76. *The Thermal Decomposition of 2-Ethyldecaborane.*

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The kinetics of the thermal decomposition of 2-ethyldecaborane have been investigated for a static system in the temperature range 210—230° and at 2-ethyldecaborane pressures of 100—600 mm. Hg. The decomposition leads initially to decaborane and diethyldecaboranes; its rate is of the second order with respect to 2-ethyldecaborane; the activation energy is 39·5 ± 1 kcal./mole. In its later stages the reaction deviates from the second-order dependence owing to side reactions which lead to non-volatile solid hydrides, alkylated non-volatile solid hydrides, hydrogen, methane, and a little ethane. 1,2-Diethyldecaborane is always present in greater concentration than 2,4-diethyldecaborane. This and other results have been interpreted in terms of hyperconjugation of the alkyl group with the B–B σ-bonds.

2-ETHYLDECABORANE is obtained by gas-phase reaction of decaborane with ethyl bromide at 230°.[1] The reaction is complex. Yields are lower than denoted by the equation

$$EtBr + B_{10}H_{14} = B_{10}H_{13}Et + HBr \qquad (1)$$

owing to side reactions such as, for example, thermal decomposition of decaborane. The present work was concerned with a study of the thermal decomposition of 2-ethyldecaborane, in order to assess its importance in the synthesis. The decomposition has been investigated in the temperature range 210—230° and a mechanism is proposed below: several side reactions were also studied at 220°. The results lead to conclusions about the electron distribution in 2-ethyldecaborane.

EXPERIMENTAL

2-Ethyldecaborane and 1,2- and 2,4-diethyldecaborane, prepared by Friedel–Crafts ethylation of decaborane, were separated by preparative gas chromatography.[2] The 2-ethyldecaborane was shown to be 99% pure by oxidation with alkaline persulphate to boric acid.[3]

1,2- and 2,4-Diethyldecaboranes were incompletely separated by the preparative column; each was shown by gas chromatography to contain about 5% of the other.

Decaborane, m. p. 99·7°, was purified by crystallisation from hexane, followed by vacuum-sublimation.[1]

The scope of the investigation was limited by the availability of the reactants.

Experiments were carried out in 150 c.c. Pyrex vessels, which consisted of a reaction bulb and an entry tube, 15 cm. long, comprising a B.10 cone on the end of a 7-cm. stem of a B.14 cone. Liquid reactants were introduced into the weighed reaction vessel of known volume by means of an Agla pipette having an 18-cm. hypodermic needle; solid decaborane was introduced by means of a funnel which prevented the sides of the entry tube from being contaminated. After weighing, the bulbs were evacuated, sealed, and heated in an " Aroclor " bath.[1]

Experiments were carried out for varying times at 210°, 220°, and 230° and at initial 2-ethyldecaborane pressures of 100—600 mm. Some experiments were carried out at 220° on the side reactions, *e.g.*, 2-ethyldecaborane with decaborane, diethyldecaborane with decaborane, diethyldecaborane with 2-ethyldecaborane, and the decomposition of diethyldecaborane alone. The products were a mixture of polyethyldecaboranes, decaborane, polymerised polyethyldecaborane, non-volatile solid hydrides, and hydrogen, methane, and a little ethane. Decaborane was occasionally observed as needle-like crystals on the side of the cooled reaction vessel.

The products were analysed as follows. The gases were shown by mass spectroscopy to consist of hydrogen and methane, with a trace of ethane. Hydrogen was determined by pressure measurements after expansion of the gas into a known volume, the reaction vessel being immersed in liquid nitrogen. For samples from the later stages of the reaction a correction was made for the vapour pressure of methane at this temperature. Methane was

[1] Owen, *J.*, 1961, 5438.
[2] Blay, Dunstan, and Williams, *J.*, 1960, 430.
[3] Dunstan and Griffiths, *Analyt. Chem.*, 1961, **33**, 1598.

then determined by allowing the reaction vessel to warm either to carbon dioxide–acetone temperature or to room temperature.

The solid and liquid products were extracted with dry benzene, a known weight of naphthalene was added, and the composition of the solution was quantitatively determined by gas chromatography.[4] In all cases, only decaborane, 2-ethyldecaborane, and the two diethyldecaboranes were recovered. The higher ethylated decaboranes had large retention volumes and were present in too small a quantity to allow their accurate determination. The solids remaining after benzene-extraction were oxidised to boric acid and titrated against aqueous barium hydroxide.[3] This method of analysis gave ∼95% recovery of boron; the 5% loss has been attributed to triethyldecaborane and tetraethyldecaboranes which are almost certainly formed in the present work and have been identified in Friedel–Crafts ethylations of decaborane.[5]

RESULTS AND DISCUSSION

Course of the Reaction.—The course of the thermal decomposition of ethyldecaborane is illustrated in Fig. 1 by a set of results which summarises the fate of the 2-ethyldecaborane
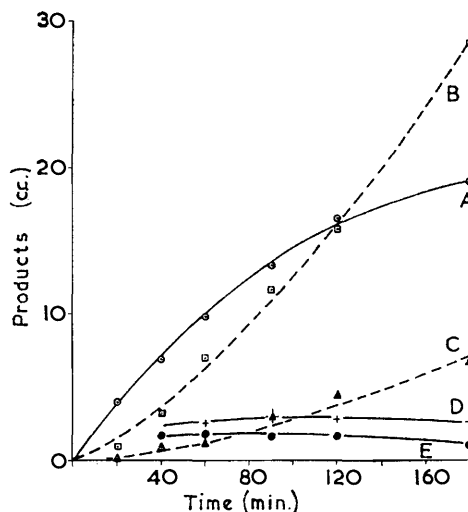

FIG. 1. Course of thermal decomposition of ethyldecaborane (200 mm.) at 210°.

(A) $C_{10}H_{13}Et$ used. (B) H_2. (C) CH_4. (D) $B_{10}H_{14}$. (E) $B_{10}H_{12}Et_2$.

at 210° and an initial decaborane pressure of 200 mm. In the initial stages of the reaction only small quantities of hydrogen and methane are produced, the main products being decaborane and diethyldecaboranes (2 pt. of 1,2- and 1 pt. of 2,4-diethyldecaborane). 2-Ethyldecaborane therefore decomposes according to the equation

$$2B_{10}H_{13}Et \rightleftharpoons B_{10}H_{14} + B_{10}H_{12}Et_2 \qquad (2)$$
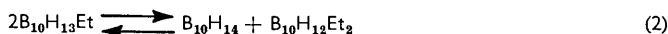
This is written as an equilibrium since 2-ethyldecaborane is a major product of the back reaction of decaborane with diethyldecaborane. At 220° the ratio of the rate of the forward to that of the back reaction leads to a value of 0·60 for the equilibrium constant for reaction (2).

As the reaction proceeds the yields of diethyldecaborane and of decaborane reach maxima. It will be shown below that these maxima result from the participation of side reactions.

Order of Reaction.—The usual second-order graphs of the ratio of 2-ethyldecaborane that reacted (x) to that unchanged ($a - x$) against the product of the initial partial pressure of 2-ethyldecaborane and time of reaction are shown in Fig. 2. The plots at each temperature, while falling on a smooth curve, refer to a range of initial pressures of 2-ethyl-decaborane, and show that the main reaction of the decomposition is of the second order.

[4] Blay, Williams, and Williams, *J.*, 1960, 424.
[5] Owen, unpublished work.

This is in agreement with the conclusion that equation (2) represents the initial step in the decomposition. The values of the rate constants k_1 obtained from the graphs are 6.1×10^{-5}, 1.34×10^{-4}, and 2.85×10^{-4} mm.$^{-1}$ min.$^{-1}$ at 210°, 220°, and 230°, respectively. Side reactions are responsible for the deviation from the usual second-order straight line and for formation of the other products.

Side Reactions.—It can be seen in Fig. 1 that only 25% of the carbon of the 2-ethyl-decaborane that reacted is recovered (as diethyldecaboranes or as methane). In the early stages of the reaction the percentage is much lower: *e.g.*, after 60 min., only 12%
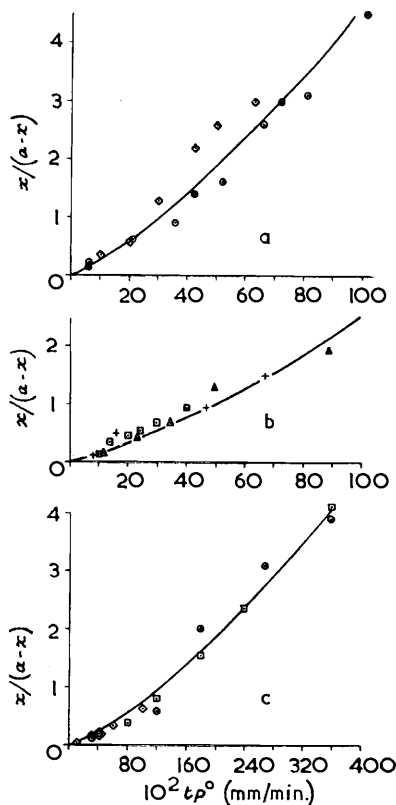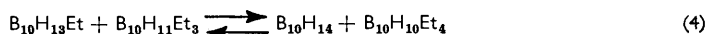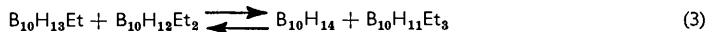

FIG. 2. Second-order plots for decomposition of ethyldecaborane at (a) 230°, (b) 220°, and (c) 210°.

Initial pressure ($p°$) of $C_{10}H_{13}Et$: $\diamond$ 100 mm. $\square$ 200 mm. o 300 mm. + 400 mm. $\triangle$ 50 mm. ● 600 mm.

of the carbon is recovered as methane. Polyalkylation must therefore occur according to the equations:

$$B_{10}H_{13}Et + B_{10}H_{12}Et_2 \rightleftharpoons B_{10}H_{14} + B_{10}H_{11}Et_3 \qquad (3)$$

$$B_{10}H_{13}Et + B_{10}H_{11}Et_3 \rightleftharpoons B_{10}H_{14} + B_{10}H_{10}Et_4 \qquad (4)$$

the higher ethylated decaboranes decompose by other routes more rapidly than 2-ethyl-decaborane. Thus, the experiments carried out at 220° with 150 mm. each of 1,2-diethyl- and 2-ethyl-decaborane gave polyethylated decaboranes, the former disappearing the more rapidly. Similar results were observed when 2,4-diethyldecaborane was used instead of the 1,2-derivative. Thermal decomposition of 2,4-diethyldecaborane yielded mainly polyethylated decaboranes and polymerised polyethylated decaborane with a 16% yield of 2-ethyldecaborane. No isomerisation of the 2,4- to 1,2-diethyldecaborane occurred. It is suggested that tetra-ethyldecaborane is the highest ethylated decaborane derivative formed in the reaction, since no higher alkylated derivative has been found in Friedel–Crafts alkylation products.

300 mm. each of decaborane and 2-ethyldecaborane react at 220° at a much faster rate than indicated by the thermal decomposition of each compound separately. The gaseous products consist of 95% of hydrogen, 4% of methane, and a little ethane. Presumably the main path of this reaction is condensation of decaborane with 2-ethyldecaborane in the 1- or 4-position:

$$B_{10}H_{14} + B_{10}H_{13}Et = B_{10}H_{13} \cdot B_{10}H_{12}Et + H_2 \qquad (5)$$
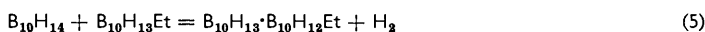
Hydrogen, besides being formed in the above reaction, is also known to be formed in the thermal decomposition of decaborane:[1]

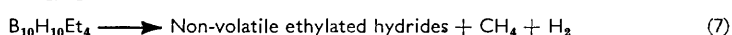$$2B_{10}H_{14} \longrightarrow B_{20}H_{26} + H_2 \longrightarrow \text{Non-volatile solid hydrides} + H_2 \qquad (6)$$
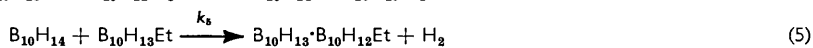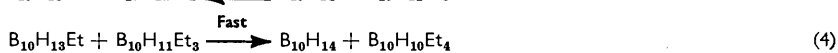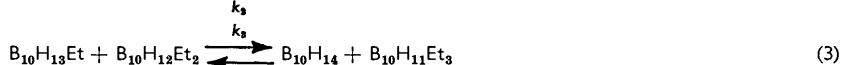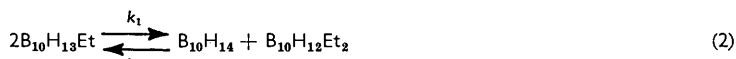
Since B–H bonds are the weakest bonds in ethyldecaboranes,[6] hydrogen is also the most likely product from the decomposition of the ethylated non-volatile solid hydrides.

Methane is not found in appreciable quantities until the later stages of the reaction; it must therefore result from a decomposition of the alkylated non-volatile solid hydrides. The mechanism of methane formation is probably similar to that which occurs in the pyrolysis of ethylbenzene,[7] *i.e.*, the side chain splits:
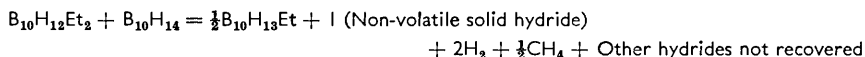
$$Ph \cdot CH_2 \cdot CH_3 \longrightarrow Ph \cdot CH_2 \cdot + CH_3 \cdot \longrightarrow CH_4$$
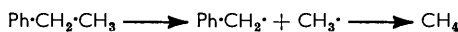
Bond dissociation energies of 89 kcal. for the B–C bond and 82·6 kcal. for the C–C bond[6] support this view and account for the low yields of ethane.

Mechanism.—The mechanism of the thermal decomposition of 2-ethyldecaborane may therefore be summarised by the equations:

$$2B_{10}H_{13}Et \underset{k_3}{\overset{k_1}{\rightleftharpoons}} B_{10}H_{14} + B_{10}H_{12}Et_2 \qquad (2)$$

$$B_{10}H_{13}Et + B_{10}H_{12}Et_2 \underset{}{\overset{k_3}{\rightleftharpoons}} B_{10}H_{14} + B_{10}H_{11}Et_3 \qquad (3)$$

$$B_{10}H_{13}Et + B_{10}H_{11}Et_3 \overset{Fast}{\longrightarrow} B_{10}H_{14} + B_{10}H_{10}Et_4 \qquad (4)$$

$$B_{10}H_{14} + B_{10}H_{13}Et \overset{k_5}{\longrightarrow} B_{10}H_{13} \cdot B_{10}H_{12}Et + H_2 \qquad (5)$$

$$B_{10}H_{14} \overset{k_4}{\longrightarrow} \text{Non-volatile solid hydrides} + H_2 \qquad (6)$$

$$B_{10}H_{10}Et_4 \longrightarrow \text{Non-volatile ethylated hydrides} + CH_4 + H_2 \qquad (7)$$

Calculations of the course of the reaction, with rate constants such that $k_5 \approx k_3 = 25\ k_1$, and k_4 values obtained previously,[1] led to the curves drawn in Fig. 2 and to the observed maximum yields of decaborane and diethyldecaborane. These rate constants are also consistent with the initial rates of disappearance of 2-ethyldecaborane obtained when reactions (3) and (5) were studied independently.

Experiments on the thermal decomposition of diethyldecaboranes have shown that this reaction can be neglected in the present system. Similarly, the back reaction between 1,2-diethyldecaborane and decaborane, which has a rate constant of $2·2 \times 10^{-4}$ mm.$^{-1}$ min.$^{-1}$, need not be considered. In this case the following stoicheiometric equation applies:

$$B_{10}H_{12}Et_2 + B_{10}H_{14} = \tfrac{1}{2}B_{10}H_{13}Et + I \text{ (Non-volatile solid hydride)}$$
$$+ 2H_2 + \tfrac{1}{2}CH_4 + \text{Other hydrides not recovered}$$

It illustrates the complexity of reactions of this type, showing that many side reactions must occur.

Activation Energy.—The Arrhenius plot leads to an activation energy of $39·5 \pm 1$ kcal./mole.

[6] Cottrell, " The Strengths of Chemical Bonds," Butterworths Scientific Publns., 2nd edn., London, 1958.

[7] Badger and Kimber, *J.*, 1961, 3407.

Effect of Alkylation on the Electron Distribution in Decaborane.—Moore, Lohr, and Lipscomb [8] have calculated the electronic structure of decaborane by a L.C.A.O. method modified by the bridge hydrogens. More recently, Moore [9] reinvestigated the treatment, assuming that the boron atom coulomb integrals were equal to the valence-state ionisation energies. The resulting electron distribution in the molecule is as shown. The excess of negative charge of $0.8e$ is contributed by the bridge hydrogen atoms. The calculation predicts the correct order of reactivity of the decaborane structure to electrophilic and nucleophilic attack. Thus the reaction of decaborane with ethyl bromide yields initially 2-ethyldecaborane.[1] Further ethylation of 2-ethyldecaborane, however, results in a predominance of 1,2-diethyldecaborane.[5] Similar results have been reported for methylation;[10] in the present work the ratio of 1,2- to 2,4-diethyldecaborane was $\sim 2 : 1$. These results allow us to infer in what way the distribution of electrons in the 2-ethyldecaborane molecule is altered from that in the decaborane molecule.
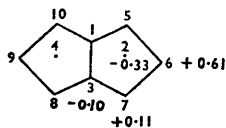
If it did not differ 1,2-diethyldecaboranes would be more reactive than 2,4-dialkyldecaboranes and, in consequence, would be present in much smaller concentrations than 2,4-derivatives. Alkyl substitution (especially in the 2-position) must therefore significantly change the charge distribution in the B_{10} nucleus. Presumably the alkyl group hyperconjugates with the σ-bonds in decaborane skeleton and activates the 1,3-positions to such an extent that they rival the reactivity of the 4-position. Hyperconjugation effects of this type would also activate the 5-, 7-, 8-, and 10-positions and would explain the presence of 1,2,3,5(or 8)-tetramethyldecaborane which has been identified in the products of a Friedel–Crafts methylation at 80°.[10]

[8] Moore, Lohr, and Lipscomb, *J. Chem. Phys.,* 1961, **35**, 1329.
[9] Moore, *J. Chem. Phys.,* 1962, **37**, 675.
[10] Williams, Dunstan, and Blay, *J.,* 1960, 5006.