KINETICS OF THE REACTION OF METAL–ALKYL COMPOUNDS WITH ALKENES
# III. DIISOBUTYLALUMINIUM HYDRIDE

J. N. HAY, G. R. JONES AND J. C. ROBB

Department of Chemistry, The University of Birmingham, P.O. Box 363, Birmingham 15 (Great Britain)
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SUMMARY

The addition of diisobutylaluminium hydride to 1-butene is investigated and the rate found to exhibit half order in aluminium hydride concentration. A mechanism is given in which the monomeric form of the aluminium hydride is active in the addition reaction.
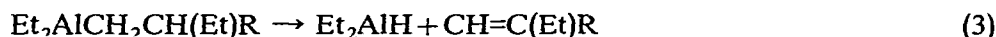
It has been shown that the addition of aluminium alkyls to n-alkenes is limited by the dissociation of the dimer[1,2], *i.e.*:

$$Al_2Et_6 \rightleftharpoons 2\,AlEt_3 \tag{1}$$
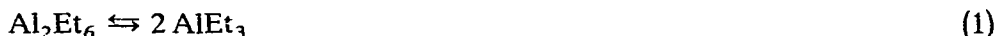
as addition proceeds through the monomer, *i.e.*:

$$AlEt_3 + CH_2{=}CHR \rightarrow Et_2AlCH_2CH(Et)R \tag{2}$$
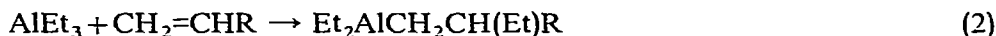
Under the conditions of the reaction, the β-branched alkyl group is eliminated and in the presence of excess n-alkene an n-alkylaluminium compound is produced. An aluminium hydride intermediate rather than direct group displacement may be involved in this reaction, *i.e.*:

$$Et_2AlCH_2CH(Et)R \rightarrow Et_2AlH + CH{=}C(Et)R \tag{3}$$

$$Et_2AlH + CH_2{=}CHR \rightarrow Et_2AlCH_2CH_2R \tag{4}$$

This overall reaction scheme was substantiated by a study of the reaction products of triethylaluminium and n-1-octene to high conversions[3]. These were 2-ethyl-1-octene-, hexadecene; n-octyl-, 2-ethyloctyl- and hexadecylaluminium compounds.

The present paper considers the evidence for the displacement reaction proceeding via a hydride intermediate in the light of the reactivity of diisobutylaluminium hydride to n-1-butene addition, and is compared with the addition reaction with triethylaluminium.

EXPERIMENTAL

Analyses, purification of the reagents, and reaction procedure were as described previously[1].

Diisobutylaluminium hydride (L. Light and Co. Ltd.) was used as obtained.

It contained 90–95 % of the theoretical hydrogen content, as measured by analysis of the gaseous hydrolysis products, and an excess of isobutyl groups, as well as traces of ethyl, propyl and n-butyl groups.
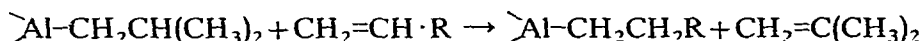
The reaction was studied in decahydronaphthalene (Decalin) (Hopkin and Williams Ltd, Micro-analytical reagent) dried and vacuum distilled. All reagents were dispensed under dry air-free nitrogen and solutions degassed *in vacuo*.

RESULTS

1. *Initial considerations*

Triisobutylaluminium was considered to be unreactive in adding to n-alkenes. Indeed at the reaction temperature 110–140° the isobutyl group was rapidly eliminated and diisobutylaluminium hydride produced. At 140°, this elimination proceeds initially as a first order rate process (half life 8 min) but the final extent of reaction was limited by the butene pressure. Under the same conditions, triethylaluminium added to 1-butene at an appreciably slower rate, see Fig. 2, accordingly any alkyl addition reaction involving isobutylaluminium groups could be neglected, and the reactivity of diisobutylaluminium hydride to alkene addition was due entirely to the hydride group.

The reaction was studied at 30–60°. Analysis of the addition products in the presence of excess 1-butene showed no trace of isobutene in the gas phase and therefore the elimination reaction :

$$\text{>Al--CH}_2\text{CH(CH}_3)_2 + \text{CH}_2\text{=CH} \cdot \text{R} \rightarrow \text{>Al--CH}_2\text{CH}_2\text{R} + \text{CH}_2\text{=C(CH}_3)_2$$

was not present. Only n- and isobutanes were obtained on hydrolysis of the reaction phase.

At the low temperature in which the reaction was studied, the measured rates were that of butenealuminium hydride addition and there were no competing side reactions.

2. *Reaction order*

The reaction system consisted of a liquid reaction phase and a gas reservoir of 1-butene whose pressure was maintained constant by means of a gas burette. The reaction was followed by decrease in volume. The rate of the reaction and solubility of 1-butene was independent of stirring rate provided this was sufficient to produce a vortex in the liquid.

By varying the concentration of aluminium hydride and temperature in the range 30–60° a reaction order of 0.50 ± 0.10 was obtained for the dependence of the initial rate on alkylaluminium concentration, see Fig. 1, and an apparent activation energy of 13.0 ± 0.5 kcal·mole^{-1}.

The reaction between triethylaluminium and butene was also studied for comparison, but in the temperature range 109–137°. Varying amounts of alkylaluminium (0.5–2.0 moles of dimer·l^{-1}) and different partial pressures of butene were used to determine reaction order. A half order dependence (0.55 ± 0.05) of initial rates on alkyl concentration and first order on butene partial pressure were accurately obeyed. (Fig. 2). An overall temperature dependence of 17.5 ± 0.4 kcal·mole^{-1} was measured. Henry's law accurately held for the system 1-butene–decalin and the concentration
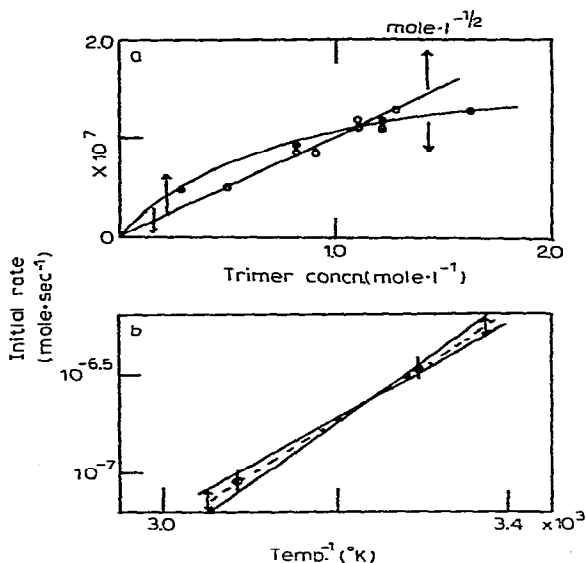
Fig. 1. a, Reaction order in aluminium hydride concentration; b, activation energy.

of alkene in decalin was directly proportional to the partial vapour pressure. The reaction was accordingly first order in 1-butene concentration.

Since a gas–liquid system was used to measure the reaction rates, the temperature dependence was not a measure of the overall activation energies of the various steps in the addition reaction but includes a term for the heat of solution of 1-butene in decalin. The heat of solution was calculated as -4.7 ± 0.1 kcal·mole^{-1} from the temperature dependence of the solubility, see Table 1.
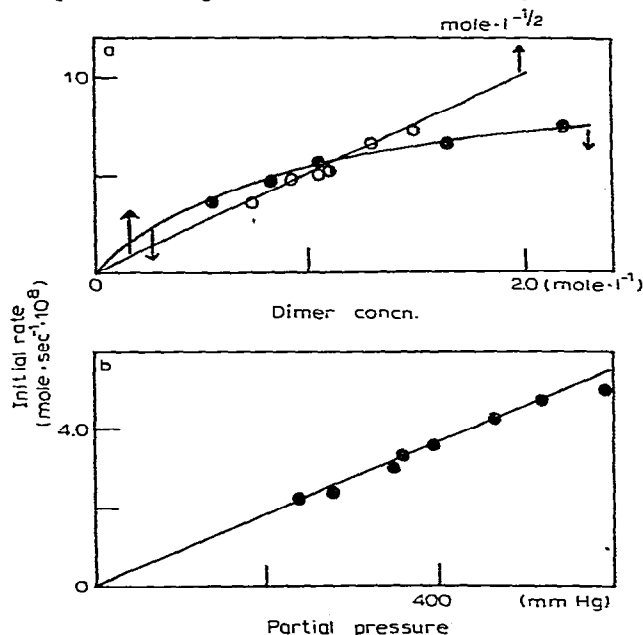

Fig. 2. Reaction order in: a, aluminium triethyl; b, butene pressure.

TABLE 1

SOLUBILITY OF 1-BUTENE IN DEKALIN
(at standard partial pressure of 1 atm)

Temp. (°C)	Solubility (mole/l)		Heat of dissolution kcal·mole^{-1}
21.0	1.79	1.76	
109.3	0.281	0.288	4.7±0.1
116.0	0.254	0.262	
130.7	0.210	0.215	
136.5	0.206	0.287	

DISCUSSION

Hoffmann from calorimetric[4], NMR[4], and cryoscopic[5] (in benzene) studies has established that dialkylaluminium hydride compounds are associated species. In particular, diisobutylaluminium hydride is trimeric in benzene at 5°, *i.e.*:
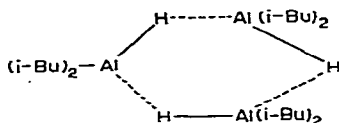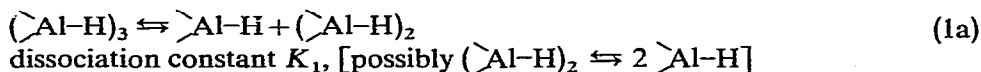

However dissociation occurs and at 100° in a 2–3% phenanthrene solution, the average association[6] is 2.5. Diisobutyl-n-alkylaluminium compounds, *i.e.* the products of the addition reaction, are dimeric with bridging n-alkyl bonds,
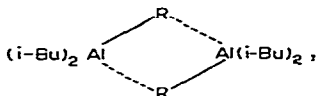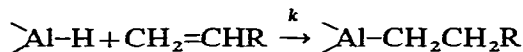

since NMR studies show that the n-alkyl bridges occur to the exclusion of isobutyl[4].
    The present kinetic order study can be interpreted in terms of dissociation of the aluminium hydride trimer prior to addition to alkene ,*i.e.*:

$$(\rangle Al-H)_3 \leftrightarrows \rangle Al-H + (\rangle Al-H)_2 \qquad (1a)$$
dissociation constant K_1, [possibly $(\rangle Al-H)_2 \leftrightarrows 2 \rangle Al-H$]

and then

$$\rangle Al-H + CH_2{=}CHR \xrightarrow{k} \rangle Al-CH_2CH_2R$$

The initial addition rate is then

$$\frac{-d}{dt} [Alkene] = kK_s p \cdot [K_1 C/3]^{\frac{1}{2}}$$

Since $K_1 = \alpha^2 (1-\alpha)^{-1} C/3$, and from Hoffmann's data $1-\alpha \simeq 1$, where K_s is alkene solubility, α the degree of dissociation and p the partial pressure of butene.

The overall temperature dependence ΔE_{obs} is then

$$\Delta E_{obs} = \Delta E_A + \Delta H_S + \tfrac{1}{2}H_d$$

where $\Delta E_{obs} = 13.0 \pm 0.5$ kcal·mole^{-1}, ΔE_A is the activation energy of the addition reaction, $\Delta H_S = -4.7 \pm 0.1$ kcal·mole^{-1} and ΔH_d is the heat of dissociation;

hence $\Delta E_A + \tfrac{1}{2}\Delta H_d = 17.7$ kcal·mole^{-1}

No value of $\Delta H_d/2$ is available but it is greater than the corresponding value for bridging methyl bonds for which $\Delta H_d/2$ lies between 6.7 and 10 kcal·mole^{-1} (Ref. 6, 7) since hydrogen bridge bonds exclusively displace methyl bonds on mixing alkyl-aluminium compounds[4,5]. By analogy it will be less than that of the corresponding bridging chlorine bonds for which $\tfrac{1}{2}\Delta H_d$ is 14.5 kcal·mole^{-1}. A comparatively low activation energy (3–11 kcal·mole^{-1}) is thus indicated for this facile addition reaction.

The reaction scheme is formally identical to that proposed for the addition of trialkylaluminium to alkenes[1,2] in that the active species is exclusively the monomeric form of the alkyl compound.

Ziegler et al.[6] have also studied the exchange reaction

$$\rangle Al-CH_2CH(CR_3)_2 + CH_2=CHR^1 \rightleftharpoons \rangle Al-CH_2CH_2R^1 + CH_2=C(CR_3)_2 \quad (5)$$
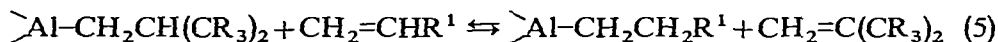
and have established that the equilibrium position is very dependent on the alkyl concentration. On applying a general equilibrium equation

$$K = \frac{\alpha^n(C)}{(1-\alpha)^{n-1}}$$

a value of n in excess of 4 was obtained.

This dependence can only be interpreted in terms of the mechanism proposed above involving hydride intermediates and invoking dissociation reactions (1) and (1a). Reaction (5) is an oversimplification.

CONCLUSIONS

Aluminium hydride compounds are intermediates in the displacement of branched with linear alkyl groups, and the unassociated form of the hydride is active in the addition to alkenes.

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