

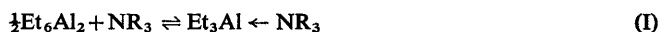
# Kinetics and Mechanism of the Reaction between Phenylacetylene and Triethylaluminium + Tertiary Amine Complexes in Hydrocarbon Solution

BY PETER E. M. ALLEN\* AND ROGER M. LOUGH†

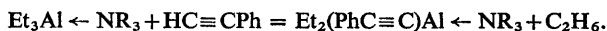
Department of Physical and Inorganic Chemistry, University of Adelaide,  
Box 498, G.P.O., Adelaide, South Australia 5001

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The reaction of phenylacetylene with triethylaluminium in solutions containing tertiary amines has been investigated using n.m.r. and kinetic methods over the temperatures 333–378 K. A binary 1 : 1 complex between triethylaluminium and the amine



reacts according to the stoichiometric equation



The apparent order of reaction of this complex, in hydrocarbon solution, is non-integral. A phenomenological rate equation :

$$v_0 = (k_1[\text{Et}_3\text{Al} \leftarrow \text{NR}_3]_0 + k_2[\text{Et}_3\text{Al} \leftarrow \text{NR}_3]_0^2)[\text{C}_6\text{H}_6]_0$$

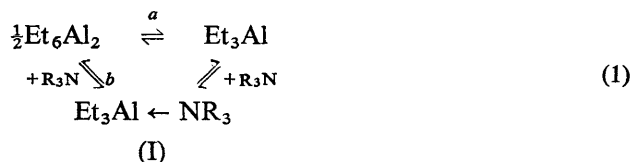
(where  $\text{R}_3\text{N} \equiv \text{Et}_3\text{N}$ ,  $\text{n-Bu}_3\text{N}$  or  $\text{Et}_2\text{NPh}$ ) is established.

Values of  $\log_{10}(k_1/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$  are  $5.0 - (62\,000 \text{ J mol}^{-1}/RT)$  for the triethylamine complex and  $11.1 - (102\,000 \text{ J mol}^{-1}/RT)$  for the tri-*n*-butylamine complex. The activation parameters are compared with those for proton-transfer reactions in non-aqueous solutions. The third order term is believed to derive from a complex parallel reaction involving a ternary complex.  $\log_{10}(k_2/\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1})$  is  $10.9 - (97\,000/RT)$  (for  $\text{Et}_3\text{N}$ ) and  $7.1 - (71\,000/RT)$  (for  $\text{n-Bu}_3\text{N}$ ).

$\text{Et}_3\text{Al}$ -pyridine and  $\text{Et}_3\text{Al}$ -tetrahydrofuran complexes did not react with phenylacetylene under these conditions.

N.m.r. spectrometry and ebulliometry were used to investigate whether any complexes other than (I) were present in the reaction mixture in significant concentrations. An ebulliometer was constructed which was capable of operating in an inert atmosphere of nitrogen at pressures 0.5–1.5 bar. The vapour pressure of  $\text{Et}_3\text{Al} \leftarrow \text{NEt}_3$  was measured over the range 294–410 K.

Triethylaluminium forms binary 1 : 1 complexes with electron donors. In the presence of tertiary amines the concentrations of the various forms of the reagent are governed by the equilibria

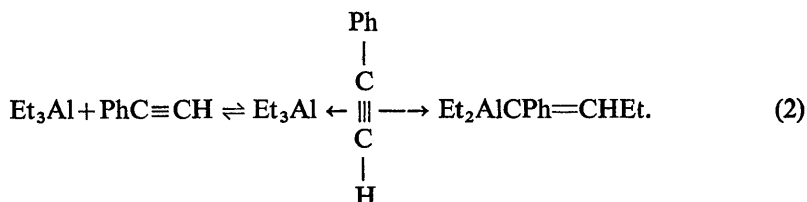


The complex (I) does not react with alkenes.<sup>1, 2</sup> The addition of  $\text{Et}_3\text{Al}$  to alkenes in hydrocarbon solution involves the formation of a  $\pi$ -complex between the alkene and a vacant fourth coordination site on the metal.<sup>3</sup> When a highly retarded reaction is observed in the presence of a very weakly basic solvent, such as diphenylether, that

† present address : Department of Defence, Box 2151, G.P.O., Adelaide, South Australia 5001.

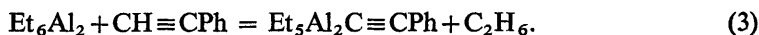
reaction proceeds exclusively from a small equilibrium concentration of unassociated  $\text{Et}_3\text{Al}$ .<sup>1</sup> In the presence of more basic ethers and amines no reaction is observed. The reaction of triethylaluminium in the absence of basic compounds also involves the unassociated  $\text{Et}_3\text{Al}$ , but only the equilibrium of eqn [1(a)] is involved.

The addition of alkynes to triethylaluminium is also a reaction of unassociated  $\text{Et}_3\text{Al}$  exclusively, and proceeds through an intermediate  $\pi$ -complex which can, in this case, be detected by n.m.r. spectrometry.<sup>4</sup>



Reaction (2) is suppressed in the presence of a stoichiometric excess ( $\text{N}/\text{Al} \geq 1$ ) of amine for a similar reason: (1) is unreactive. Ethers also inhibit reaction (2).

Phenylacetylene is considerably more acidic than the alkenes, so there is an important difference in its reactions with triethylaluminium: the addition reaction (2) is accompanied by evolution of ethane from a reaction of stoichiometry



In our previous paper,<sup>4</sup> we have shown that in hydrocarbon solution this is a second order reaction of  $\text{Et}_6\text{Al}_2$ , the predominating species of equilibrium 1(a), with phenylacetylene. The evolution of ethane is suppressed by the presence of ethers, but only reduced by tertiary amines. In the present work we investigated the kinetics and mechanism of this reaction in the presence of tertiary amines, under conditions where reaction (2) is completely inhibited.

## EXPERIMENTAL

The rate of reaction was estimated from the rate of evolution of ethane measured by an automatically recording manometer as in our previous work.<sup>4</sup> The reaction vessel and a connected ballast volume of 300 cm<sup>3</sup> were enclosed in the thermostat bath. The amount of ethane evolved was estimated from the increase in pressure in the system. A correction was made for a small volume of gas in the manometer arm which was at ambient temperature. Decahydronaphthalene was used as solvent. Neither this nor the  $\text{Et}_3\text{Al} \leftarrow \text{NR}_3$  complexes were sufficiently volatile for their loss to the vapour phase to be significant at the temperature used.  $\text{Et}_3\text{Al} \leftarrow \text{Nn-Bu}_3$  was involatile up to 410 K. The vapour pressure of  $\text{Et}_3\text{Al} \rightarrow \text{NEt}_3$  was measured between 294 and 410 K and found to fit an Antoine equation

$$\log_{10}(p/\text{Torr}) = 5.50 - 1740 \text{ K}/T. \quad (4)$$

At higher temperatures it was necessary to make a small correction to allow for the decrease in concentration of phenylacetylene arising from its vapour pressure. Details of the design of the manometer and recording circuit are given elsewhere.<sup>6</sup>

The nature of the complexes present in the reaction mixture was investigated by proton n.m.r. spectrometry on a Varian DA-IL 60 MHz spectrometer and by ebulliometry. An ebulliometer was constructed which consisted of two interconnecting vessels, one for solvent, one for solution. Each vessel was supplied with a Cottrell pump. Steady boiling was ensured by the presence of powdered glass and a tungsten rod sealed through the base of the vessel, which was heated during the experiment. The Cottrell pumps discharged on to matched thermistors which were connected into a resistance bridge circuit incorporating a Leeds and Northrup d.c. Null-detector. Measurements were made in a closed system. This departure from normal practice was dictated by the air-sensitivity of the solutes.

Advantage was taken to vary the pressure over a range, 0.5–1.5 bar, thereby obtaining measurements of apparent molecular weights at different temperatures at each fixed concentration. The closed system was completed by connecting the ebulliometers to a 20 dm<sup>3</sup> ballast vessel which effectively damped out random pressure fluctuation. The system was evacuated and then filled with dry nitrogen three times before use. Solvent was injected through a septum cap. The solute was introduced through breakseal capsules. The measurements were corrected for the hold-up of solvent vapour. A correction was made to allow for the volatility of  $\text{Et}_3\text{Al} \leftarrow \text{NEt}_3$  at the higher temperatures only.

Amines of AnalaR grade (Pfaltz and Bauer) were dried over calcium hydride for 24 h and distilled on a high-vacuum apparatus into breakseal capsules. Decahydronaphthalene (AnalaR grade Decalin, Unilab) was similarly treated, but decanted from the calcium hydride before distilling in order to avoid frothing. Other reagents were treated as described previously.<sup>1-4</sup>

Amine, pyridine and tetrahydrofuran 1 : 1 complexes of triethylaluminium were prepared using a slight excess of donor, and dispensed into breakseal capsules.

## RESULTS AND DISCUSSION

### EVIDENCE CONCERNING THE COMPLEX $\text{Et}_3\text{Al} \leftarrow \text{NR}_3(\text{I})$

The chemical shifts of the methylene protons of triethylaluminium and triethylamine are shown in fig. 1 as a function of N/Al mole ratio. The shifts are taken from the midpoint of the quartet and are referred to an internal reference. Our preferred method of using the internal methyl-methylene shift<sup>4</sup> was inapplicable because of the overlap of Al-Et and N-Et methyl protons.

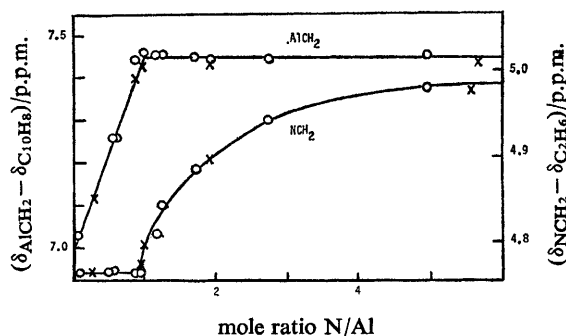
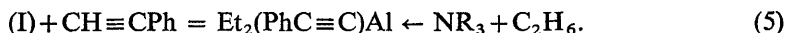


FIG. 1.—Chemical shifts,  $\delta_{\text{CH}_2}$ , of the methylene protons of the ethyl groups of triethylaluminium (left hand scale) and triethylamine (right hand scale) in binary mixtures as a function of mole ratio N/Al at 378 K (○) and 393 K (×).

The sharp discontinuity at unit mole ratio confirms not only the stoichiometry but the stability of complex (I). The equilibria of eqn (1) are such that, once triethylamine is in stoichiometric equivalence, complex (I) is in overwhelming preponderance over uncomplexed organoaluminium compounds. It is assumed, therefore, that the reaction observed under these conditions is a reaction of (I) according to the stoichiometry



On reducing the temperature (at N/Al = 2) the N—CH<sub>2</sub> resonance coalesced to a broad singlet at 302 K. Below 302 K, two separate quartets corresponding to free and complexed  $\text{Et}_3\text{N}$  appeared. At ambient temperature,  $\text{Et}_3\text{N}$  groups in complex (I) must be exchanging rapidly with free  $\text{Et}_3\text{N}$  molecules. Et—Al groups also exchange rapidly with each other at these temperatures.

The  $\text{CH}_2\text{-Al}$  shift in mixtures of triethylaluminium and tri-*n*-butylamine depended on the mole ratio in exactly the same way, confirming the presence of a strong binary 1 : 1 complex.

#### EVIDENCE CONCERNING OTHER COMPLEXES BETWEEN $\text{Et}_3\text{Al}$ AND $\text{NR}_3$

The spectrum of a 1 : 2  $\text{Et}_3\text{Al} : \text{NEt}_3$  mixture was scanned, at maximum power and 343 K, 100 Hz downfield of the  $\text{N-CH}_2$  quartet. Additional quartets centred at approximately 0.6 and 1.1 p.p.m. downfield from the main quartet could be discerned. Their integrated intensities did not amount to more than 1 % of the total  $\text{N-CH}_2$  spectrum. At this temperature, amine groups must be present in two different magnetic environments other than complex (I) and free  $\text{NEt}_3$ . Furthermore, these additional amine groups are not exchanging rapidly with (I) or free  $\text{NEt}_3$ .

#### EVIDENCE CONCERNING ASSOCIATED COMPLEXES

Kinetic data, described below, could be interpreted on the assumption that associated forms of complex (I) were present. The question arises as to whether such species are responsible for the two weak  $\text{N-CH}_2$  resonances. The disappearance of these peaks at low temperatures all but negates their assignment to associated species, though it is possible that the lines might be lost through line-broadening rather than disappearance of the species. The absence of any change in the shifts or relative intensities of the  $^1\text{H}$  n.m.r. spectrum when the mixtures were diluted by a factor of 10 with cyclohexane, while maintaining the  $\text{N/Al}$  mole ratio, rules out the possibility that any of the species being observed were involved in association equilibria.

Extensive ebullioscopic measurements were made on solutions of Complex (I) (both  $\text{Et}_3\text{N}$  and  $n\text{-Bu}_3\text{N}$  complexes) in cyclohexane and *n*-heptane over the temperature range 350–370 K. Both complexes were monomeric in both solvents over this temperature range.

Neither n.m.r. nor ebullioscopic experiments provide any evidence that associated forms of complex (I) are present in significant proportions.

#### EVIDENCE CONCERNING TERNARY $\text{Et}_3\text{Al} : \text{NR}_3 : \text{C}_6\text{H}_6$ COMPLEXES

The rate eqn (8) can be interpreted on the assumption that a ternary  $\text{Et}_3\text{Al} : \text{NR}_3 : \text{CH}\equiv\text{CPh}$  complex was present. We sought evidence for this in the n.m.r. spectra of reaction mixtures. The chemical shifts of the phenylacetylene protons were measured using the cyclohexane resonance as reference. The experiments were carried out in cyclohexane solution at a constant concentration of phenylacetylene in the absence and presence of (I). In the presence of a molar excess of (I), the phenyl-acetylene resonances were shifted downfield, but the shifts were small: 0.06 p.p.m. for the acetylenic proton resonance and 0.03 p.p.m. for the aromatic resonances.

While the observed shift indicates some interaction between phenylacetylene and  $\text{Et}_3\text{Al} \leftarrow \text{NEt}_3$ , it is small compared with the interaction between phenylacetylene and triethylaluminium in the absence of complexing solvents, when shifts of the order of 0.13 p.p.m. are observed.<sup>4</sup> The value of the equilibrium constant for the formation of a ternary complex consistent with the observed shifts could not exceed  $0.06 \text{ dm}^6 \text{ mol}^{-2}$ .

#### APPARENT ORDERS OF REACTION

The kinetic measurements were carried out in decahydronaphthalene, since cyclohexane is too volatile to use in the manometric experiments. Both solvents

have similar solubility parameters, 36.8 and 36.7  $\text{J cm}^{-3}$ , and similar non-polar characters. It is assumed that results obtained in the two solvents are comparable.

The rate of reaction,  $v$ , was determined from the rate of evolution of ethane as in previous studies. The dependence of the initial rate of reaction  $v_0$  ( $= \{d[\text{C}_2\text{H}_6]/dt\}_{t=0}$ ) on the initial concentration of triethylaluminium, in all forms,  $a$ , and of phenylacetylene,  $b$ , was determined, where

$$a = \frac{1}{2}[\text{Et}_6\text{Al}_2]_0 + [\text{Et}_3\text{Al}]_0 + [\text{I}]_0 \quad (6)$$

However, all kinetic experiments were carried out under conditions where  $\text{N/Al} \geq 1$  where the equilibria of eqn (1) are such that

$$a = [\text{I}]_0 \quad (7)$$

Experiments at constant  $a$  and  $b$  showed that the rate of reaction was independent of the concentration of trialkylamine once  $\text{N/Al} \geq 1$ . In experiments at constant  $a$ , the reaction was found to be first order in the concentration of phenylacetylene,  $b$ . This was established at 343 K for both triethylamine and tri-*n*-butylamine complexes. However at this temperature, and a constant concentration of phenylacetylene,  $b = 2.0 \text{ mol dm}^{-3}$ , the order with respect to  $[\text{I}]_0$  was non-integral.

#### THE RATE EQUATION FOR REACTION OF $\text{Et}_3\text{Al} \leftarrow \text{NR}_3$ COMPLEXES

This is the first case in which an apparent order of reaction with respect to triethylaluminium greater than unity has been encountered. It could be attributed to the participation in the reaction of an associated form of the predominant form of the reagent (in this case I). As reported above, there is no evidence of the presence of the dimer of (I)  $(\text{Et}_3\text{Al} \leftarrow \text{NR}_3)_2$ . There is evidence for the presence of a weak ternary complex between  $\text{Et}_3\text{Al}$ ,  $\text{NR}_3$  and  $\text{C}_8\text{H}_6$  which could account for the apparent order of reaction if its stoichiometry was 2 : 2 : 1 or 2 : 1 : 1.

The equilibrium constant of this complex cannot be calculated directly with adequate precision. We attempted to calculate a value of the equilibrium constant by numerical analysis of the kinetic data, assuming that the complex was the sole reactive species. The method was applied successfully to deal with a non-integral order of reaction encountered in the reaction with styrene.<sup>3</sup> In the present case, the rate was not linearly dependent on the calculated concentration of the complex. It was concluded that the exclusive reaction of a ternary complex is not a tenable hypothesis.

A parallel-reaction-path mechanism was tested using the rate equation

$$v_0 = d[\text{C}_2\text{H}_6]/dt = k_1ab + k_2a^2b \quad (8)$$

where  $a = [\text{Et}_3\text{Al} \leftarrow \text{NR}_3]_0$  (under experimental conditions) and  $b$  is the initial concentration of phenylacetylene.

Eqn (8) was tested by regression analysis of  $v_0/ab$  against  $a$ . Good linear fits were obtained for the reaction of three amine complexes (triethylamine, tri-*n*-butylamine and *N,N'*-diethylaniline) in decahydronaphthalene. The slopes,  $k_1$ , and intercepts,  $k_2$ , are shown in table 1. The standard errors are confined to the last digit cited. No reaction could be detected with the pyridine and tetrahydrofuran complexes.

#### ARRHENIUS PARAMETERS

Fig. 2 shows the Arrhenius plot of  $k_1$  for the triethylamine and tri-*n*-butylamine complexes.  $A$ -factors and apparent energies of activation are given in table 2. The Arrhenius plots of the rate coefficient for the third-order term,  $k_2$ , were also linear. The parameters are shown in table 2.

TABLE 1.—RATE COEFFICIENTS DETERMINED FOR EQN (8) BY REGRESSION ANALYSIS  
(THE STANDARD ERROR LYING IN THE LAST DIGIT CITED)

$a/\text{mol dm}^{-3}$	$pK_a^*$	$T/\text{K}$	no. runs	$k_1/\text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$	$k_2/\text{dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$
$[\text{Et}_3\text{Al} \leftarrow \text{NEt}_3]_0$ = 0.1-1.5	10.8	333	9	0.001 02	0.027 8
		343	9	0.001 99	0.011 8
		353	9	0.004 77	0.020 4
		363	9	0.005 28	0.066 0
		373	9	0.012 5	0.124
$[\text{Et}_3\text{Al} \leftarrow \text{Nn-Bu}_3]_0$ = 0.1-1.0	9.9	343	9	0.002 93	0.012 1
		353	9	0.004 50	0.031 9
		363	9	0.016 2	0.062 8
		373	9	0.046 2	0.103 5
		378	9	0.064 2	0.120 7
$[\text{Et}_3\text{Al} \leftarrow \text{NPhEt}_2]_0$ = 0.1-1.0	6.6	353	6	0.002 1	0.017 5
$\text{Et}_3\text{Al} \leftarrow \text{N} \begin{array}{c} \text{[CH]}_5 \\ \text{[ ]} \end{array}$	5.2	353	2	no reaction	
$\text{Et}_3\text{Al} \leftarrow \text{O} \begin{array}{c} \text{[CH}_2\text{]}_4 \\ \text{[ ]} \end{array}$		353	2	no reaction	

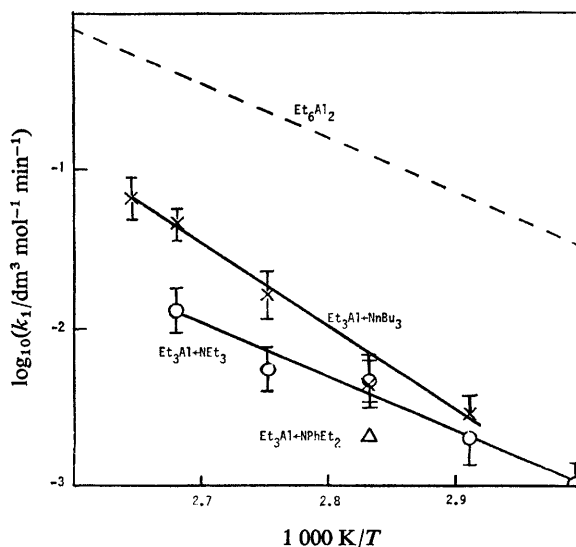
\* of donor in aqueous solution at 298 K.<sup>7</sup>FIG. 2.—Arrhenius plots of  $k_1$  [reaction (9)]. The error bars indicate standard errors on the intercept of eqn (2). The broken line is the Arrhenius plot, extrapolated from lower temperatures, for the bimolecular reaction of dimeric, uncomplexed  $\text{Et}_6\text{Al}_2$  [reaction (3)].



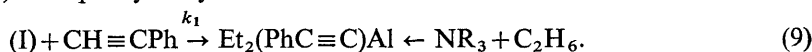
TABLE 2.—ARRHENIUS PARAMETERS FOR THE BIMOLECULAR REACTIONS (3) AND (9) ( $A_1$ ,  $E_1$ ) AND APPARENT ARRHENIUS PARAMETERS FOR THE COMPLEX REACTION RESPONSIBLE FOR THE THIRD ORDER TERM IN THE RATE EQN (8) ( $A_2$ ,  $E_2$ )

	$E_1 \pm \text{s.e.}(E_1) / \text{kJ mol}^{-1}$	$\log_{10} A_1 \pm \text{s.e.}(A_1) / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$E_2 \pm \text{s.e.}(E_2) / \text{kJ mol}^{-1}$	$\log_{10} A_2 \pm \text{s.e.}(A_2) / \text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$
Et <sub>3</sub> Al $\leftarrow$ NEt <sub>3</sub>	62 $\pm$ 7	5.0 $\pm$ 1.0	97 $\pm$ 7	10.9 $\pm$ 1.1
Et <sub>3</sub> Al $\leftarrow$ Nn-Bu <sub>3</sub>	102 $\pm$ 10	11.1 $\pm$ 1.4	71 $\pm$ 6	7.1 $\pm$ 0.9
Et <sub>6</sub> Al <sub>2</sub> [ref. (4)]	64 $\pm$ 3	6.8 $\pm$ 1.5	—	—

### CONCLUSIONS AND DISCUSSION

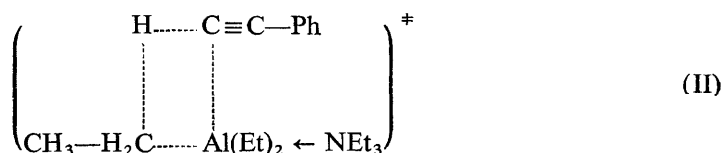
At the temperatures investigated we found that complex (I) was less reactive than Et<sub>6</sub>Al<sub>2</sub> (table 1). The reactivity of complex (I) depended on its constituent donor component; the rate of reaction (5) increased in the order of increasing basicity of the donor (table 1). The effect is probably associated with an increase in the polarity of the Al-C bonds with increase in the basicity of the donor.<sup>2</sup>

Reaction (3) is a second-order reaction.<sup>4</sup> Its Arrhenius parameters (table 2) are compatible with a simple bimolecular reaction between Et<sub>6</sub>Al<sub>2</sub> and phenylacetylene. Reaction (5) is not simple, consisting of parallel second and third order mechanisms according to eqn (8). The second-order term probably arises from the bimolecular reaction of (I) with phenylacetylene



However, if this is the case, the difference in the Arrhenius  $A$ -factors for the reactions of Et<sub>3</sub>Al  $\leftarrow$  NEt<sub>3</sub> and Et<sub>3</sub>Al  $\leftarrow$  Nn-Bu<sub>3</sub> (table 2) implies that there is significant difference in reaction path.

The low value of  $A_1$  found for reaction of Et<sub>3</sub>Al  $\leftarrow$  NEt<sub>3</sub> is in the same range as those found for the addition of Et<sub>3</sub>Al to alkenes which are not sterically encumbered. In the present case, the low value is not subject to external uncertainties, such as the value chosen for  $\Delta S^\circ \{\text{Et}_6\text{Al}_2 \rightleftharpoons 2\text{Et}_3\text{Al}\}$  on which the  $A$ -factors for the addition reactions depend.<sup>3</sup> We conclude that the  $A_1$  for the reaction of Et<sub>3</sub>Al  $\leftarrow$  NEt<sub>3</sub> refers to a bimolecular reaction proceeding through a tight four centre complex (II)

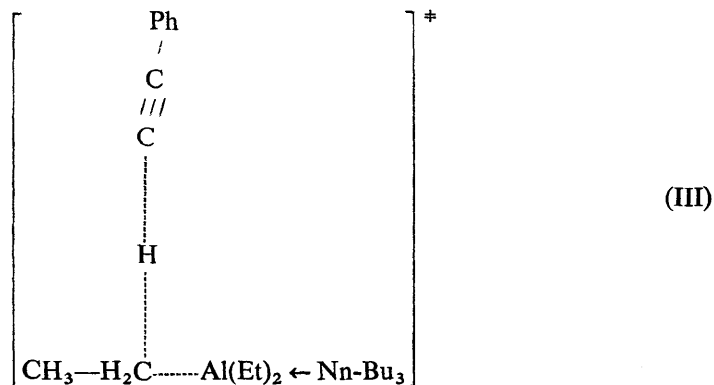


The value of  $10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  is nevertheless very low for a bimolecular  $A$ -factor. However, while methods for predicting entropies of activation for gas reactions have been developed<sup>8</sup> to the level of precision where they can be used with confidence to cull dubious experimental values,<sup>9</sup> this is not the case for reactions in liquid solution. There is a much greater element of doubt about the magnitude of  $A$  for these reactions, which has been discussed elsewhere.<sup>10</sup>

It seems likely, from general reactivity considerations, that when the acidic hydrogen of the phenylacetylene migrates to the methylene carbon of an ethyl group, it does so as a proton. We, therefore, sought comparable data in the field of proton exchange reactions in non-aqueous media. Entropies of activation commensurate with our value of  $A_1$  have been reported by Caldin and Mateo<sup>11</sup> for proton exchange from 4-nitrophenyl-nitromethane to tertiary amines in toluene.

The high value of  $A_1$  for the reaction of Et<sub>3</sub>Al  $\leftarrow$  Nn-Bu<sub>3</sub> is also probably a simple bimolecular reaction. If it is, the transition state is much looser. We suggest that

the reaction path involves a direct, end-on attack of the acidic hydrogen of the acetylene on an ethyl group, without any assistance in the transition state from interaction between the methine carbon and aluminium (III). The change in reaction path is



likely to be dictated by steric effects, the clash of the acetylene phenyl and the bulky Nn-Bu<sub>3</sub> groups preventing the formation of a tight four-centre transition state (II) involving any of the three Al-C bonds.

*A*-factors in the 10<sup>10</sup>-10<sup>11</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> range have been reported for proton exchange from tetrabromophenylphthalen to tertiary amines.<sup>12</sup> It is possible that these are diffusion-controlled reactions (the energies of activation are very low), but, even if this is so, the *A*-factor for the chemical step must lie at the top of the bimolecular range because, if it did not, the overall reaction would not be diffusion-controlled.

The lack of positive evidence for associated forms of (I), and the unlikelihood of a direct termolecular reaction, leaves two possible mechanisms for the third-order step: bimolecular reaction between a weak Et<sub>3</sub>Al:NR<sub>3</sub>:C<sub>2</sub>HPh complex and (I) or spontaneous reaction of a weak (Et<sub>2</sub>Al)<sub>2</sub>:(NR<sub>3</sub>)<sub>2</sub>:C<sub>2</sub>HPh complex. Both ternary complexes must involve five-coordinate aluminium. A possible structure for the 2:2:1 complex would involve complexing of the aromatic and alkyne  $\pi$ -systems to separate aluminium atoms. We cannot distinguish between the two mechanisms.

We acknowledge support by the Australian Research Grants Committee. R. M. L. was supported by the Australian Government Public Service Board and Departments of Defence and Education.

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<sup>4</sup> P. E. M. Allen and R. M. Lough, *J.C.S. Faraday I*, 1973, **69**, 849.

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