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Reactions of Group 3 Metal Alkyls in the Gas Phase*

Part 8.—Homogeneous Thermal Unimolecular Elimination of Ethylene from Triethylaluminium

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Received 6 *September*, 1971

The kinetics of the homogeneous gas-phase elimination of ethylene from triethylaluminium have been studied in the presence of excess propene in the temperature range 426-488 K. The observed first-order rate constants k_0 based on the loss of ethyl groups fit the Arrhenius relationship, $\log k_0/s^{-1} = 10.93 \pm 0.13 - (30.05 \pm 0.27)/\theta$, where $\theta = 4.58 \times 10^{-3}\,T$ in units of kcal mol^{-1} ‡ [$= 10.93 \pm 0.13 - (125.7 \pm 1.1)/19.15 \times 10^{-3}\,T$ in units of kJ mol^{-1}]. These activation parameters are compatible with the 4-centre polar transition state proposed for olefin eliminations from other Group 3 metal alkyls, and the effect of β-substitution on the rate of elimination is additive. The activation energy for the back-addition of ethylene to dialkylaluminium hydride is estimated to be 4.9 kcal mol^{-1}.

The kinetic parameters for the homogeneous unimolecular gas phase olefin eliminations from trialkylaluminium, [1-3], trialkylgallium,[4] and trialkylboron compounds,[5,6] substantiate the concept of a polar 4-centre transition state for these reactions. It has been proposed [6] that the effect of β-substitution on $\Delta G^{\ddagger}$ may be additive. The present study was undertaken to test this prediction and to extend the thermochemical kinetic data for Group 3 metal alkyls. An earlier gas-phase study of the decomposition of triethylaluminium in glass reaction vessels [7] yielded results which were interpreted in terms of a heterogeneous first-order reaction. In the present study, a Teflon coated stainless steel vessel was used to eliminate any heterogeneous component of the reaction.

EXPERIMENTAL

MATERIALS

Triethylaluminium was obtained from Schering A.G., Bergkamen, Germany. Hydrolysis indicated that it contained a small quantity (5 %) of aluminium-butyl bonds. The ratio of ethyl to butyl groups in the starting material was shown to remain constant throughout the study and hence a simple correction could be applied to the kinetics to factor out the contribution due to the elimination of butene. To facilitate handling, a 30 % solution of triethylaluminium in n-hexane was used as starting material throughout this work. Propylene (99.9 %) was obtained from Fluka A.G., Buchs, Switzerland.

APPARATUS AND PROCEDURE

The static reaction system and 0.802 l. Teflon-coated stainless steel reaction vessel were essentially the same as described previously.[1] To check the homogeneity of the reaction the vessel was packed with Teflon tubing, resulting in a 56-fold increase of the surface-to-volume ratio. A 30 % solution of triethylaluminium in n-hexane was introduced into the evacuated reaction volume through a silicone rubber septum followed by immediate addition

* Part 7: A. T. Cocks and K. W. Egger, *J. Chem. Soc. A*, 1971, 3606.

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‡ throughout this paper, 1 cal = 4.184 J.

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of propene. For the experiments carried out in the packed reaction vessel, propene had to be preheated to 170°C prior to addition in order to establish temperature equilibrium in the reaction system fast enough.

The reaction vessel was isolated from the injection volume by means of a Teflon valve and all propene and aluminium alkyl remaining in the dead space were condensed out. An experiment was quenched by condensing the contents of the reaction vessel into a trap cooled in liquid nitrogen. Negligible amounts of non-condensable products were observed. The gaseous hydrocarbons and the n-hexane were removed at −20°C and the remaining aluminium alkyl fraction was hydrolyzed with excess water. The gaseous hydrolysis products were transferred to a gas burette by means of an automatic Toepler pump and were analyzed by gas chromatography. An F+M 810 gas chromatograph fitted with T.C. detectors was employed. A 30 ft × 0.25 in. column packed with 20 % bis-(2-methoxyethyl) adipate on 60-80 mesh chromosorb W, operated at 0°C with a helium flow rate of 80 ml min^{-1} gave a quantitative separation of the hydrolysis products. Peak areas were measured with a Disc integrator and all analyses were performed in duplicate. From calibration mixtures, the relative response factors for ethane, propane, and butane were 1.533 : 1.225 : 1.

RESULTS

In the presence of propene, triethylaluminium decomposes in the temperature range 426-488 K to give ethylene and mixed aluminium alkyls containing ethyl and propyl groups. Difficulties in quantitatively separating and measuring small quantities of ethylene in the presence of excess propene and the small but variable amount of heterogeneous decomposition yielding ethane, ethylene and aluminium on introduction [1] precluded the use of ethylene production as a measure of the extent of reaction. The reaction was followed, therefore, by measuring the rate of replacement of ethyl groups by propyl groups, which was determined from the composition of the hydrolysis gases from the aluminium alkyl products.

Under the conditions of this study, the triethylaluminium was almost completely dissociated into the monomeric form. The calculated concentration of dimer [8] under the most favourable conditions for its existence is less than 1.5 % of the monomer, and in most experiments is considerably smaller than this.

The overall reaction mechanism is summarized below:

$$\mathrm{Alet_3} \underset{-1}{\overset{1}{\rightleftharpoons}} \mathrm{HAlet_2} + \mathrm{C_2H_4}$$

$$\mathrm{prAlet_2} \underset{-2}{\overset{2}{\rightleftharpoons}} \mathrm{pr(H)Alet} + \mathrm{C_2H_4}$$

$$\mathrm{pr_2Alet} \underset{-3}{\overset{3}{\rightleftharpoons}} \mathrm{pr_2AlH} + \mathrm{C_2H_4}$$

$$\mathrm{R_2AlH} + \mathrm{C_3H_6} \underset{-4}{\overset{4}{\rightleftharpoons}} \mathrm{R_2Alpr}$$

where et stands for ethyl and pr for propyl groups, and R = et or pr. The experimental methods employed precluded the direct observation of the consecutive mechanism but this observation has been made for triisobutylboron.[6]

Under the experimental conditions, $r_4 \gg r_{-n} > r_{-4} \approx r_n$, where r denotes rate and n = 1, 2, 3, and hence the mechanism simplifies to

$$\mathrm{Alet_3} \overset{1}{\rightarrow} \mathrm{prAlet_2} \overset{2}{\rightarrow} \mathrm{pr_2Alet} \overset{3}{\rightarrow} \mathrm{pr_3Al}.$$

Possible side-reactions involving the addition of olefins to the aluminium-ethyl bond [9] are unimportant under the reaction conditions employed.

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The rate constant for the rate of loss of ethyl groups k_0 is given by:

$$k_0 = -2.303/t \log \{[C_2H_6]/([C_2H_6]+[C_3H_8])\}.$$

As has been shown previously,[6] if $k_1 : k_2 : k_3 = 3 : 2 : 1$, k_0 calculated from the above formula is time-invariant and equal to $k_1/3$, i.e., the rate constant for the initial step corrected for the path-degeneracy factor due to the number of groups. Path-degeneracy considerations and the time invariance of k_0 obtained in other group 3 metal alkyl systems,[1-4] indicates that the rate constant ratio is close to 3 : 2 : 1.

TABLE 1.—GAS-PHASE ELIMINATION OF ETHYLENE FROM TRIETHYLALUMINIUM IN THE PRESENCE OF PROPENE

temp./K	time/min	starting materials mol. × 10⁴ AlR_3 [a]	propene	conversion %	$k/10^{-4}$ s^{-1}
426.0	60	0.191	120	11.50	0.358
426.7	120	0.307	106	20.65	0.321
426.9	45	2.11	113	9.95	0.389
427.0	15	2.70	134	3.29	0.336
436.4	15	0.470	137	6.01	0.688
436.4	30	0.278	106	12.89	0.766
436.9	45	0.849	64.8	18.38	0.752
436.9	60	0.587	83.2	22.64	0.713
443.5	50	0.447	68.7	31.14	1.27
443.6	5	0.600	98.9	3.84	1.31
443.6	15	0.483	130	11.92	1.41
443.7	10	0.817	178	7.99	1.39
443.9	20	1.03	136	15.63	1.42
456.2	5	1.88	157	10.69	3.77
456.2	20	0.231	131	33.41	3.39
456.4	10	0.221	121	17.57	3.22
456.4	15	0.318	103	24.86	3.18
460.9 [b]	20	0.201	45.0	30.72	3.06
460.4 [b]	10	0.462	34.8	19.55	3.63
466.5	5	0.191	83.0	21.68	8.15
467.0	7	0.845	132	24.72	6.76
467.0	10	0.444	159	36.27	7.51
469.0	3	0.281	189	13.24	7.92
478.2	3	0.493	99.7	27.75	18.1
478.2	4	0.697	119	31.71	15.9
478.5	5	0.437	142	38.20	16.0
478.7	2	1.74	83.4	26.97	15.5
478.7	6	0.420	67.8	41.43	14.9
488.4	2.5	0.633	148	35.35	29.1
488.5	1.5	1.87	120	24.45	31.2
488.5	2	0.443	160	30.10	29.8
488.5	3	0.743	135	41.25	29.6

[a] based on hydrolysis products. [b] packed reaction vessel; not included in least squares analysis.

The results for k_0 in the triethylaluminium system and the experimental conditions are summarized in table 1. No significant variation of k_0 with time, amount of starting material, propene-to-triethylaluminium ratio, or the final calculated propene-to-ethylene ratio was observed. No pressure changes were observed during the reaction and no non-condensable reaction products or hydrolysis products were

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found. Duplicate g.c. analyses generally agreed within 0.5 %. The typical standard deviation of k_0 within a temperature block is ± 6 %. This scatter is due to uncertainties introduced in the hydrolysis and collection procedures. Fig. 1 shows the Arrhenius plot of the data.

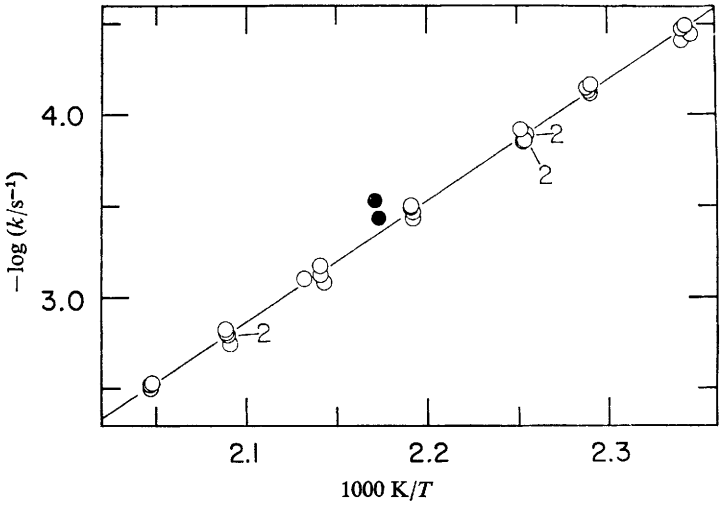

FIG. 1.—Arrhenius plot for the elimination of ethylene from triethylaluminium. Filled circles denote runs carried out in the packed vessel and numerals indicate overlapping points.

Least-squares analysis yielded the following Arrhenius relationship: $\log k_0/s^{-1} = 10.93 \pm 0.13 - (30.05 \pm 0.27)/\theta$, where $\theta = 4.58 \times 10^{-3}\, T$ in units of kcal mol^{-1}; or $\log k_0/s^{-1} = 10.93 \pm 0.13 - (125.7 \pm 1.1)/\theta$, where $\theta = 19.15 \times 10^{-3}\, T$ in units of kJ mol^{-1}. (The quoted errors are standard deviations). The maximum likely error [10] in the activation energy is estimated to be ± 700 cal mol^{-1}. Runs carried out with the packed reaction vessel with a 56-fold larger surface-to-volume ratio yielded rate constants within 22-35 % of those calculated from the Arrhenius equation obtained in the unpacked vessel. Any heterogeneous component of the reaction is, therefore, small.

Initial runs in the study of triethylaluminium were carried out with pent-1-yne as a hydride trap. The results for k_0 were similar to those obtained with propene but were more scattered. The reaction in the presence of pentyne is complicated by a secondary reaction of the pentenyldialkylaluminium, formed by addition of pentyne to the hydride, with a further molecule of pent-1-yne [11] to give the pentynyldialkylaluminium and pent-1-ene. Pent-1-yne was the major C_5 hydrolysis product from these studies and pent-1-ene was observed as a reaction product. This secondary reaction is surprisingly fast, and the scattered results were probably due to small variable amounts of pent-1-yne trapped in the aluminium alkyl fraction.

DISCUSSION

The observed Arrhenius parameters for the homogeneous elimination of ethylene from triethylaluminium substantiate the concept of a polar 4-centre transition state proposed earlier for the elimination of olefins from other Group 3 metal alkyls.[1-4, 6] This transition state is considered to be similar, except for tightness to that proposed

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by Benson and Haugen for the addition of H—X to olefins,[12, 13] in which the α-carbon is negatively charged and the β-carbon positively charged.

Values of k_0 are already path-degeneracy-corrected with respect to the number of alkyl groups but a further correction is necessary for n-butyl and ethyl groups for the number of hydrogen atoms available for elimination (2 and 3 respectively). Table 2 shows the fully corrected kinetic parameters for the group 3 metal alkyl elimination reactions studied to date.

TABLE 2.—PATH DEGENERACY CORRECTED ACTIVATION PARAMETERS FOR OLEFIN ELIMINATIONS FROM GROUP 3 METAL ALKYLS

compound	log A	E_a/(kcal mol^{-1})	$\Delta G^{\ddagger}_{450}$/(kcal mol^{-1}	ref.
triisobutylaluminium	11.2 ± 0.3	26.6 ± 0.7	30.2	1
dimethyl-n-butylaluminium	10.6 ± 0.2	27.8 ± 0.4	32.7	3
triethylaluminium	10.5 ± 0.1	30.1 ± 0.3	35.2	this work
triisobutylgallium	11.6 ± 0.3	30.4 ± 0.6	33.2	4
triisobutylboron	11.8 ± 0.5 *	30.4 ± 1.0	32.7	6
triethylboron	10.6 ± 0.6 *	33.7 ± 1.2	38.5	5

* obtained by applying path degeneracy corrections to k_1.

The A factor appears to increase with a decrease in electronegativity of the central atom and the A factors for ethyl and n-butyl compounds are markedly lower than those for the isobutyl derivatives. These effects are almost certainly real. The effects of the electronegativity of the central atom on the A factor are difficult to predict as the precise nature of the transition state cannot be defined due to the lack of data concerning the electrostatic effects involved. The difference between isobutyl and n-butyl and ethyl derivatives can be rationalized on the basis of increased steric repulsion in the isobutyl compounds resulting in $\Delta G^{\ddagger}$ being minimized by a higher A factor and consequently higher activation energy (after taking the extra electronic stabilization into account).

For a detailed comparison of the results it is better to consider the effects on $\Delta G^{\ddagger}$ at a temperature within the range of all the studies (450 K in this case), as this quantity is subject to less error than the derived Arrhenius parameters. From the values for $\Delta G^{\ddagger}_{450}$ listed in table 2, in the aluminium alkyl series, the effect of a single β-alkyl substituent is to lower $\Delta G^{\ddagger}_{450}$ by 2.5 kcal mol^{-1} and the effect of dialkyl β-substitution is to lower $\Delta G^{\ddagger}_{450}$ by 5.0 kcal mol^{-1}.

The effect of β-substitution is, therefore, additive although such exact agreement is probably fortuitous. In the boron series, the difference in $\Delta G^{\ddagger}_{450}$ between the unsubstituted and di-β-substituted compound is 5.8 kcal mol^{-1}, thus indicating that similar effects are operating in both boron and aluminium systems. The slightly greater substituent effect in the boron system may reflect a slightly greater polarity difference between the ground and transition states. The substituent effects on the positive charge are not as pronounced as in the elimination reactions of alkyl halides (6 kcal per substituent)[12] and would indicate a decreased polar character in the transition state for Group 3 metal alkyl elimination reactions with respect to that in the alkyl halide series. A lower polarity should result in a tighter transition state and this is indicated by the much lower A factors observed in the Group 3 metal alkyl series.

The heat of reaction for the triethylaluminium→diethylaluminium hydride+ethylene system has been estimated [3] to be 25.2 kcal mol^{-1}. The activation energy for the addition of ethylene to dialkylaluminium hydride is, therefore, estimated

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to be 30.1-25.2 = 4.9 kcal mol^{-1}. Values for the hydride addition reaction of n-butene and 2-methylpropene have been estimated [3] to be 5 and 5.9 kcal mol^{-1} respectively. Thus, little difference in activation energy is predicted for the different olefins.

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