Kinetics of Reaction of Triethylaluminium with Oct-1-ene in Diphenyl Ether and Thermodynamic Parameters for the Stability of the Triethylaluminium–Diphenyl Ether Complex

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Parameters for the equilibrium: $\frac{1}{2}Et_6Al_2 + Ph_2O \overset{K_4}{\rightleftharpoons} Et_3Al,OPh_2$ have been estimated by the n.m.r. chemical shift method: $\Delta H_4^{\circ} = -16{\cdot}3 \pm 1{\cdot}3$ KJ mol^{-1} and $\Delta S_4^{\ominus} = -42{\cdot}7 \pm 1{\cdot}7$ J mol^{-1} K^{-1} (molar scale). The complex does not participate in the reaction with oct-1-ene. The retarded reaction in the presence of Ph_2O proceeds from the reduced concentration of the reactive, monomeric Et_3Al. The rate coefficient for the rate-controlling step $Et_3Al + C_8H_{16} \xrightarrow{k_2} Et_2Al(Decyl)$ is the same in Ph_2O and hydrocarbon solutions. If Smith's values of K_3 for $Et_6Al_2 \rightleftharpoons 2Et_3Al$ are used, $A_2 = 10^{4{\cdot}7 \pm 0{\cdot}1}$ l mol^{-1} s^{-1}, $E_2 = 63{\cdot}5 \pm 1{\cdot}2$ kJ mol^{-1}. An error in previous calculations of k_2 for hydrocarbon solutions is corrected.

REACTIONS between triethylaluminium and n-alk-1-enes in hydrocarbon solution are well characterized.[1-3] The overall rate is described by equation (1), where

$$v = -d[RCH{:}CH_2]/dt = k_1 a^{\frac{1}{2}}[RCH{:}CH_2] \quad (1)$$

a is the total concentration of all forms of triethylaluminium estimated according to the formula Et_6Al_2. It has been thoroughly established that the reaction proceeds from the monomeric Et_3Al and that the rate-controlling step is the addition of this to the alkene. A second molecule of alkene is consumed in a sequence of rapid subsequent reactions (2). The overall rate

$$Et_3Al + CH_2{:}CHR \xrightarrow{k_2} Et_2AlCH_2CHREt \xrightarrow{+CH_2:CHR} Et_2AlCH_2CH_2R + CH_2{:}CREt \quad (2)$$

coefficient k_1 is determined by k_2 and K_3, the equilibrium coefficient for equilibrium (3).

$$Et_6Al_2 \rightleftharpoons 2Et_3Al \quad (3)$$

In co-ordinating solvents, such as ethers, the overall reaction is either suppressed, as in the case of dioxan, or retarded as in the more weakly co-ordinating diphenyl ether. It is of considerable significance in the understanding of reactivity factors controlling organometallic reactions to determine whether the reduced reactivity proceeds from the Et_3Al–ether adduct or from the reduced concentration of free Et_3Al. In diphenyl ether the relevant equilibria are shown in (4).

$$\begin{tikzcd} \frac{1}{2}Al_2Et_6 + Ph_2O \arrow[rr, shift left, "K_4"] \arrow[dr, shift left, "K_3^{\frac{1}{2}}"] & & Et_3AlOPh_2 \arrow[ll, shift left] \arrow[dl, shift left] \\ & Et_3Al + Ph_2O \arrow[ul, shift left] \arrow[ur, shift left] & \end{tikzcd}$$

We applied the methods described in our previous paper to elucidate the mechanism of the reaction with n-oct-1-ene.

EXPERIMENTAL

Previously described[3] purification, manipulation, and spectrometric procedures were followed throughout. K_4 Was estimated from the dependence of the internal chemical shift (δ_{int}) of the methyl and methylene n.m.r. of Et_3Al on reagent ratio.[4,5] δ_{int} Was measured from the central line of the CH_3 triplet to the downfield, inner line of the CH_2 quartet. Mol ratios of $Ph_2O{:}Et_3Al$ were measured at 302 K from the integrated spectra on a 500 Hz scan locked onto the cyclohexane resonance off-set 130 Hz downfield. At other temperatures a 250 Hz scan was used and a Ph_2O lock, off-set to 850 Hz. Previous procedures[3] were followed in kinetic measurements except

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[1] P. E. M. Allen, J. N. Hay, G. R. Jones, and J. C. Robb, *Trans. Faraday Soc.*, 1967, **63**, 1636.

[2] J. N. Hay, P. G. Hooper, and J. C. Robb, *Trans. Faraday Soc.*, 1969, **65**, 1635; 1970, **66**, 2045.

[3] P. E. M. Allen and A. E. Byers, *Trans. Faraday Soc.*, 1971, **67**, 1718.

[4] K. Hataba and H. Yuki, *Tetrahedron Letters*, 1968, 213.

[5] B. A. Casey and P. E. M. Allen, *European Polymer J.*, 1970, **6**, 793.

that benzene was always, and cyclohexane normally, omitted; Ph_2O was used as the integration reference and the centre line of the Et_3Al triplet as the internal lock. Reaction rates were measured from the rate of decay of the integrated oct-1-ene $CH_2=$ resonance and the rate of appearance of the product $CH_2=$ resonance as previously.

RESULTS AND DISCUSSION

Equilibrium Parameters for the Et_3Al,OPh_2 *Complex.*—For a 1 : 1 Et_3Al,OPh_2 complex

$$K_4 = \frac{[Et_3Al,OPh_2]}{[Et_6Al_2]^{\frac{1}{2}}[Ph_2O]} = \frac{\Delta(\Delta + 1)^{\frac{1}{2}}}{a^{\frac{1}{2}}\{r + (r - 1)\Delta\}} \quad (5)$$

where $\Delta = (\delta_{obs} - \delta_f)/(\delta_c - \delta_{obs})$, δ_{obs} is the internal chemical shift, δ_{int}, observed at the mol ratio $Ph_2O{\cdot}Al = r$. δ_f is the value for free Et_6Al_2, which is assumed to be δ_{int} when $r = 0$ and δ_c is that for the complex: $\underset{r \to \infty}{\text{Lim}}\,\delta_{obs}$. The dependence of δ_{int} on r at 302 K is shown in Figure 1 The 1 : 1 stoicheiometry of the complex is confirmed by the intersection of the limiting straight lines. Similar curves were obtained at six temperatures from 323—383 K. The intersection in all cases lay between r = 1·0—1·4. A program written in Fortan IV for use on a CDC 6400 computer was used to calculate K_4.[6]

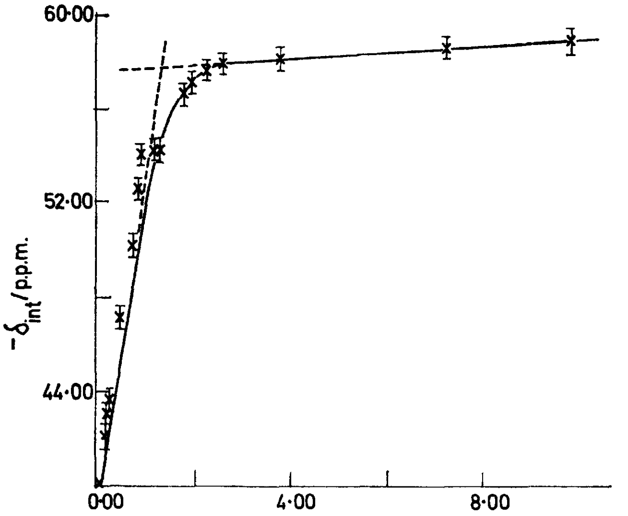

FIGURE 1 The internal chemical shift of the triethylaluminium ethyl n.m.r. resonances: $-\delta_{int} = \delta_{CH_2} - \delta_{CH_3}$ as a function of r, the Ph_2O : Al ratio, at 302 K

The linear, least-squares, regression line of log K_4 against $1/T$ (Figure 2) gave $\Delta H_4^\circ \pm$ S.E.$(\Delta H_4^\circ) = -16{\cdot}3 \pm 1{\cdot}3$ kJ mol^{-1}, which may be compared with a calorimetric value of $-11{\cdot}2$ KJ mol^{-1},[7] and $\Delta S_4^\ominus \pm$ S.E.$(\Delta S_4^\ominus) = -42{\cdot}7 \pm 1{\cdot}7$ J mol^{-1} K^{-1} (1M standard state).

*Kinetics and Mechanism of the Reaction with Oct-*1*-ene.*—The rate of reaction was estimated from the rate of consumption of octene at $Ph_2O{\cdot}Al$ mol ratios in the range: r = 0·1—10 at six temperatures between 373 and 398 K. Duplicate data were obtained at four of these temperatures. The experiments were carried out at initial octene concentrations: $b \simeq 2$M using samples of the same initial volume.

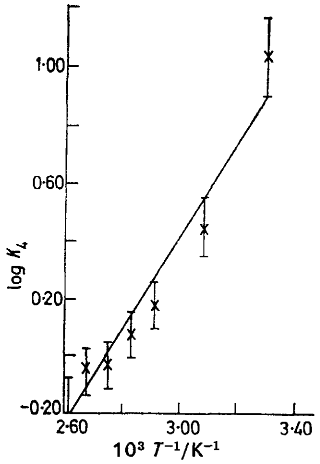

FIGURE 2 Least-squares regression of the van't Hoff plot of the molar scale equilibrium constant: K_4 for $\frac{1}{2}Et_6Al_2 + PhO_2 \rightleftharpoons Et_3Al,OPh_2$. The bars on data points indicate log {S.D.(K_4)}.

External Order of Reaction.—If the complex is the reactive species, the initial overall rate

$$v_0 = 2k_6[Et_3Al,OPh_2]_0[C_8H_{16}]_0 \quad (6)$$

where k_6 is the second-order rate coefficient for the addition of oct-1-ene to the complex. If monomeric triethylaluminium is the reactive species:

$$v_0 = 2k_2\,[Et_3Al]_0[C_8H_{16}]_0 \quad (7)$$

Both equations were tested. The reactant decay curves were fitted to a second-degree polynomial, which, provided the data were restricted to low conversion, gave reliable values for the initial rates v_0. Concentrations of the species Et_3Al and Et_3Al,OPh_2 were computed from our values of K_4 (Figure 2) and Smith's value of K_3,[8] assuming that it is unaffected by

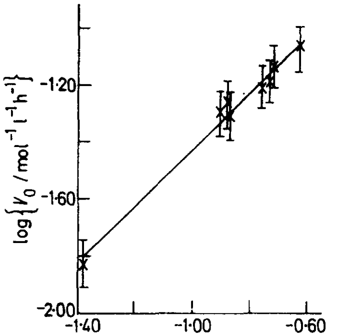

FIGURE 3 Dependence of initial rate of reaction, v_0, on the initial equilibrium concentration of the species Et_3Al at 388 K. The octene concentration was maintained nearly constant. Error bars indicate log {S.D.(v_0)} of the fitted polynomial used to estimate v_0

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[6] R. M. Lough, Honours Thesis, University of Adelaide, 1970.
[7] E. Bonitz, *Chem. Ber.*, 1955, **88**, 742.
[8] M. B. Smith, *J. Phys. Chem.*, 1967, **71**, 364.

the presence of Ph_2O. Figure 3 shows a log–log plot according to equation (7). The slope of the least-squares regression was 0·996. A direct plot of equation (7) was a straight line through the origin. The data thus fit equation (7). The slope of the plot of log v_0 against log $[Et_3Al,OPh_2]_0[C_8H_{16}]_0$ was $-0{\cdot}663$ showing that the data do not fit equation (6).

Integrated Rate Equations.—The stoicheiometric coefficient of 2 in equations (6) and (7) arises from the consumption of a second molecule of octene in reactions subsequent to the rate-controlling step [see equation (2)]. At very low conversions this value is not exact due to the delay in establishment of steady state conditions. However at low conversion the integrated rate equation is insensitive to deviations in stoicheiometry.

If the complex is the reactive form, the stoicheiometric equations and relationships are

$$\left.\begin{array}{lllll} \tfrac{1}{2}Al_2Et_6 \; + & Ph_2O & \overset{K_4}{\rightleftharpoons} Et_3Al,OPh_2 & (+2C_8H_{16}) & \longrightarrow \text{product} \\ 1.\; a - x_0/2 & d - x_0 & x_0 & b & 0 \\ 2.\; a - x/2 & d - x & x - y & b - 2y & y \end{array}\right\} \quad (8)$$

1. Initial conc. 2. Conc. at time t.

and the kinetic equation is

$$-\mathrm{d}[C_8H_{16}]/2\mathrm{d}t = \mathrm{d}y/\mathrm{d}t = k_6(x - y)(b - 2y) \qquad (9)$$

The variables in the equilibrium equation

$$(x - y)/(a - x/2)^{\frac{1}{2}}(d - x) = K_4 \qquad (10)$$

cannot be separated to give a closed form relationship $x = f(y)$ so the following procedure was adopted. The cubic in x was solved for the experimental values of y. The resulting points (x_n, y_n) were fitted to a sixth-degree polynomial in y to give $x = f(y)$ and the kinetic equation

$$\mathrm{d}y/\{f(y) - y\}(b - 2y) = k_6\mathrm{d}t \qquad (11)$$

was integrated numerically using Gaussian quadratures, order 22 and 100 intervals. The dependence of the integrated function of y on t is shown in Figure 4; the curvature shows that the data do not fit equation (11) and the mechanism cannot be equation (8).

If monomeric Et_3Al is the reactive species, the kinetics are simplified by the insensitivity of the concentration of this species to extent of reaction. To a reasonable approximation, over the extents of reaction studied, this concentration (m) may be regarded as constant and pseudo-first-order equations applied:

$$-\mathrm{d}[C_8H_{16}]/2\mathrm{d}t = \mathrm{d}y/\mathrm{d}t = k_2m(b - 2y) \qquad (12)$$

$$-\frac{1}{2m}\ln(1 - 2y/b) = k_2t \qquad (13)$$

Figure 5 shows a typical set of kinetic data fitted to equation (13). The hyperbolae show the 90% confidence limits of the fit of the linear least-squares regression. All sets of data fitted well, the origins lay within the 90% confidence limits, and the rate coefficients were independent of the value of m calculated from our values of K_4 and Smith's values of K_3.[8] At 373 K, for example, k_2 varied in a random fashion within the range $(5{\cdot}20$—$5{\cdot}88) \times 10^{-5}$ mol^{-1} s^{-1}, while the computed value of m ranged from 0·026—0·132M. At the six temperatures investigated between 373 and 398 K S.D.(k_2) did not exceed 0·1 k_2, confirming the fit of equations (13), (12), and (7) and a mechanism involving uncomplexed monomeric Et_3Al as the reagent.

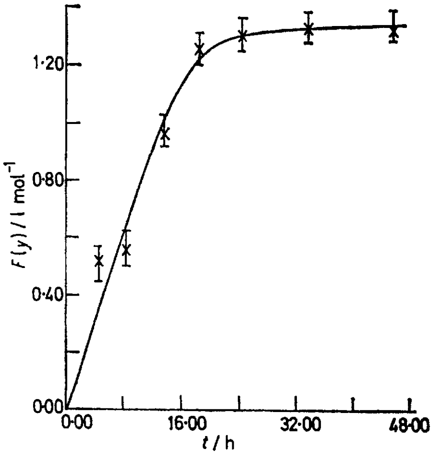

FIGURE 4 The dependence of values of:

$$F(y) = \int_0^y \mathrm{d}y/f(\{y) - y\}\,(b - 2y),$$

obtained by numerical integration of equation(11), on reaction time t

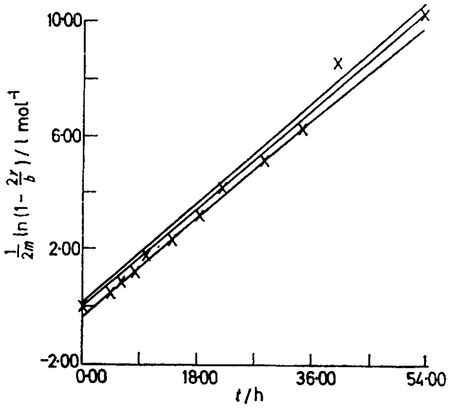

FIGURE 5 The dependence of the integrated rate function, equation (13), on time t. The hyperbolae show the 90% confidence limits of the unweighted, linear, least-squares regression. The straight line is a linear regression, weighted to pass through the origin

Arrhenius Parameters.—Figure 6 shows the fit of the data to the Arrhenius equation. Three sets of data are distinguished. Set A refer to diphenyl ether solution with *ca.* 2M octene and the Ph_2O : Al ratio varied from $r = 0{\cdot}1$—10. Set B refer to stoicheiometric mixtures of Ph_2O and alkylaluminium ($r = 1{\cdot}0$) at concentrations ($d = a/2$) in the range 0·8—3·2M with *ca.* 1·6M octene in cyclohexane. The third set have been recalculated from the data of Allen and Byers[3] and refer to hydrocarbon solutions with Ph_2O absent. A stoicheiometric coefficient was omitted in the original calculations so that values of k_1 and k_2 reported in this source must be multiplied by 2. The Table shows the Arrhenius parameters of each set and the combined set in which all data points from all three sets are equally weighted. There is little significant difference and the parameters of the combined set adequately represent the data of each individual set.

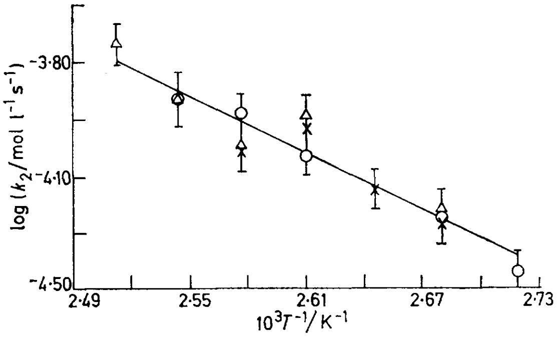

FIGURE 6 Arrhenius plots of k_2, for the following data sets: △ set A: Ph_2O solution, Ph_2O : Al varied r = 0·1—10; × set B: cyclohexane solution, r = 1; ○ hydrocarbon solution: Ph_2O absent, ref. 3; the error bars indicate log {S.D.(k_2)}

Arrhenius parameters and standard errors for the reaction:

$$Et_3Al + C_8H_{16} \xrightarrow{k_2} Et_2AlC_{10}H_{21}$$

A, In diphenyl ether solution with Ph_2O:Al between 0·1 and 10; *B*, in cyclohexane with Ph_2O:Al = 1 and in hydrocarbon solution in the absence of Ph_2O (calculated from the data of Allen and Byers, ref. 3).

	$\log_{10}\left(\frac{A_2}{\text{l mol}^{-1}\text{ s}^{-1}}\right)$	$\frac{E_2}{\text{KJ mol}^{-1}}$
Set A	6·2 ± 0·7	64·6 ± 2·4
Set B	4·5 ± 0·5	62·3 ± 2·4
Ph_2O absent	5·3 ± 0·2	68·6 ± 3·8
Combined	4·7 ± 0·1	63·5 ± 1·2

CONCLUSIONS

The retarding influence exerted on the reaction by Ph_2O is solely due to the depression of the concentration of reactive, monomeric Et_3Al. The complex Et_3Al,OPh_2 is unreactive. It is most unlikely that nearly identical kinetic parameters would have been obtained for such varied solvent compositions if the procedure for calculating equilibrium concentrations was unsound. This result confirms the validity of the procedure and in particular the assumption that K_3 is unaffected by the presence of Ph_2O. The values of the kinetic parameters of each set of data depend on Smith's value of K_3. The preference for this value has been explained elsewhere,[3] but the case is by no means conclusive. If other values were preferred the kinetic parameters would change accordingly.

The absence of a solvent effect on k_2 in diphenyl ether suggests that reaction (2) is essentially non-polar. The low A factor must, therefore, arise entirely from the loss of entropy associated with a compact, rigid transition state such as a four-centre structure. The lack of reactivity of Et_3Al,OPh_2 and other species in which Al has four-fold co-ordination (*e.g.* Et_6Al_2) suggests that the reaction path involves co-ordination of the alkene to the vacant fourth site of Et_3Al.

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