

A GAS-CHROMATOGRAPHIC STUDY OF THE DIBORANE PYROLYSIS

K. BORER*, A. B. LITTLEWOOD† and C. S. G. PHILLIPS
Inorganic Chemistry Laboratory, Oxford

(Received 26 January 1960)

Abstract—The use of gas-liquid chromatographic techniques for the study of volatile reactive inorganic substances is illustrated by an investigation of diborane pyrolyses over a range of temperature from 50 to 188°C.

WHEN diborane is heated alone at temperatures between about 70 and 200°C, it decomposes slowly into hydrogen, a mixture of more complex volatile hydrides, and a solid polymer of variable composition.⁽¹⁻³⁾ The reaction has been followed by the rise in pressure,^(2,3) by the pressure of hydrogen produced, and by mass-spectrometry.⁽³⁾ This paper describes the study of the reaction by gas-liquid chromatography. This method of analysis is particularly suitable for the detection and determination of small amounts and small proportions of volatile substances. Its use for the separation of boron hydrides has been reported by LITTLEWOOD⁽⁴⁾, and by KAUFMAN *et al.*⁽⁵⁾

APPARATUS AND EXPERIMENTAL TECHNIQUE

Chromatographic apparatus. This was similar to that already described.⁽⁶⁾ Column and katharometer were contained in a vapour jacket, which for the analysis of boron hydrides contained ether at 34.5°C. Oxygen-free nitrogen, dried with magnesium perchlorate, was used as carrier gas. Since the various reaction products are easily separated, only a short column is required, and indeed a short column is desirable in order to avoid long residence times for unstable hydrides within it. In most of the analytical work, the column was 40 cm in length, 5 mm internal diameter, and contained 0.59 g of Silicone 702 (Midland Silicones Ltd.) supported on 1.47 g. of Celite 535 (Johns-Manville). A column capable of handling up to about 0.5 g of crude diborane per run was also used to purify the diborane used for the pyrolyses; it was 150 cm in length, 12 mm internal diameter, and contained 18.9 g of Silicone 702 on 47.1 g of Celite.

Apparatus. Crude diborane was prepared by the method of SCHLESINGER *et al.*⁽⁷⁾ The apparatus for the preparation, purification and pyrolysis of diborane, and for the analysis of reaction products was arranged so that all handling was carried out *in vitro*, either *in vacuo* or in a stream of the carrier gas (Fig. 1). Pyrolyses were performed in a glass vessel A of about 500 ml capacity, held at the required temperature by a vapour jacket. As pyrolysis proceeded, samples were collected at known intervals in the previously-evacuated sampling vessel B, which was small (about 10 ml) compared to A, and though the abstraction of each sample produced a measurable drop in the pressure measured by the manometer C, it did not sensibly change the rate of reaction. The sample in B was frozen at liquid oxygen temperature, and hydrogen was pumped off; the remainder was then transferred *in vacuo* to the trap D. The normal path of the carrier gas is through stopcocks G, H and I. The sample

* Present address: Imperial Chemical Industries, Billingham.

† Present address: Department of Chemistry, University of Durham, Newcastle-upon-Tyne.

(1) A. STOCK, *Hydrides of Boron and Silicon*. Cornell University Press (1933).

(2) R. P. CLARKE and R. N. PEASE, *J. Amer. Chem. Soc.* **73**, 2132 (1951).

(3) J. K. BRAGG, L. V. MCCARTY and F. J. NORTON, *J. Amer. Chem. Soc.* **73**, 2134 (1951).

(4) A. B. LITTLEWOOD, *Analyst*, **81**, 55 (1956).

(5) J. J. KAUFMAN, J. E. TODD and W. S. KOSKI, *Analyt. Chem.* **29**, 1032 (1957).

(6) A. B. LITTLEWOOD, C. S. G. PHILLIPS and D. T. PRICE, *J. Chem. Soc.* 1480 (1955).

(7) H. I. SCHLESINGER, H. C. BROWN, J. R. GILBREATH and J. J. KATZ, *J. Amer. Chem. Soc.* **75**, 195 (1953).

was introduced to the column by operating G, H and E so that carrier gas was deflected to sweep out D. After passage through the column, components were trapped at liquid oxygen temperature either separately (traps L, M, N and O) or together (trap J). Individual hydrides could then be transferred *in vacuo* to other analytical apparatus when required. When all the components were condensed together at the outlet of the column, the chromatogram could be repeated by removing the liquid oxygen and reversing the flow of carrier gas by turning G and I. In cases where there was not time to chromatograph one sample before taking another, it could be transferred *in vacuo* to storage traps (not shown) and chromatographed later.

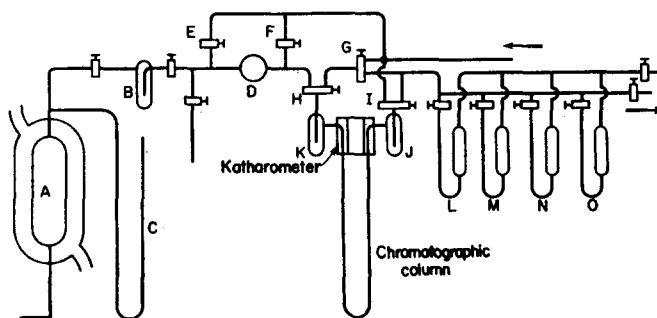


FIG. 1.—Diagram of apparatus.

Analytical methods. Three methods were used to identify the components emerging from the column.

(a) *Complete pyrolysis.* The component producing a peak was heated to bright red heat in a thick Pyrex tube, and the number of hydrogen atoms produced per molecule of the component determined from the rise in pressure.

(b) *Hydrolysis.* Diborane was analysed by hydrolysis, followed by measurement of the volume of hydrogen produced.

(c) *Microeffusimetry.* A microeffusimeter similar to that of NASH⁽⁸⁾ was used to determine the molecular weights of components. Calibration with substances of known molecular weights showed that molecular weights could be determined with an accuracy of 2 per cent (mean deviation), as claimed by NASH; by careful adjustment so that the apparatus worked at the lowest possible pressures, the molecular weights of quantities down to six micromoles could be determined.

EXPERIMENTAL RESULTS

Chromatographic results. In general, the chromatogram obtained from a pyrolysed sample of diborane had four peaks, as in the example shown in Fig. 2. These were identified in order of increasing retention volume as diborane, tetraborane, penta-borane and dihydropentaborane. Specific retention volumes⁽⁹⁾ (V_g values⁽⁶⁾) for Silicone 702 oil at 34.5°C were found to be 12, 65, 254 and 355 ml g⁻¹.

In order to determine whether any hydrides were decomposing in the column, samples of mixed boron hydrides were passed back and forth through the column, using the reversing procedure described above, and the areas of the peaks on each successive chromatogram were measured. In the case of diborane, tetraborane and pentaborane, no decrease in area occurred in at least six passages through the column. However with dihydropentaborane, successive passages led to a diminution in area of 10 ± 2 per cent per passage. This corresponds to a half-life of the order of 100 min for dihydropentaborane in the column at 34.5°C. When pure dihydropentaborane was run back and forth, small peaks corresponding to tetraborane and pentaborane were

⁽⁸⁾ L. K. NASH, *Analyt. Chem.* **20**, 258 (1948).

⁽⁹⁾ D. AMBROSE, A. I. M. KEULEMANS and J. H. PURNELL, *Analyt. Chem.* **30**, 1582 (1958).

observed on the second passage and grew after succeeding passages. Since none appears after the first passage, the decomposition occurs in the column and not in the katharometer, through the reference half of which pure dihydropentaborane must pass on its first passage through the column. In contrast to the results of KAUFMAN *et al.*⁽⁵⁾ we do not find that the decomposition of dihydropentaborane is too rapid to be able to make measurements, and we find no diborane in the decomposition products. Recently BOONE and BURG⁽¹⁰⁾ have shown that the decomposition of dihydropentaborane in

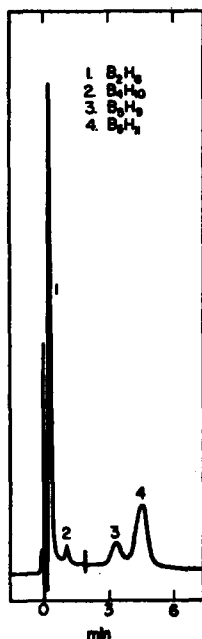


FIG. 2.—A typical chromatogram.

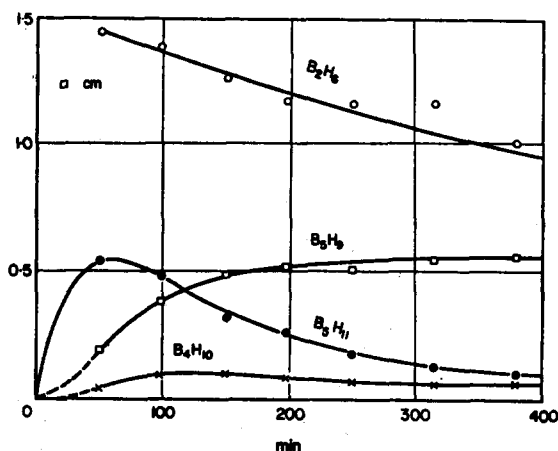


FIG. 3.—Pyrolysis of B_5H_9 at $111^\circ C$. Chromatogram peak areas plotted against time.

the condensed phase at low temperatures is sharply affected by liquid catalysts, especially if they are basic, and this may account for the differences in the behaviour of dihydropentaborane.

Kinetic results. Diborane was pyrolysed at temperatures ranging from 50 to $188^\circ C$. At $50^\circ C$ no reaction could be detected after 5 hr. At higher temperatures the reaction, was easily measurable, and was directly demonstrable by the continuously increasing pressure in the pyrolyser. Samples were abstracted at intervals and chromatographed, and the areas of the peaks of diborane and of the higher hydrides were plotted against time. In general the plots resembled that in Fig. 3, which gives the results for $111^\circ C$. The area of a peak due to any one hydride is proportional to its mass, and the proportionality constants between area and mass could be shown to be very approximately the same for B_4H_{10} , B_5H_9 and B_5H_{11} , so that the areas in Fig. 3 are approximately proportional to weight proportions. At the same time as the higher hydrides were formed, hydrogen was produced, together with crystals of a slightly volatile compound (presumably decaborane) which condensed in the cool tubes leading to the pyrolyser, and a yellow deposit which collected largely on the bottom of the pyrolyser.

⁽¹⁰⁾ J. L. BOONE and A. B. BURG, *J. Amer. Chem. Soc.* **80**, 1519 (1958); **81**, 1766 (1959).

The effect of increase in temperature was to compress the abscissa of Fig. 3 but not to alter the overall shape of the curves. The first product of pyrolysis is always dihydropentaborane, and though only a few runs showed dihydropentaborane without any pentaborane or tetraborane, the plots of the type shown in Fig. 3 suggest that B_5H_{11} is the only hydride which is formed initially. Measurements from plots of composition against time show that the rate of formation of pentaborane is almost exactly proportional to the concentration of dihydropentaborane, and that the same is true of tetraborane up to the shallow maximum in its concentration. At 157°C pentaborane is completely stable for at least 1 hr, but at 188°C it reaches a maximum concentration after about 25 min, the concentration declining thereafter. At this temperature, if any dihydropentaborane is formed in the early stages of the reaction, its concentration has fallen below the level of detection by the time the first sample was taken. The activation energy of the reaction was measured from the rate of increase of pressure at different temperatures and found to be $29 \text{ kcal mole}^{-1}$.

The effect of increase in the initial pressure of diborane was to expand the ordinate of Fig. 3, but not to alter the overall shape of the curves. Pressures from about 12 to 60 cm of diborane were used, and at 111°C the order of the reaction was found to be 1.5 ± 0.1 .

The kinetic results are in general agreement with those of BRAGG *et al.*⁽³⁾ The gas chromatographic analyses however give a more complete picture than the mass-spectroscopic data, showing for example a considerable proportion of tetraborane throughout the reaction.

Acknowledgements—One of us (A. B. L.) is indebted to the Department of Scientific and Industrial Research for a maintenance grant and to the Harmsworth Trust, Merton College, for a senior scholarship. We thank Imperial Chemical Industries for the loan of a recorder.