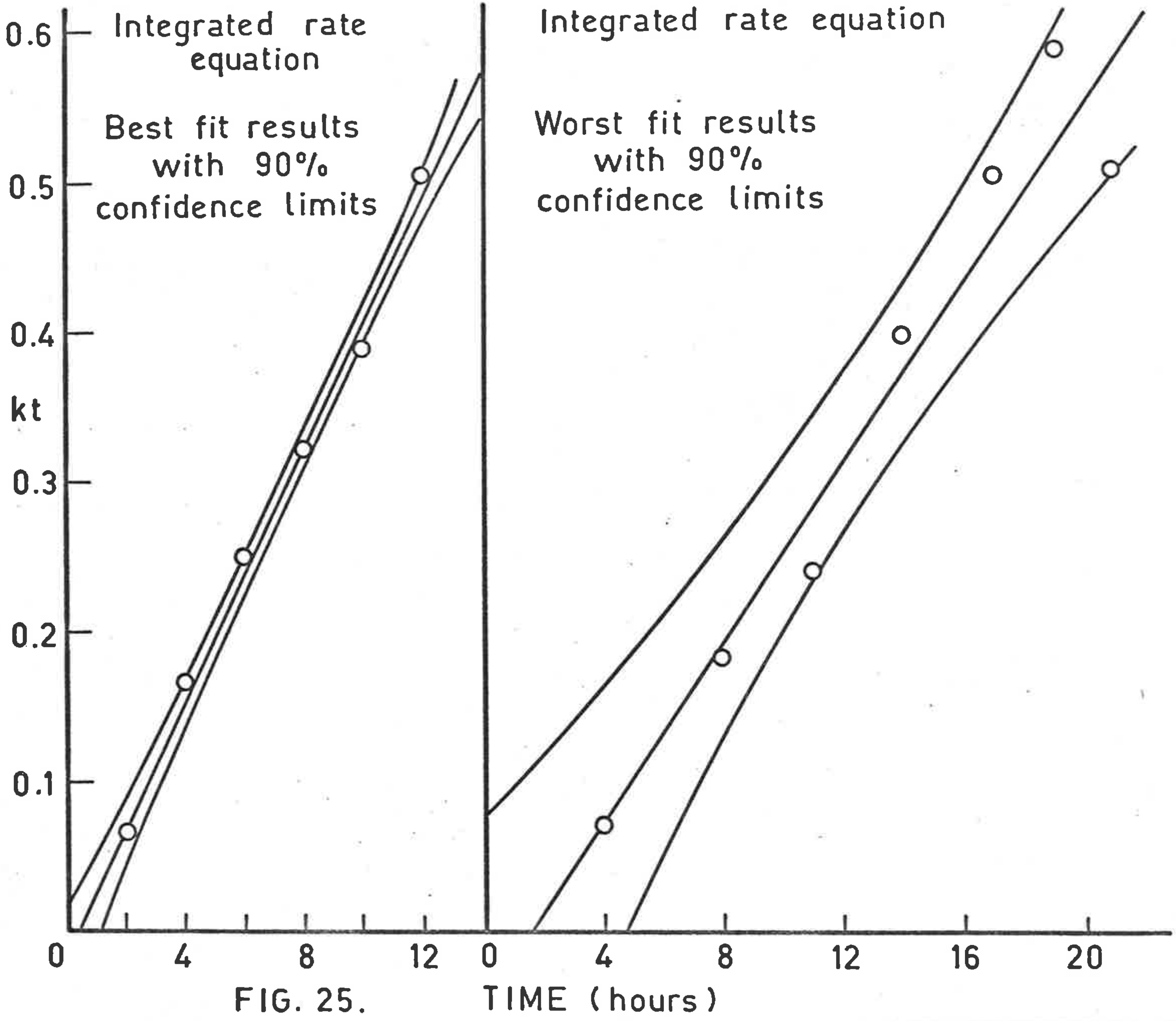

Integrated rate equation
Best fit results with 90% confidence limits
Integrated rate equation
Worst fit results with 90% confidence limits
kt
0.6
0.5
0.4
0.3
0.2
0.1
0
4
8
12
0
4
8
12
16
20
TIME (hours)

FIG. 25.

The Arrhenius plot of log $\bar{k}_n$ versus the reciprocal of temperature in degrees absolute is shown in Fig. 26. The graph shows a linear dependence of the reaction rate with temperature, the least squares slope of this straight line realising an activation energy E_n of 23.0 ± 1.5 kcal/mole. The pre-exponential factor A_n, equal to the intercept was calculated as $10^{7.9 \pm 1.0}$ litre $\text{mole}^{-1}\text{deg}^{-1}$.

Conclusion Discussion

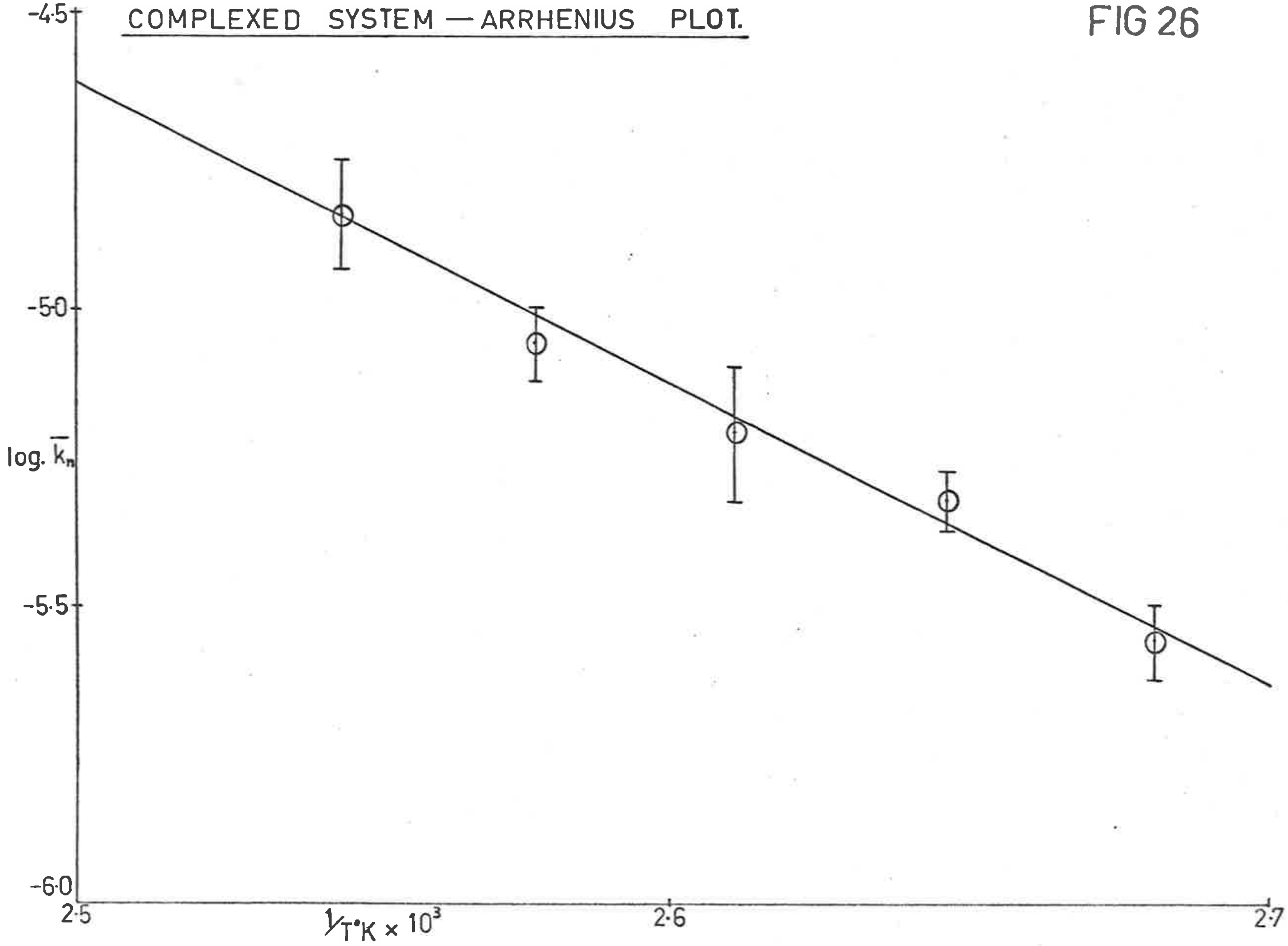
An estimation of the extent of complexing at the kinetic reaction temperature, based on the extrapolation of K_c (29.0°C) using the heat of complex formation (2.70 kcal/mole[57]), suggests that at the reaction temperature the molar concentration of $AlEt_3$.D.P.E. complex is significantly in excess of free triethylaluminium dimer. If then, the reaction observed is due to complex participation, then the observed kinetics should correspond to a second order rate equation, as is observed.

$$AlEt_3.D.P.E. + \text{1-octene} \xrightarrow{k_n} \text{products}$$

$$\begin{aligned} \text{Rate} &= k_n[\text{complex}][\text{1-octene}] \\ &= k_n\, C_{Al}[\text{1-octene}] \end{aligned}$$

However, it must be stated that the complexed form of triethylaluminium is by no means overwhelmingly predominant and we would

FIG 26



COMPLEXED SYSTEM — ARRHENIUS PLOT.

not expect this approximate rate law to hold rigidly over a wide concentration range.

If the mechanism applies, then the observed reaction rate is to a reasonable approximation at the concentrations and temperatures used, the rate of a simple bimolecular reaction. The A factor of $10^{7.9 \pm 1.0}$ lies within the range commonly observed for reactions of this type.[68]

An alternative mechanism assumes that the complex is unreactive, the observed reaction being due to the equilibrium concentration of uncomplexed monomer. The following equilibria illustrate the possibility of the two mechanisms:

$$\begin{tikzcd} & 2\,Et_3Al + 2\,D.P.E. \arrow[dl, leftrightarrow, "K_d"'] \arrow[dr, leftrightarrow, "K'"] & \\ Et_6Al_2 + 2\,D.P.E. \arrow[rr, leftrightarrow, "K_c"] & & 2\,Et_3Al.D.P.E. \end{tikzcd}$$

A detailed kinetic analysis of the favoured mechanism is exceedingly complex. No simple general rate equation applies and analysis would have to be made by numerical methods and would require precise values of K_c and K_d. Our data to hand is insufficient to warrant such an analysis. Although the mechanism does not give a simple closed form solution for a rate equation, we cannot rule out the possibility that an approximate second order relationship might arise over the limited concentration range. Thus the approximate agreement between the observed rate equation and the mechanism involving the reaction

$$AlEt_3.D.P.E. + 1\text{-octene} \rightarrow \text{products}$$

does not uniquely establish this mechanism. There is no doubt that our results need refinement before the mechanism can be confirmed. The evidence for the first mechanism seems quite strong, but it cannot be entirely accepted until more precise measurements enable the alternative mechanism to be evaluated.

CHAPTER VI - CONCLUSION

The reaction between triethylaluminium and 1-octene has been examined kinetically in two environments; in inert hydrocarbon solution only and in the presence of a coordinating ether.

The rate data for the hydrocarbon system, as tabulated in Chapter III, applies to the postulated overall mechanism and is defined by an apparent rate coefficient

$$Al_2Et_6 + 2,1\text{-octene} \xrightarrow{k_{APP}} Al_2Et_5.\text{octyl} + 2\text{-Et-1-octene}$$

However, we wish to characterise the addition step itself, by the calculation of individual Arrhenius parameters and the derived activation parameters for the rate determining step

$$AlEt_3 + 1\text{-octene} \xrightarrow{k_2} \text{adduct.}$$

The mechanism of reactions 1→4 (Chapter III) shows that the apparent rate constant k_{APP} is related to the addition rate constant k_2 as follows:

$$k_{APP} = k_2 K_d^{\frac{1}{2}} \quad \text{or} \quad k_2 = \frac{k_{APP}}{K_d^{\frac{1}{2}}}$$

Thus the initial dimer dissociation has to be taken into account when calculating rate constants for the addition reaction only.

Hence

$$A_{APP}e^{-E_{APP}/RT} = A_{APP}e^{-E_2/RT}\ e^{-\Delta H_d/2RT}$$

$$\therefore \quad E_2 = E_{APP} - \frac{\Delta H_d}{2}$$

The heat of dimer dissociation was estimated from the molecular weight measurements of Chapter IV and recorded as -12.6 ± 1.0 kcal/mole. The apparent activation energy measured in Chapter III was 24.0 ± 0.6 kcal/mole. Hence the activation energy for the rate determining step is

$$E_2 = 24.0 - 6.3 = \underline{17.7 \pm 1.6\ \text{kcal/mole}}$$

Table of Addition Rate Data

Temp. °C	$\bar{k}_{APP} \times 10^6$ (litre/mole sec.)	$K_d^{\frac{1}{2}*}$ (moles/litre)	$\bar{k}_2 \times 10^5$ (litre^2/mole^{2}sec.)
95	2.94	0.26	1.14
100	5.13	0.29	1.78
110	10.8	0.35	3.05
115	18.6	0.39	4.78
120	25.0	0.44	5.67

* $K_d^{\frac{1}{2}}$ at the above temperatures calculated from the least squares slope of the log K_d versus $1/T^o$ K plot (Fig. 18).

The determination of the intercept of the least squares slope of the graph of log $\bar{k}_2$ versus 1/T° K produced a pre-exponential factor for the addition reaction of $A = 10^{5.9 - 6.9}$ litre mole^{-1} sec^{-1}.

In general, the errors associated with the above rate data are the sums of errors from reactant and solvent dispensing, triethylaluminium concentration determinations, p.m.r. spectrometer instrument errors (more specifically integration errors). These are possibly the cause of the random variance in each set of rate constants measured at a particular temperature.

Comparing our results with those of previous workers; Hay et al.[13,14] examined the reactions between triethylaluminium and 1-alkenes ranging in carbon number from C_3-C_6. If one expects an "homologous series" of activation energies with carbon number increase, then our results do not quite fit the pattern established by Hay et al., although there is some agreement with their value for the triethylaluminium/1-hexene system.

Hay-Jones: $E_{APP} = 24.3 \pm 0.5$ kcal/mole

Ours: $E_{APP} = 24.0 \pm 0.6$ kcal/mole.

For the addition step above, the difference is increased.

Hay-Jones: $E_2 = 18.2 \pm 2.0$ kcal/mole; $A_2 = 10^{6.5-7.5}$ litre mole^{-1} sec^{-1}

Ours: $E_2 = 17.7 \pm 1.6$ kcal/mole; $A_2 = 10^{5.9-6.9}$ litre mole^{-1} sec^{-1}

The discrepancy is due, no doubt, to the different estimations (and methods therein) of K_d and ΔH_d for dimer dissociation. If we use the Hay-Hooper K_d and ΔH_d estimates in the calculation of Arrhenius parameters from our data, then the values obtained are:

$$E_2 = 18.9 \text{ kcal/mole} \qquad A_2 = 10^{7.4} \text{ litre mole}^{-1}\text{sec}^{-1}.$$

Thus, our Arrhenius parameters for the addition reaction enclose Hay et al. data, depending on the dimer dissociation data chosen and we have already discussed the merits of gas or liquid phase estimations and their application to our kinetics.

In a comparison with Allison's results, our overall parameters are even more removed. However, the mechanism used by this author has now been shown to be incorrect.

Our results can be further utilised to calculate the entropy of activation ΔS^{o}_{+}, which presents us with an indication of the transition state structure. The knowledge of this structure is fundamental in describing the reactivity and the reaction path through the activated complex. The entropy of activation can be related, by the theory of Absolute Reaction Rates, to the frequency factor A which, in turn, can be quoted in several ways; as a temperature independent factor, a steric factor or formally as an entropy of activation.

Now the rate constant $k = K\frac{kT}{h}\,e^{\Delta S^{o}_{+}/R}\;e^{-\Delta H^{o}_{+}/RT}$

where K = the transmission coefficient $\simeq 1$

k = Boltzmann's constant = 1.38×10^{-16} erg/°K

h = Planck's constant = 6.625×10^{-27} erg/sec.

Approximating and substituting the above constants at 25°C

$$e^{\frac{\Delta S^{o}_{+}}{R}} = \frac{A}{10^{12.8}}$$

or

$$\Delta S^{o}_{+} = 2.303\, R\, (\log_{10} A - 12.8).$$

Substitution of the relevant A factors produces the corresponding entropies of activation at the standard state of one mole/litre.

$\Delta S^{o}_{+\ APP} = -16.0$ cal. mole^{-1} deg. K^{-1} (our apparent entropy of activation),

$\Delta S^{o}_{+\ 2} = -29.3$ cal. mole^{-1} deg. K^{-1} (our addition reaction entropy of activation),

$\Delta S^{o}_{+\ H} = -24.7$ cal. mole^{-1} deg. K^{-1} (our addition reaction entropy of activation from our apparent frequency factor corrected by Hay-Hooper's dimer dissociation results),

$\Delta S^{o}_{+\ n} = -22.4$ cal. mole^{-1} deg. K^{-1} (our apparent entropy of activation for the complexed alkyl system).

Both $\Delta S^{o}_{+\ APP}$ and $\Delta S^{o}_{+\ n}$ place a numerical estimate on the overall or apparent reaction rate in each particular system studied. The rate in the complexed alkyl system is slower, as indicated by the more negative entropy of activation.

Our data is a good example of the insensitivity of activation energy as a criterion for reactivity comparison. The apparent activation energies E_{APP} and E_n are very similar, yet the entropies of activation are quite different and make sense if we initially assume the reactivity between triethylaluminium and 1-octene is a function of the electronic content of the Al-C bond and a steric factor. The agreement in apparent activation energies possibly exhibits a similarity in the mode of reactant interaction. However, we emphasise only a possible inference as the sole accurate data available is for the addition step in hydrocarbon solution.

Absolute estimates of the frequency factor provide more reliable information on transition state structure. The so-called "normal" frequency factor for a gas phase bimolecular reaction of rigid elastic spherical molecules is 10^{11} litre $mole^{-1}$ sec^{-1} and is observed for a number of reactions in solution. It could be suggested that our lower than "normal" frequency factors might involve a forbidden transition by quantum mechanical selection rules. However, it seems more likely that the low frequency factors are a consequence of large entropy decreases that occur in association-type reactions. More specifically, the numerical value of the frequency factor can be related to the molecule like transition state which varies little in structure from the resulting product molecule. Frost and Pearson[69] have tabulated empirical expressions and values of bimolecular rate constants of different types of reactants and the complexes they form.

Here a frequency factor formula defined as

$$\frac{kT}{h}\frac{fr^2}{ft^3}$$

for a model of two reactant atoms has a steric factor of unity (fr is a partition function for one degree of rotational freedom, having a value typical of a typical molecular rotation; fr^3 is three degrees of translational freedom). For a model of two non-linear molecules interacting to form a non-linear complex (the model for both of our systems), the frequency factor formula is now

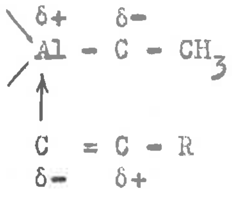
$$\frac{kT}{h}\frac{fv^5}{ft^3fr^3} ;$$

the steric factor formula now being $\frac{fv^5}{fr^5}$ and calculated as 10^{-5}; (fv^5 is five degrees of vibrational freedom). This steric factor is a multiplier and when applied to the "normal" frequency factor, it produces a new estimate for our model of $A = 10^6$ litre $mole^{-1}$ sec^{-1}. Initially, the decrease in A factors is due to the fact that "typical" fr values exceed "typical" fv values by a factor of 10. Thus the lower A factors obtained experimentally could be attributed largely to the loss of rotations of reactants on forming the transition state. However, this analysis fails to account for certain specific factors concerned with the liquid state, e.g. the free volume effect and solvation effects. Frequency factors of this magnitude ($\sim 10^{6}$) are observed in the addition reactions of vinyl compounds with radicals, nucleophiles and electrophiles.

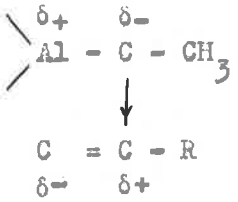
The nucleophilic addition of 4-substituted 2-nitro benzene sulphonyl halides to cyclohexene disubstituted styrenes[70,71] produces A factors in the range $10^{6.0}$ to $10^{7.9}$. The electrophilic addition of bromine to substituted styrenes in anhydrous acetic acid[72] produces a range of frequency factors of $10^{6.0}$ to $10^{7.4}$. Radical addition to various unsaturates[73] shows an A factor range of $10^{8.3}$ to $10^{11.7}$.

Again, comparing the two systems we have examined, the complexed alkyl/1-octene transition state is a more loosely held unit which is illustrated as a more negative entropy of activation and infers the formation of the transition state is less probable and the rate is correspondingly slower.

The mechanism of interaction between triethylaluminium and 1-octene is broadly classified by two alternatives; the electrophilic attack through the aluminium atom via an electron rich carbon atom (1) or a π system (4); the nucleophilic attack through the alkyl group attached to the aluminium atom (2).

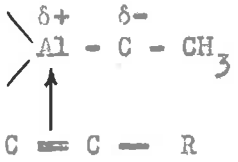


(1)



(2)

(3)



(4)

The above two alternatives are extremes and the situation is probably best described by case (3) in which both nucleophilic and electrophilic attacks occur simultaneously to form a four-centre transition state complex. In addition, there are modes of attack which are intermediate between these, for instance, the nucleophilic attack of the alkyl group on the substrate olefin (2) assisted by the coordination of the substrate olefin to the metal ((1) and (4)). With this mechanism the relative reactivities may be a function of the ability of the aluminium atom to complex with the substrate. We have attempted to observe such complexing by p.m.r. spectroscopy, however, even at low temperatures ($-40^{\circ}C$) no shifts in any likely affected peaks were apparent. Possible evidence is obtained from Hata's work,[21] where intramolecular complexing between the π bond system and the Al atom was observed by p.m.r. spectroscopy in 4-alkenyl-aluminium dialkyls.

The kinetic evidence for the coordinated anionic mechanism depends on an assumption that the mechanism cases (2) and (3) above should proceed with both monomer and dimer of triethylaluminium. However, the coordinated mechanism is supposed to be a reaction involving monomer participation only, because of the availability of the vacant sp^3 orbital for coordination purposes. No such vulnerable site is present in the dimer, where bridge bonds effectively incorporate these empty orbitals into three-centre bonds. The combination of our observed heat of dimer dissociation and the non-observance of any 1-alkene/-triethylaluminium complexing shows that if any complexing is to be assumed, the equilibrium constant must be very small, the complex having an equally reduced lifetime and hence is unlikely to affect the monomer-dimer equilibrium. This coordinated anionic mechanism is confirmed by our determination of monomer only participation in the addition step.

A further distinction between nucleophilic and electrophilic attack may come to light in reactions of triethylaluminium with 1-alkenes, substituted in the 2 position.

If the addition mechanism occurs by electrophilic attack then the rate of reaction should be advanced over that involving the non-substituted 1-alkene. Conversely if the nucleophilic mechanism applies, the reaction rate should be reduced. This is a result of the inductive effect of the alkyl substituent which tends to increase the electron content of the double bond. In fact a comparison of the relative yields of the products of substituted ethylenes[74] has lead to the conclusion that alkyl groups deactivate the double bond towards nucleophilic attack.

We have shown that the rate of reaction is reduced in the presence of coordinating solvents, specifically diphenylether, even though we have proved that the monomer exists as an integral part of the 1:1 complex with the ether. This is further support for the coordinated mechanism, as the orbital normally available for coordination with the 1-olefin substrate is now occupied in bond formation with the ether oxygen. In addition, it confirms that no discrete alkyl carbanion formation and participation in the addition step occurs. Brownstein et al.[54] and Takashi,[55] using p.m.r. measurements on triethylaluminium etherates, calculated the reduced electronegativity of the complexed aluminium atom and its effectively reduced electron withdrawing power. The donation of electrons by the oxygen atom increases the electron density about the Al atom and reduces its tendency to share electrons of the Al-C bond. This in itself is experimental proof of the reduced carbanionic character of the alkyl group. Apparently the reverse effect is observed in the reactions of alkyl lithiums with 1-alkenes. However, there is considerable disagreement about the association number of the lithium alkyl initiating species.

Evidence for carbanionic character has been tendered in the form of a measured residual conductivity of triethylaluminium alone and the measured specific conductance of triethylaluminium etherates. The former effect is explained as the ability of triethylaluminium to self-ionise

$$Al_2Et_6 \rightleftharpoons AlEt_2^+ + AlEt_4^- .$$

However, the conductivity has also been attributed to impurities present with the alkyl. The conductivities of complexed triethylaluminiums are remarkably high. Takashi[55] concludes that their ionic properties and the polarised nature of the Al-C bond might "significantly affect the reactivity". Again there is still no absolute evidence that any aluminium compounds produce carbanions <u>in solution</u>. The coordinated mechanism predominates on the evidence available at present.

In the above discussion, we have attempted to outline the correct mechanism for reactions between triethylaluminium and 1-octene by; initially measuring the rate parameters of a particular reaction and tabulating them as characteristic indeces; discussing the difference in these indeces by comparing the mode of reagent attack and the alkylaluminium environment in each example; finally, by postulating a mechanism which supports the experimental data which justifies it against a carbanionic alternative. All the evidence confirms the participation of monomer only, in the reaction in hydrocarbon solution alone. The activation parameters calculated for this reaction are eminently reasonable, irrespective of any doubt about the position of the monomer-dimer equilibrium under kinetic temperature conditions. However, this latter question is obviously one which requires urgent investigation by different methods to those employed to date. The other point which requires clarification is the distinction between two possible mechanisms in etherated solvents. We think that this problem can be solved by a more extensive investigation along the lines of our preliminary experiments.

In conclusion, it must be emphasised that the knowledge of the path of a chemical reaction in terms of the Transition State Theory is still not secure. Many theoretically derived models have been put forward in an attempt to correlate empiricism with experimental observation. As Laidler[75] states: "A large number of calculations have been made with the object of comparing calculated and experimental rate constants, activation energies and frequency factors". The remarkable feature (after all this time) of each empirical theory is that while one particular chemical system can be predicted by a model, in all likelihood, the next system chosen cannot. Unfortunately, the discrepancies are usually attributed to steric or polar effects.

BIBLIOGRAPHY

1. G.B. Buckton and W. Odling, Ann. Supplementum 4, 109 (1865).
2. K. Ziegler, H. Gellert, K. Zosel, H. Lehmkuhl and W. Pfohl, Angew. Chem. 67, 424 (1955).
3. K. Ziegler, ibid. 64, 323 (1952).
4. R. Koster and P. Binger, Advances in Inorganic Chem. and Radiochem. 17, 311 (1965).
5. K. Zosel, Brennstoff. Chem. 41, 321 (1960).
6. E. Perry and H.A. Ory, J. Org. Chem. 25, 1685 (1960).
7. P.G. Hooper - unpublished results - cited in reference 12.
8. K. Ziegler, Angew. Chem. 71, 623 (1959).
9. K. Ziegler, H. Gellart, K. Zosel, E. Holtzkamp, J. Schneider, W. Kroll and M. Soll, Liebigs. Ann. De. Chemie. 629, 121 (1960).
10. G. Natta, M. Farino and P. Pino, Ricerca Sci. Suppl. A25, 120 (1955); Chem. Zentr. 12182 (1957).
11. P.E.M. Allen, J.P. Allison, J.R. Majer and J.C. Robb, Trans. Farad. Soc. 59, 2080 (1963).
12. A.W. Laubengayer and W.F. Gilliam, J. Amer. Chem. Soc. 63, 477 (1941).
13. P.E.M. Allen, J.N. Hay, G.R. Jones and J.C. Robb, Trans. Farad. Soc. 63, 1636 (1967).
14. J.N. Hay, P.G. Hooper and J.C. Robb, ibid, 65, 1365 (1969).

15. A.A. Bothner-by and C. Naar-Colin, J. Amer. Chem. Soc. 83, 231 (1961).

16. Varian N.M.R. Spectra Catalogue, Varian Associates Palo Alto California.

17. J.W. Elmsley, J. Feeney and L.H. Sutcliffe in "High Resolution Nuclear Magnetic Resonance Spectroscopy" (2 vols.) Pergamon (1965).

18. Mass Spectral Data, American Petroleum Inst. Research Project 44, National Bureau of Standards, Washington D.C.

19. Selected Values of Physical and Thermodynamic Properties of Hydrocarbons, American Petroleum Inst. Research Project, Carnegie Press.

20. Calculation from data of reference 12.

21. G. Hata, Chem. Comm. 7, 1115 (1968).

22. P.E.M. Allen and B.A. Casey, Europ. Pol. J. 2, 9 (1966).

23. K.J. Laidler "Chemical Kinetics" 2nd ed. McGraw-Hill (1965).

24. K.S. Pitzer and R.K. Sheline, J. Chem. Phys. 16, 552 (1948).

25. K. Kohlrausch and J. Wagner, Z. Physik. Chem. B52, 185 (1942).

26. T. Mole, Aust. J. Chem. 16, 794 (1963).

27. K.S. Pitzer and H.S. Gutowsky, J. Amer. Chem. Soc. 68, 2204 (1946).

28. E.G. Hoffman, Liebigs Ann. De. Chemie, 104 629 (1960).

29. C.H. Henrickson and D.P. Eyman, Inorg. Chem. 6, 1461 (1967).

30. N.S. Davidson and T.L. Brown, J. Amer. Chem. Soc. <u>64</u>, 316 (1942).

31. P.H. Lewis and R.E. Rundle, J. Chem. Phys. <u>21</u>, 986 (1953).

32. R.G. Vranka and E.L. Amma, J. Amer. Chem. Soc. <u>89</u>, 3121 (1967).

33. N. Muller and D.E. Pritchard, ibid, <u>82</u>, 248 (1960).

34. K. Ramey, J. O'Brien, I. Hasegawa and A. Borchert, J. Chem. Phys. <u>69</u>, 3418 (1965).

35. O. Yamamoto, Bull. Chem. Soc. Japan, <u>37</u>, 1125 (1964).

36. K. Ziegler in "Organometallic Chemistry" Chapter 5 "Organoaluminium Compounds" (A.C.S. Monograph No. 147) Edit. H. Zeiss, Reinhold (1960).

37. G.E. Coates and K.L. Wade in "Organometallic Compounds" Vol. 1, 3rd ed. Methuen.

38. H. Martin and W. Kliene-Dopke, cited in reference 4.

39. J.F. Malone and W.S. McDonald, Chem. Comm. 444 (1967).

40. E.A. Jeffery, T. Mole and J.K. Saunders, Aust. J. Chem. <u>21</u>, 137 (1968).

41. D.A. Sanders and J.P. Oliver, J. Amer. Chem. Soc. <u>90</u>, 5910 (1968).

42. E.G. Hoffman, Bull. Soc. Chim. France, 3917, 1467 (1963).

43. A.W. Laubengayer and W.F. Schirmer, J. Amer. Chem. Soc. <u>62</u>, 1578 (1940).

44. A.W. Weissberger in "Techniques of Organic Chemistry", Physical Methods Part 1.

45. W. Sweitoslawski in "Ebulliometric Methods" Reinhold (1945).

46. R.S. Lehrle, "Ebulliometry Applied to Polymer Solutions" Progress in High Polymers I (1961).

47. A.J. Davies, A.E. Phillpotts and B.W. Swanson (1955) - Proc. 4th World Petroleum Congress, Rome 1955, Sect. 5, p. 351.

48. S. Tanaka, Bull. Chem. Soc. Japan, 41, 723 (1968).

49. from Standard Telephones and Cables Thermistor Handbook (1959).

50. J.M. Pugh and R.H. Stokes, Aust. J. Chem. 16, 211 (1963).

51. Handbook of Chemistry and Physics, 47th edition.

51a. A.A. Frost and R.G. Pearson in "Kinetics and Mechanism" p. 126, 2nd ed. Wiley (1962).

52. L. Reich and A. Schindler "Polymerisation by Organometallic Compounds", Polymer Reviews 12, Interscience.

53. J. Boor Jr., Macromolecular Reviews, Vol. 2, p. 115, Interscience.

54. S. Brownstein, B. Smith, C. Ehrlich and A.W. Laubengayer, J. Amer. Chem. Soc. 81, 3826 (1959).

55. Y. Takashi, Bull. Chem. Soc. Japan, 40, 612 (1967).

56. K. Hatada and H. Yuki, Tetrahedron Letters, 2, 213 (1968).

57. cited in reference 37.

58. F.J. Welch, J. Amer. Chem. Soc. 81, 1345 (1959).

59. cited in reference 55.

60. J.P. Allison, Ph.D. Thesis, Birmingham (1961).

61. P.J. Narashimham and M.T. Rogers, J. Amer. Chem. Soc. 82, 5983 (1960).

62. E. Bonitz, Chem. Berichte, 88, 742 (1955).

63. J.L. Atwood and G.D. Stucky, J. Amer. Chem. Soc. 89, 5362 (1967).

64. T.E. Hogen-Esch and J. Smid, ibid, 88, 307 (1966).

65. C.H. Wadelin, Talanta, 10, 97 (1963).

66. D.F. Hagen and W. Leslie, Analyt. Chem. 35, 814 (1963).

67. J.H. Mitchen, ibid, 33, 1331 (1961).

68. S.W. Benson in "The Foundations of Chemical Kinetics", p. 302 McGraw-Hill (1960).

69. A.A. Frost and R.G. Pearson in "Kinetics and Mechanism" p. 94, 2nd ed. Wiley (1962).

70. D.R. Hogg, Quarterly Rev. Sulfur Chemistry (Intrascience, Santa Monica, Calif.) 2, No. 4, 340 (1967).

71. N. Kharasch and W.L. Orr, J. Amer. Chem. Soc. 78, 1201 (1956).

72. K. Yates and W.V. Wright, Canad. J. Chem. 45, 167 (1967).

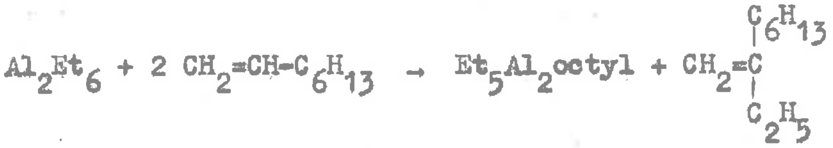
73. J.A. Kerr in Annual Reports of the Chemical Society, p. 99, Vol. 64 (1967).

74. S. Patai in "Chemistry of Alkenes" p. 469, Chapter 8, Interscience (1964).

75. K.J. Laidler and J.C. Polanyi in Progress in Reaction Kinetics, Vol. III, ed. G. Porter (1965).

APPENDIX I - DERIVATION OF THE INTEGRATED RATE EQUATION

Stoichiometrically the observed reaction is defined as



$$Al_2Et_6 + 2\,CH_2{=}CH{-}C_6H_{13} \rightarrow Et_5Al_2\text{octyl} + CH_2{=}\underset{\substack{|\\C_2H_5}}{\overset{\substack{C_6H_{13}\\|}}{C}}$$

The initial concentrations of alkyl and olefin are a and b. If x is defined as the amount of kinetic product formed in time t, then the reduced reactant concentrations are (a-x) and (b-2x).

The rate of reaction can be defined as

$$R = -\frac{d[Al_2Et_6]}{dt} = -\frac{1}{2}\,\frac{d[\text{octene}]}{dt}$$

$$= k_{APP}[Al_2Et_6]\,[CH_2{=}CH{-}C_6H_{13}]$$

(k_{APP}, C_{Al} and k_2 are defined in Chapter III)

or

$$\frac{dx}{dt} = k_2K_d^{\frac{1}{2}}(C_{Al})^{\frac{1}{2}}[CH_2{=}CH{-}C_6H_{13}]$$

$$= k_2K_d^{\frac{1}{2}}(a-x)^{\frac{1}{2}}(b-2x)$$

$$\therefore\ k_2K_d^{\frac{1}{2}}.dt \text{ or } k_{APP}\,dt = \frac{dx}{(a-x)^{\frac{1}{2}}(b-2x)}\ .$$

This is the differential form of the rate equation which now has to be integrated.

For convenience, let $\frac{dx}{dt} = k_{APP}(a-x)^{\frac{1}{2}}(b-2x)$

and let $u = (a-x)^{\frac{1}{2}}$

$$\therefore \frac{du}{dx} = -\frac{1}{2(a-x)^{\frac{1}{2}}} = -\frac{1}{2u}$$

$\therefore$ $dx = -2u.du.$

Now $u^2 = a-x$ or $-x = u^2-a$ or $b-2x = 2(u^2-a) + b$

$\therefore$ Substituting expressions for x in terms of u into the differential equation

$$-\int_0^t k_{APP}.dt = \int_0^u \frac{2u.du}{u[2(u^2-a) + b]}$$

$$\therefore \qquad -k_{APP}.t = \int_0^u \frac{du}{u^2-a+\frac{b}{2}} \qquad (1)$$

This general expression (1) can now be integrated depending on the relative magnitudes of a and $\frac{b}{2}$.

(a) when $a > \frac{b}{2}$ expression (1) becomes

$$-k_{APP}.t = \int \frac{du}{u^2 - (a - \frac{b}{2})}$$

Integrating by partial fractions

$$\frac{1}{u^2 - (a - \frac{b}{2})} = \frac{A}{u + (a - \frac{b}{2})^{\frac{1}{2}}} + \frac{B}{u - (a - \frac{b}{2})^{\frac{1}{2}}}$$

$\therefore\ 1 = A(u - (a - \frac{b}{2})^{\frac{1}{2}}) + B(u + (a - \frac{b}{2})^{\frac{1}{2}})$

$\therefore$ when $u = (a - \frac{b}{2})^{\frac{1}{2}}$, $2B(a - \frac{b}{2})^{\frac{1}{2}} = 1$ $\qquad \therefore\ B = \dfrac{1}{2(a - \frac{b}{2})^{\frac{1}{2}}}$

and when $u = -(a - \frac{b}{2})^{\frac{1}{2}}$, $-2A(a - \frac{b}{2})^{\frac{1}{2}} = 1$ $\qquad \therefore\ A = -\dfrac{1}{2(a - \frac{b}{2})^{\frac{1}{2}}}$

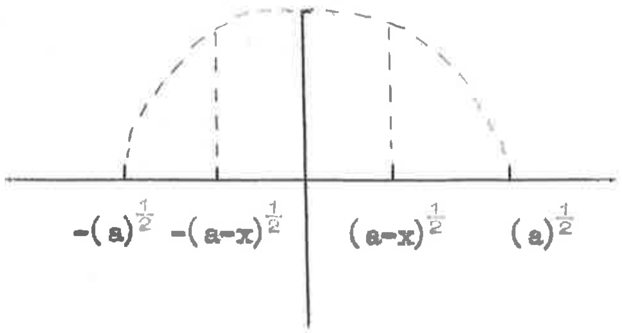
$\therefore$ Substituting for A and B

$$-k_{APP}t = \int \frac{-\frac{1}{2(a - \frac{b}{2})^{\frac{1}{2}}}}{u + (a - \frac{b}{2})^{\frac{1}{2}}} \cdot du + \int \frac{\frac{1}{2(a - \frac{b}{2})^{\frac{1}{2}}}}{u - (a - \frac{b}{2})^{\frac{1}{2}}} \cdot du$$

or

$$k_{APP}t = \frac{1}{2(a - \frac{b}{2})^{\frac{1}{2}}} \left[\int \frac{du}{u + (a - \frac{b}{2})^{\frac{1}{2}}} - \int \frac{du}{u - (a - \frac{b}{2})^{\frac{1}{2}}}\right]$$

Because of the shape of such a function, graphically the limits exist between $-(a-x)^{\frac{1}{2}}$ to $-(a)^{\frac{1}{2}}$ and from $(a-x)^{\frac{1}{2}}$ to $(a)^{\frac{1}{2}}$. As these areas are the same, this is modified to twice the integrated area from $(a-x)^{\frac{1}{2}}$ to $(a)^{\frac{1}{2}}$



$$\therefore\ k_{APP}t = \frac{1}{(a - \frac{b}{2})^{\frac{1}{2}}}\left[\ln\frac{u + (a - \frac{b}{2})^{\frac{1}{2}}}{u - (a - \frac{b}{2})^{\frac{1}{2}}}\right]_{(a)^{\frac{1}{2}}}^{(a-x)^{\frac{1}{2}}}$$

$$\therefore\ k_{APP}t = \frac{1}{(a - \frac{b}{2})^{\frac{1}{2}}}\ \ln\left(\frac{(a-x)^{\frac{1}{2}} + (a - \frac{b}{2})^{\frac{1}{2}}}{(a-x)^{\frac{1}{2}} - (a - \frac{b}{2})^{\frac{1}{2}}} \times \frac{(a)^{\frac{1}{2}} - (a - \frac{b}{2})^{\frac{1}{2}}}{(a)^{\frac{1}{2}} + (a - \frac{b}{2})^{\frac{1}{2}}}\right.$$

$$= \frac{1}{(a - \frac{b}{2})^{\frac{1}{2}}}\left\{\ln\left(\frac{(a-x)^{\frac{1}{2}} + (a - \frac{b}{2})^{\frac{1}{2}}}{(a-x)^{\frac{1}{2}} - (a - \frac{b}{2})^{\frac{1}{2}}}\right) - \ln\left(\frac{(a)^{\frac{1}{2}} + (a - \frac{b}{2})^{\frac{1}{2}}}{(a)^{\frac{1}{2}} - (a - \frac{b}{2})^{\frac{1}{2}}}\right)\right\}$$

$$\text{or } k_{APP}t = \frac{1}{(a - \frac{b}{2})^{\frac{1}{2}}}\left[\ln\left\{\frac{1+\left(\frac{a - \frac{b}{2}}{a - x}\right)^{\frac{1}{2}}}{1-\left(\frac{a - \frac{b}{2}}{a - x}\right)^{\frac{1}{2}}}\right\} - \ln\left\{\frac{1+\left(\frac{a - \frac{b}{2}}{a}\right)^{\frac{1}{2}}}{1-\left(\frac{a - \frac{b}{2}}{a}\right)^{\frac{1}{2}}}\right\}\right]$$

When $a = b$

$$-k_{APP}t = \int\frac{du}{u^2}$$

$$= 2\left[\frac{1}{u}\right]_{(a-x)^{\frac{1}{2}}}^{(a)^{\frac{1}{2}}}$$

$$= 2\left(\frac{1}{(a-x)^{\frac{1}{2}}} - \frac{1}{(a)^{\frac{1}{2}}}\right)$$

or

$$k_{APP}t = 2\left(\frac{1}{(a)^{\frac{1}{2}}} - \frac{1}{(a-x)^{\frac{1}{2}}}\right) \qquad (3)$$

when $a < \frac{b}{2}$

$$k_{APP}t = \int\frac{du}{u^2 + (\frac{b}{2} - a)}$$

This integral is a standard form of the integral

$$\int \frac{dx}{x^2 + a^2} = \frac{1}{a} \arctan \frac{x}{a}$$

∴ Converting

$$k_{APP}t = \frac{1}{(\frac{b}{2} - a)^{\frac{1}{2}}} \left[\arctan \frac{x}{(\frac{b}{2} - a)^{\frac{1}{2}}}\right]_{(a-x)^{\frac{1}{2}}}^{(a)^{\frac{1}{2}}}$$

$$\therefore \quad k_{APP}t = \frac{2}{(\frac{b}{2} - a)^{\frac{1}{2}}} \left[\arctan \left(\frac{a}{\frac{b}{2} - a}\right)^{\frac{1}{2}} - \arctan\left(\frac{a - x}{\frac{b}{2} - a}\right)^{\frac{1}{2}}\right] \qquad (4)$$

APPENDIX II - DEVELOPMENT OF INTEGRATED RATE EQUATION FOR COMPLEXED SYSTEM

We assume the reaction to be (in brief)

$$AlEt_3.D.P.E. + 2,1\text{-octene} \xrightarrow{k_n} \text{products}$$

$\therefore$ Rate = k_n[complex][1-octene]

However the experimental conditions are such that $[\text{complex}]_{init} \simeq C_{Al}$, the total triethylaluminium concentration expressed as monomer.

$\therefore$ Rate = $k_n C_{Al}$[1-octene]

If the initial concentrations of alkyl and olefin are a and b and x is the kinetic product formed after time t, then the reduced concentration of reactants are (a-x) and (b-2x).

Thus the differential form of the rate equation is

$$\frac{dx}{dt} = k_n(a-x)(b-2x).$$

Integrating with respect to x

$$\int k_n dt = \int \frac{dx}{(a-x)(b-2x)}$$

and integrating by partial fractions one obtains two solutions for the integrated rate equation, depending on which reactant is in stoichiometric excess.

When $a > \frac{b}{2}$

$$k_n t = \frac{2.303}{(2a-b)} \log \frac{b(a-x)}{a(b-2x)} .$$

When $a < \frac{b}{2}$

$$k_n t = \frac{2.303}{(b-2a)} \log \frac{a(b-2x)}{b(a-x)}$$

APPENDIX III - CONFIDENCE LIMITS AS AN ESTIMATE OF RESULT RELIABILITY

Before commencing a discussion of the practical application of confidence limits as a statistical tool, one must initially define the basis of result significance, which in turn, leads to a definition of confidence limits. The application of these limits to type examples can then be illustrated.

If one considers two separate populations, both derived from the same measurement source, the purpose of significance tests is to separate chance differences from those which could not easily occur by chance.

Statistical significance infers the difference which could not easily have occurred by chance.

Initially, a hypothesis is made that no difference occurs, and then the probability that an observed difference could be equalled or exceeded by chance if the hypothesis is true.

Once the level of significance is decided, the results can then be rejected or accepted. The accepted divisions of probability are (probability range $0 \rightarrow 1$):

$p \geq 0.1$ - not a significant difference - hypothesis accepted

$0.1 > p > 0.05$ - possibly significant - hypothesis suspect

$p < 0.05$ - a significant difference - hypothesis rejected

It is convenient to define degrees of freedom here, a term used to express the reliability of any calculated statistic. Each parameter from a group of data consumes one degree of freedom. Thus for n observations, one has n degrees of freedom. If a total or mean value is calculated, then a degree of freedom is lost and any variance is based on (n-1) degrees of freedom. In regression analysis, another degree of freedom would be lost in calculating the slope; hence any variance of slope utilising mean values will be subject to (n-2) degrees of freedom.

Development of Confidence Limits

The development will first be confined to populations of y at measured x. Once confidence limits are defined in these terms, the formula can then be applied to regression analysis.

Let us assume a population y_i with a mean value $\bar{y}_i$ and a standard deviation S_i.

$$\text{S.D. defined as } \sqrt{\sum_{i=1}^{n} \frac{(y_i - \bar{y})^2}{n}}$$

Assume also a similarly measured population y_j with mean $\bar{y}_j$.

Our sample y_k with mean $\bar{y}_k$ is drawn from the y_j measured population. Summarising, we have two populations; known y_j is coincident with known y_i.

The alternative hypothesis to test for any difference, and if so, in a particular direction. Consider a real increase where

original hypothesis $H_0 \equiv y_j = y_i$

alternative hypothesis $H_1 \equiv y_j > y_i$

where the population mean $\bar{y}_j$ is determined by the sample mean $\bar{y}_k$.

Now because of the experimental variance, $\bar{y}_k$ will not always be equal to $\bar{y}_i$. The original hypothesis implies that indefinite sampling (a large amount of data) must occur before these two values approach equality and therefore $\bar{y}_j = \bar{y}_i$.

To determine if the observed value is consistent with the hypothesis, the probability that a sample with a mean as great as $\bar{y}_k$ could have been drawn from a population with a mean y_i, is calculated.

Any assumed normal distribution of y's can be transformed to the standard form by a suitable change in unit.

$$\therefore \quad y_j = \frac{\bar{y}_k - \bar{y}_i}{(\text{standard error in } y_k)}$$

The probability of exceeding y_i is found from standard normal tables, i.e. the probability of exceeding $(\bar{y}_k - \bar{y}_i)$ and hence the probability of the original hypothesis being true.

Since y_k and its error are known, one can calculate the limits within which the true value of y_j is expected to be. These limits are termed Confidence Limits.

Assuming a risk, a, that the true value of $\bar{y}_j$ is outside these limits, and this risk is divided into $\frac{1}{2}$ a above the upper limit and $\frac{1}{2}$ a below the lower limit. Thus we allow $\bar{y}_{j(\frac{a}{2})}$ to be the value of $\bar{y}_j$ which is exceeded with probability $\frac{a}{2}$.

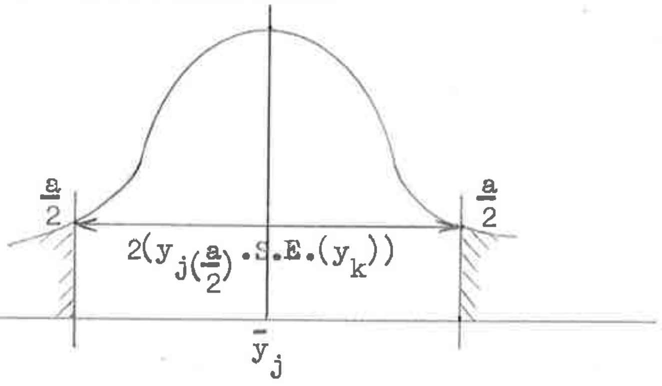
If a sample is drawn from a normal distribution with a mean $\bar{y}_j$, then the probability is $^a{}_2$, that the sample mean will exceed $\bar{y}_{k_1}$, where y_{k_1} is given by

$$y_{j(\frac{a}{2})} = \frac{\bar{y}_{k_1} - \bar{y}_j}{S.E.\ (y_k)}$$

or $\quad \bar{y}_{k_1} = \bar{y}_j + \bar{y}_{j(\frac{a}{2})} \cdot S.E.(y_k)$

Similarly $\bar{y}_{k_2} = \bar{y}_j - y_{j(\frac{a}{2})} \cdot S.E.(y_k)$

Shown on the distribution curve



The probability that $\bar{y}_k$ lies outside the limits is

$$\bar{y}_j \pm y_{j(\frac{a}{2})} \cdot S.E.\ y_k$$

where S.E. $y_k = \sigma_d/n$.

Conversely, if y_k is known and used to estimate y_j, then there is a probability that y_j will be outside the limits

$$\bar{y}_k \pm y_{j(\frac{a}{2})} \cdot \text{S.E.}\ y_k \quad .$$

These limits are the 100 (1-p) % confidence limits.

Confidence Limits in Regression Analysis

Our experimental results (rate constants, Arrhenius parameters etc.) rely on slopes of graphs of y population data at measured x values. It is important to know the significance of such results, a significance readily illustrated by confidence limits.

Initially, we are interested in the relationship between $\bar{y}$ and x, especially from the mathematical model and tested with the data available. The slope b (the regression coefficient) is usually determined by the method of Least Squares. However, the least squares method by itself gives no indication of the data reliability.

Now assuming a normal distribution of measured y values, and without prior knowledge of the regression equation, a sample of n values is drawn from the y population. The best estimate of any further y value drawn at random is $\bar{y}$. The error in this predicted y value is the sum of

$$\text{squares} = \Sigma(y_i - \bar{y})^2.$$

Briefly, once the regression equation of y or x is known and having measured x_i, the best estimate of any y_i is

$$\hat{y}_i = \bar{y}_i + b(x_i - \bar{x}).$$

The error in any y_i is given a minimum value equal to

$$\text{(sum of squares) } U = \Sigma(y_i - \bar{y})^2 - \frac{[\Sigma(x_i - \bar{x})(y_i - \bar{y})]^2}{\Sigma(x_i - \bar{x})^2}.$$

The difference between the sum of squares above represents L, the sum of squares accounted for by the regression

$$L = \frac{[\Sigma(x_i - \bar{x})(y_i - \bar{y})]^2}{\Sigma(x_i - \bar{x})^2}.$$

The parameter evolved by the linear regression equation will be subject to variance in the measured y population. This error variance will be given by the mean square about the regression line, S_o^2.

Now the regression coefficient b can be shown to be

$$b = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\Sigma(x_i - \bar{x})^2}.$$

Rewriting this equation and knowing

(a) $\sum_{i=1}^{n} (x_i - \bar{x}) = 0$,

(b) S^2 = experimental error variance in the observed y value, one can then show

$$\text{the variance in b} = \frac{S_o^2}{\sum_{i=1}^{n}(x_i - \bar{x})^2}$$

and the standard error in b

$$= \frac{S_o}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2}}$$

The 100 (1 - p) % confidence limits in b will be

$$b \pm t\,\tfrac{a}{2}(n - 2).\ \frac{S_o}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2}}$$

The line of best fit between estimated y_i for measured x_i is

$$\hat{y}_i = \bar{y}_i + b(x_i - \bar{x}).$$

The variance in this line is

$$= \text{variance } (\bar{y}_i) + \text{variance } (b).(x_i - \bar{x})^2$$

$$= \frac{S_o^2}{n} + (x_i - \bar{x})^2 \cdot \frac{S_o^2}{\sum_{i=1}^{n}(x_i - \bar{x})^2}$$

$$\therefore \text{ standard error in } \hat{y}_i = S_o\left(\frac{1}{n} + \frac{(x_i - \bar{x})^2}{\sum_{i=1}^{n}(x_i - \bar{x})^2}\right)^{\frac{1}{2}}$$

The standard error will be a minimum when $x_i = \bar{x}$ and increases as $(x_i - \bar{x})^2$ increases.

The confidence limits on y will be

$$\bar{y}_{C.L.} = \bar{y}_i \pm t\frac{a}{2}(n - 2).S_o\left(\frac{1}{n} + \frac{(x_i - \bar{x})^2}{\sum\limits_{i=1}^{n} (x_i - \bar{x})^2}\right)^{\frac{1}{2}}$$

Experimentally, the following steps were made:

A calculation of the least squares slope b; the drawing of the line of best fit, substituting known x values into the equation for the line of best fit; the calculation of the standard deviation between y fitted (i.e. y least squares fitted) and y measured values; the calculation and drawing of the confidence limit hyperbolas about the least squares line; finally a plot of the measured y data about the least squares line and within the confidence limit curves.

References used in the above discussion were:

"The Handling of Chemical Data"
by P.D. Lark, B.R. Craven and R.C.L. Bosworth - Pergamon
"The Analysis of Straight Line Data"
by F.S. Acton - Wiley Publication in Statistics
"Mathematics and Statistics for Chemists"
by C.J. Brookes, I.G. Betteley and S.M. Loxston - Wiley