Reactions of Group III Metal Alkyls in the Gas Phase. Part VII.† The Thermal Unimolecular Decomposition of Tri-isobutylboron

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The kinetics and mechanism of the gas-phase thermal decomposition of tri-isobutylboron in the presence of excess of ethylene have been studied in the temperature range 407—469 K. Elimination of 2-methylpropene and rapid addition of ethylene to the resulting hydride leads to the formation of ethyldi-isobutylboron, diethylisobutylboron,

$$BBu^i_3 \xrightarrow{k_1} EtBBu^i_2 \xrightarrow{k_2} Et_2BBu^i \xrightarrow{k_3} Et_3B \qquad (A)$$

and triethylboron by a consecutive mechanism (A). The rate constants are those for the elimination of 2-methylpropene from the trialkylboron species and fit the following Arrhenius relationships:

$$\log k_1/s^{-1} = 12{\cdot}3 \pm 0{\cdot}5 - (30{\cdot}4 \pm 1{\cdot}0)/\theta$$
$$\log k_2/s^{-1} = 12{\cdot}5 \pm 0{\cdot}6 - (30{\cdot}7 \pm 1{\cdot}1)/\theta$$
$$\log k_3/s^{-1} = 11{\cdot}4 \pm 0{\cdot}8 - (28{\cdot}9 \pm 1{\cdot}6)/\theta$$

where $\theta = 4{\cdot}58 \times 10^{-3}T$ in units of kcal mol^{-1}.‡

The rate constant for the *overall loss* of isobutyl groups (k_0) fits the equation

$$\log k_0/s^{-1} = 12{\cdot}3 \pm 0{\cdot}5 - (31{\cdot}1 \pm 1{\cdot}0)/\theta$$

These results are compared with those from studies of other Group III metal alkyls in the gas phase and are shown to be consistent with a polar 4-centre transition state.

THE kinetic parameters for the gas-phase unimolecular olefin eliminations from tri-isobutylaluminium,[1,2] dimethyl-n-butylaluminium,[3] and tri-isobutylgallium [4] are compatible with a 4-centre polar transition state. The present study was undertaken to examine further the effect of the electronegativity of the central atom on the rate of elimination in the Group III metal alkyls.

EXPERIMENTAL

Tri-isobutylboron was prepared by the dropwise addition of tri-isobutylaluminium to triethyl borate under nitrogen followed by refluxing for 3 h at 68 °C.[5] The product was separated by reduced-pressure distillation (b.p. 64 °C at

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† Part VI, K. W. Egger and A. T. Cocks, *J. Amer. Chem. Soc.*, in the press.

‡ Throughout this paper, 1 cal = 4·184 J and 1 Torr = 101·325/760 kN m^{-2}.

[1] K. W. Egger, *J. Amer. Chem. Soc.*, 1969, **91**, 2867.

[2] K. W. Egger, *Internat. J. Chem. Kinetics*, 1969, **1**, 459.

[3] K. W. Egger and A. T. Cocks, *Trans. Faraday Soc.*, 1971, **67**, 2629.

[4] K. W. Egger, preceding paper.

[5] R. Köster, *Annalen*, 1958, **618**, 31.

10 Torr) and further purified by slow distillation on the vacuum line to yield a sample of tri-isobutylboron of 97% purity (g.l.c.). The structure was confirmed by n.m.r. spectroscopy. The impurities appeared to be thermally stable.

Apparatus and Procedures.—The static high-vacuum system and Teflon-coated stainless steel reaction vessel were essentially as described.[1-3] A 25% solution of tri-isobutylboron in n-hexane was introduced into the evacuated reaction volume through a silicone rubber septum followed by immediate addition of an excess of ethylene. The reaction vessel was isolated from the injection system by means of a Teflon valve, and all ethylene and tri-isobutylboron remaining in the dead-space was condensed out. An experiment was quenched by condensing the contents of the reaction vessel into a trap cooled with liquid nitrogen. Ethylene and most of the 2-methylpropene were removed at 223 K, and the remaining products were condensed into a collection vessel fitted with a rubber septum. The vessel was pressurised with nitrogen and the contents analysed by g.l.c. by use of liquid injections. An F and M 810 Gas Chromatograph fitted with T.C. detectors was employed. A 12 ft × 0·25 in column packed with 20% silicone oil (D.C. 710) on Chromosorb P operated at 85 °C with a helium flow rate of 100 ml min^{-1} quantitatively separated the products. Peak areas were measured with a ' disc ' integrator.

RESULTS

The decomposition was studied in the temperature range 407—469 K. In excess of ethylene, the principal reaction products are 2-methylpropene, ethyldi-isobutylboron, diethylisobutylboron, and triethylboron. Because of their extreme susceptibility to oxidation[6,7] the trialkylboron products could not be identified unambiguously. However, Et_3B had identical retention times to that of an authentic sample on silicone oil and Carbowax columns, and the retention times of $EtBBu^i_2$ and Et_2BBu^i were compatible with the identification. The product–time distributions were consistent with a consecutive first-order mechanism. Pressure changes during the reaction were negligible. Initial experiments in which tri-isobutylboron together with undecane as internal standard were injected into the reaction volume and immediately condensed out resulted in an almost quantitative recovery of BBu^i_3. This indicates that BBu^i_3 is not as susceptible to heterogeneous decomposition in the inlet system as aluminium alkyls.[1-3]

The homogeneous mechanism in the presence of excess of ethylene is shown in reactions (1)—(4) where R = Bu^i or Et.

$$BBu^i_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Bu^i_2BH + Me_2C{:}CH_2 \qquad (1)$$

$$EtBBu^i_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} EtBu^iBH + Me_2C{:}CH_2 \qquad (2)$$

$$Et_2BBu^i \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Et_2BH + Me_2C{:}CH_2 \qquad (3)$$

$$R_2BH + C_2H_4 \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} R_2BEt \qquad (4)$$

As $r_a \gg r_{-n} > r_n > r_{-a}$ (where r denotes rate and n = 1, 2, or 3), the overall mechanism becomes (5).

$$BBu^i_3 \xrightarrow{k_1} EtBBu^i_2 \xrightarrow{k_2} Et_2BBu^i \xrightarrow{k_3} BEt_3 \qquad (5)$$

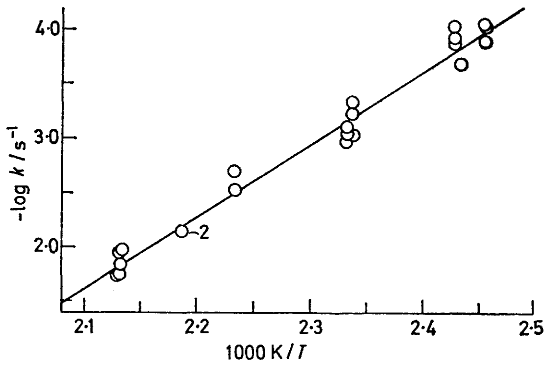
k_1 is thus given by equation (6).

$$k_1 = -\frac{2{\cdot}303}{t} \times \log\left(\frac{[BBu^i_3]}{[BBu^i_3] + [EtBBu^i_2] + [Et_2BBu^i] + [BEt_3]}\right) \qquad (6)$$

k_0, the rate constant for the *overall elimination* of isobutyl groups was evaluated from expression (7).

$$k_0 = -\frac{2{\cdot}303}{t} \times \log\left(\frac{3[BBu^i_3] + 2[EtBBu^i_2] + [Et_2BBu^i]}{3([BBu^i_3] + [EtBBu^i_2] + [Et_2BBu^i] + [BEt_3])}\right) \qquad (7)$$

Response factors were assumed to be inversely proportional to molecular weight. This has been shown to hold for homologous hydrocarbons.



Arrhenius plot for the elimination of 2-methylpropene from tri-isobutylboron. The numeral 2 indicates overlapping points

Values obtained for k_1 and k_0 at various temperatures, together with relevant data, are in Table 1. There appears to be no systematic variation of rate constants with conversion or ethylene : BBu^i_3 ratio. The scatter in the results (typical standard deviation within a temperature bloc ± 25%) is due to uncertainties introduced in the collection and analysis procedures. In many of the runs, undecane was added as an internal standard and the mass balances obtained by this method were satisfactory within experimental error. The extreme oxygen sensitivity of the trialkylborons is demonstrated by the fact that despite precautions to keep the reaction products under nitrogen throughout, duplicate injections often revealed further products, presumably oxygenated compounds, with longer retention times than BBu^i_3.

k_2 and k_3 were obtained by numerical solution of the integrated rate equations[8] and are subject to larger errors than k_1 and k_0. The values are in Table 1. The Figure shows the Arrhenius plot for k_1. The Arrhenius equations, in logarithmic form, obtained by least-squares analysis are (8)—(11) where $\theta = 4{\cdot}58 \times 10^{-3}T$ kcal mol^{-1}. The quoted errors are standard deviations. The maximum likely error in the activation energy for k_1 and k_0 is estimated to

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[6] J. Grotewold, J. Hernandez, and E. A. Lissi, *J. Chem. Soc.* (*B*), 1971, 182 and references therein.

[7] A. G. Davies, K. U. Ingold, B. P. Roberts, and R. Trudor, *J. Chem. Soc.* (*B*), 1971, 698, and references therein.

[8] A. Rakowski, *Z. phys. Chem.*, 1907, **57**, 321.

TABLE 1

Gas-phase elimination of 2-methylpropene from tri-isobutylboron in the presence of ethylene

	Time	Starting materials/Torr		Butyl group conversion				
T/K	min.	BBu^i_3 [a]	C_2H_4	(%)	$10^4k_1/s^{-1}$	$10^4k_2/s^{-1}$	$10^4k_3/s^{-1}$ [b]	$10^4k_0/s^{-1}$
406·7	240	1·8	210	40·6	0·985	0·881	0·355	0·362
406·9	60	1·8	255	10·2	0·919	0·918	7·66 *	0·301
406·9	180	1·8	210	40·2	1·34	1·00	0·669	0·476
410·5	30	1·4	349	13·1	2·16	2·36	1·75	0·779
411·3	15	1·6	547	4·7	1·37	1·37	1·35	0·530
411·3	60	1·6	439	15·4	1·24	1·54	1·22	0·466
411·3	120	1·6	132	24·0	0·977	1·21	0·977	0·381
427·6	10	2·5	311	19·0	9·54	9·99	6·76	3·50
427·6	20	2·5	349	18·7	4·89	3·33	12·7 *	1·72
427·6	45	2·5	193	38·1	6·11	5·01	3·23	2·27
428·5	5	1·8	333	7·8	8·03	6·17	6·17	2·70
428·5	10	1·8	94	18·4	9·38	9·14	4·36	3·36
428·5	15	1·8	306	29·9	11·0	8·23	4·69	3·79
447·5	5·2	2·4	286	27·0	30·4	20·6	8·77	10·1
447·5	10	1·6	436	39·6	20·7	23·2	13·5	8·40
457·0	5	1·8	249	61·4	72·8	79·0	45·1	31·8
457·1	3	1·8	510	42·6	73·4	87·5	53·7	30·8
468·4	2·5	1·2	154	56·0	108	180	96·1	54·7
468·7	4	2·4	345	84·6	147	188	111	78·0
468·8	3·7	1·8	346	96·1	181	119	42·2	45·8
468·9	2	1·8	230	69·5	116	111	22·2 *	41·9
469·3	3	3·5	154	76·4	185	175	105	80·2

[a] Based on material injected. [b] Data marked with asterisks were not included in the least-squares analysis.

be[9] ±2 kcal mol⁻¹. This error is greater for k_2 and particularly k_3.

$$\log k_1/\mathrm{s}^{-1} = 12{\cdot}33 \pm 0{\cdot}52 - (30{\cdot}35 \pm 1{\cdot}01)/\theta \qquad (8)$$

$$\log k_2/\mathrm{s}^{-1} = 12{\cdot}48 \pm 0{\cdot}55 - (30{\cdot}69 \pm 1{\cdot}09)/\theta \qquad (9)$$

$$\log k_3/\mathrm{s}^{-1} = 11{\cdot}40 \pm 0{\cdot}81 - (28{\cdot}90 \pm 1{\cdot}59)/\theta \qquad (10)$$

$$\log k_0/\mathrm{s}^{-1} = 12{\cdot}27 \pm 0{\cdot}51 - (31{\cdot}08 \pm 1{\cdot}01)/\theta \qquad (11)$$

DISCUSSION

The rate constants for the consecutive elimination steps k_1, k_2, and k_3 have similar magnitudes. *A priori*, it would be expected that the activation energy for the elimination of 2-methylpropene from a dialkylisobutylboron species would not be greatly dependent on the nature of the alkyl groups. The relative rates for mono-, di-, and tri-isobutyl species would be expected to depend mainly on the path degeneracies and therefore be in the approximate ratio 1 : 2 : 3. This ratio has been observed in liquid-phase isomerisations of trialkylborons[10] which almost certainly occur *via* an elimination–addition mechanism. The observed ratio for $k_3 : k_2 : k_1$ obtained at the mean temperature of the present study is 1 : 1·47 : 1·53. Most of the discrepancy is almost certainly due to the errors in the rate constants, although a small rate enhancement in the ethyl substituted isobutylboron compounds cannot be ruled out.

If the ratio $k_3 : k_2 : k_1$ is $Z : Y : 1$, the integrated rate equations[8] for the concentrations of BBu^i_3, $EtBBu^i_2$, and Et_2BBu^i can be written as (12)—(14). k_0 is thus given by equation (15). If $Y = \frac{2}{3}$ and $Z = \frac{1}{3}$, then $k_0 = Zk_1$ and hence the value for k_0 is time-invariant. The studies on the aluminium alkyls[1-3] and tri-isobutylgallium,[4] which were subject to smaller errors than the present study, showed no systematic variation in k_0 up to 96% conversion of alkyl groups. Therefore, in these systems, the rate-constant ratio does not differ greatly from 1 : 2 : 3. In the present study, from use of the rate-constant ratio obtained at the mean temperature, k_0 would be expected to increase with time. At 50% conversion of BBu^i_3 the theoretical value for k_0 is 10% greater than at low conversion, increasing to 20% at 80% conversion and 38% at 98% conversion. As Table 1 shows, this trend is generally masked by experimental errors. At the mean temperature of the study, $k_1/k_0 =$ 2·73 instead of 3, a deviation of 9%.

$$[BBu^i_3] = [BBu^i_3]_0 \exp(-k_1t) \qquad (12)$$

$$[EtBBu^i_2] = \{[BBu^i_3]_0[\exp(-k_1t) - \exp(-Yk_1t)]\}/(Y-1) \qquad (13)$$

$$[Et_2BBu^i] = [BBu^i_3]_0 Y\left(\frac{\exp(-k_1t)}{(Y-1)(Z-1)} - \frac{\exp(-Yk_1t)}{(Y-1)(Z-Y)} + \frac{\exp(-Zk_1t)}{(Z-Y)(Z-1)}\right) \qquad (14)$$

$$k_0 = -\frac{2{\cdot}303}{t}\log\left(\exp(-k_1t) + \frac{2\exp(-k_1t)}{3(Y-1)} + \frac{Y\exp(-k_1t)}{3(Y-1)(Z-1)} - \frac{Y\exp(-Yk_1t)}{3(Y-1)(Z-Y)} - \frac{2\exp(-Yk_1t)}{3(Y-1)} + \frac{Y\exp(-Zk_1t)}{3(Z-Y)(Z-1)}\right) \qquad (15)$$

The gas-phase studies of aluminium and gallium alkyls yielded only values for k_0. The Arrhenius parameters obtained are shown in Table 2. It appears that the transition state in the case of the tri-isobutylboron is looser than that for the aluminium and gallium alkyls. As theoretically k_1/k_0 should be a constant factor of 3, the lower limits for the Arrhenius parameters for k_0 are

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[9] S. W. Benson, 'The Foundations of Chemical Kinetics,' McGraw-Hill, New York, 1960, p. 91.

[10] F. M. Rossi, P. A. McCusker, and G. F. Hennion, *J. Org. Chem.*, 1967, **32**, 450.

probably to be preferred in the case of tri-isobutylboron. It appears that a decrease in the electropositive character of the central atom is paralleled by a decrease in the tightness of the transition state for olefin elimination.

TABLE 2

Activation parameters for olefin elimination from Group III metal alkyls

Compound	log A	E_a/kcal mol^{-1}	$\Delta G^{\ddagger}_{450}$ [a]/kcal mol^{-1}	Ref.
Tri-isobutylaluminium	$11{\cdot}2 \pm 0{\cdot}4$	$26{\cdot}6 \pm 0{\cdot}7$	30·2	1
Dimethyl-n-butylaluminium	$10{\cdot}9 \pm 0{\cdot}2$	$27{\cdot}8 \pm 0{\cdot}4$	32·7	3
Tri-isobutylgallium	$11{\cdot}6 \pm 0{\cdot}3$	$30{\cdot}4 \pm 0{\cdot}6$	33·2	4
Tri-isobutylboron	$12{\cdot}3 \pm 0{\cdot}5$	$31{\cdot}1 \pm 1{\cdot}0$	32·5	This work

[a] Corrected for path degeneracy.

The A factors in the Group III trialkyls are consistent with a 4-centre transition state.[1-3]

From the electrostatic model of Benson and Haugen [11] for 4-centre reactions, the activation energy depends on the energy required to form a quadrupolar-type transition state. This energy depends largely on the ground-state electrostatic energy and polarisability of the bonds involved. The difference in activation energy between isobutylaluminium and isobutylgallium may be rationalised on the basis of the difference in the ground-state dipoles of the metal–carbon bonds. On this basis, however, a larger difference in activation energy between isobutylgallium and isobutylboron would be predicted because of the greater electronegativity differences. However, the rate of elimination for tri-isobutylboron is *ca.* 2·2 times that for isobutylgallium. There is evidence for an appreciable π-character in the B–C bond [12] which would increase the polarisability and the effect of this term may be sufficient to overcome the ground-state dipole deficiency.

For detailed consideration of substituent effects in the Group III trialkylmetals, it is probably better to consider $\Delta G^{\ddagger}$ values at a mean temperature (450 K in this case) as these quantities are subject to less error than the derived Arrhenius parameters. The $\Delta G^{\ddagger}_{450}$ values (corrected for path degeneracy) in Table 2 show that in the trialkylaluminium series, the effect of an additional methyl group on the β-carbon atom is to decrease $\Delta G^{\ddagger}_{450}$ by 2·5 kcal mol^{-1}.

The only other gas-phase study of the elimination reactions of boron alkyls is that of the unimolecular decomposition of triethylboron with acetylene as a hydride trap.[13] In this work, the kinetics were obtained by assuming no further elimination from the initially formed vinyldiethylboron. This reaction almost certainly does perturb the kinetic results to some extent. The Arrhenius equation reported for the primary elimination was (16). After correcting for path degeneracy,

$$\log k_1/\mathrm{s}^{-1} = (11{\cdot}6 \pm 0{\cdot}6) - (33{\cdot}7 \pm 1{\cdot}2)/\theta \qquad (16)$$

$\Delta G^{\ddagger}_{450}$ for this elimination is 37·5 kcal mol^{-1} compared with 31·8 for the analogous step in the decomposition of tri-isobutylboron. The stabilising effect of a β-alkyl group is, therefore, (5·7)/2 kcal mol^{-1}, in good agreement with the value obtained from the aluminium alkyls. This indicates that the same effects are operative in the boron and aluminium systems. On this basis, we predict a value of *ca.* $30{\cdot}2 + 5 = 35{\cdot}2$ kcal mol^{-1} for $\Delta G^{\ddagger}_{450}$ for the elimination of ethylene from triethylaluminium. Work is in progress to test this prediction.

Thus we conclude that the eliminations of trialkylboron compounds, like those of other Group III metal alkyls, occur *via* similar polar 4-centre transition states, and a recent suggestion that transalkylations of alkylboron compounds occur not by an addition–elimination reaction but *via* a bimolecular displacement [14] cannot be supported. More information as to the nature of the polar transition state is given by the activation energy for the reverse reaction, the addition of olefin to the dialkyl hydride. Unfortunately, in the case of boron alkyls, there are few thermochemical data from which to estimate the heat of reaction.

From a consideration of group additivity trends in other elements,[15] and application of bond-additivity principles,[16] a range of -38 to -45 kcal mol^{-1} is obtained for ΔH_f° ($\mathrm{Bu^i_2BH}$). This yields a back-activation energy of 5—12 kcal mol^{-1}. The values for the analogous aluminium and gallium compounds are 6 and 10 kcal mol^{-1} respectively.

[1/1229 *Received, July 19th*, 1971]

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[16] A. E. Pope and H. A. Skinner, *J. Chem. Soc.*, 1963, 3704.