

labels each contribution and optionally prints out either the entire calculated and labeled mass spectrum or just the monoisotopic fragmentation pattern.

Conclusion.—One most important feature of the method in which the appearance potential data on fragments from the boron hydrides are treated in order to calculate ionization potentials is that it is quite independent of the correct bond structure of the original parent boron hydride. All that is postulated is what particular types of bonds rupture on electron impact and what other types of bonds are formed or rearranged. If the original structure of a parent boron hydride should prove to be different from the one accepted now, this would in no way alter the calculations performed. Also, if the principle of the constancy of the bond energies of B—H terminal or B—H—B bridge bonds or B—B or B—B—B bonds should prove to be only an approximately valid assumption, the calculations for the potentials are set up in such a way that it will be a simple matter to insert the modified bond energy.

When more independent data become available on heats of formation of the boron hydrides themselves and then heats of formation of some of the fragments, it will become possible to check the validity of some of the assumptions in the calculations of their ionization potentials.

The method employed does seem to have given

quite self-consistent results for the boron hydrides and BY_3 compounds and should prove generally applicable to any other types of compounds, most particularly aluminum, silicon and phosphorus compounds in which there is a great deal of interest and a great scarcity of thermochemical data.

It is postulated that there is a similarity between processes which take place in ionization and fragmentation mass spectroscopically and those which may take place in radiation studies. Calculations performed on the boron hydrides where there are so few independent thermochemical data available necessitated development of general procedures for interpretation of such processes, and these may aid in interpreting the mass spectra and radiation studies of compounds for which there are so few other data.¹⁷

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(17) W. F. Libby, *J. Chem. Phys.*, **35**, 1714 (1961).

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On the Nature of Some Higher Boron Hydrides Produced in Radiation-Induced Reactions in Penta- and Decaborane¹

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The mass spectra of the solid products produced by deuteron irradiation of mixtures of various known boron hydrides reveal several groups of peaks attributed to some new higher hydrides of boron. Small amounts of these hydrides were obtained by separation in a vapor-phase chromatograph. The mass spectra of the isolated materials yield molecular weights which suggest that these new higher hydrides are produced by the coupling of smaller polyhedral units. The irradiation of pure pentaborane-9 and decaborane-14 is shown to produce two new hydrides identifiable from their mass spectra as decaborane-16 and icosaborane-26.

Introduction

Three years ago, Schmied and Koski³ reported some results on products obtained from proton radiation-induced reactions in pentaborane-9. Indication was obtained that at least some of the higher hydrides of boron were produced by the coupling of two simpler polyhedral boron hydride molecules. For example, evidence was obtained that two pentaborane-9 units could couple across the apical borons to produce a decaborane different in structure from decaborane-14. Mass spectroscopic measurements which were made at a variety of laboratories were used for the analyses. Unfortunately, only small amounts of materials were available and since the compounds were not

separated and also contained small amounts of organic impurities, the results obtained were not completely unambiguous. Recently, with the acquisition of appropriate instrumental facilities in our laboratories, we have resumed our activities in this field. This paper is a brief summary of our exploratory results to date on the products obtained by deuteron irradiation of mixtures of several volatile hydrides, of pentaborane-9, and of decaborane-14. In this study many of the earlier results are confirmed and extended.

Experimental

The mass spectra were made on a Consolidated Electrodynamics Mass Spectrometer Model 21-103C supplied with a heated inlet system. The mass ranges scanned are as indicated in Figs. 1 and 2 using a slit on the collector of 7 mil width. The temperature of both the inlet system and gold leak were maintained at 100°. The hydride vapors were admitted to the expansion volume by heating the solids to 95° in the external sample outlet with a small tubular

(1) This work was done under the auspices of the United States Atomic Energy Commission and the National Science Foundation.

(2) Lever Brothers Company Foundation Fellow.

(3) H. Schmied and W. S. Koski, Abstracts of Papers, 135th Meeting of ACS, 1959, p. 38-M.

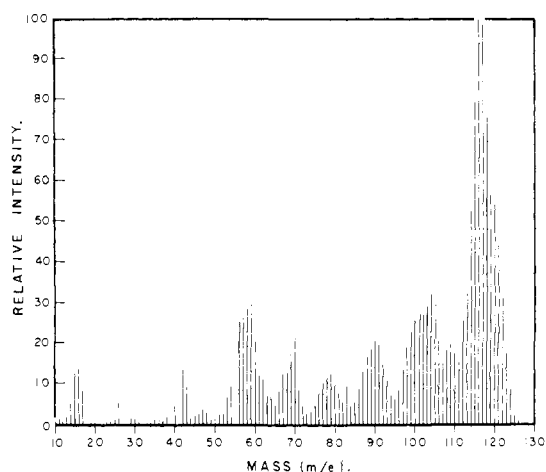


Fig. 1.—Complete mass spectrum of decaborane-16 produced by deuteron irradiation of pentaborane-9; the spectrum is normalized so that m/e 116 = 100.

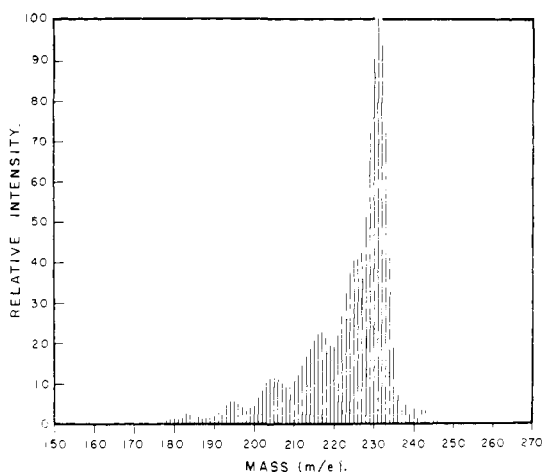


Fig. 2.—Partial mass spectrum of icosaborane-26 produced by deuteron irradiation of decaborane-14, including the mass range from 178 to 246; the spectrum is normalized so that m/e 231 = 100.

furnace. Pressures in the expansion volume obtained were in the 30 to 100 μ range.

The vapor-phase chromatograms were obtained from a Barber-Colman Chromatograph Model 21 with an argon detector and using silicone oil as the liquid phase. Chromatograms were made under a large variety of operating conditions. The chromatogram in Fig. 3 was made under the following conditions: Argon flow rate, 60 ml./min.; column temperature, 157°; flash heater, 250°; detector block, 190°; detector voltage, 800 volts.

The hydrides were introduced as solids or they were dissolved in Skellysolve and injected by a hypodermic needle into the stream of flow gas by standard techniques. The various separated components were diverted from the leak-proof detector block by a small heated and insulated tube maintained at 180° into a U-tube immersed in a slush bath maintained at -120°. The collected sample was then admitted to the mass spectrometer for identification.

The irradiation of the hydrides was carried out in special Pyrex cells in our electrostatic generator. A 0.1 μ amp. deuteron beam at 2 Mev. was used as the source of radiation. The time of irradiation varied from 30 min. to one hour. The cell used consisted of a 400 cc. Pyrex vessel connected to a brass flange by means of a Kovar to glass seal. It could be evacuated by means of a Hoke high vacuum metal valve. A nickel foil of 0.0001 in. thickness was used as the window for the deuterons. The cell was evacuated and filled with pentaborane vapor at 20 cm. pressure or with

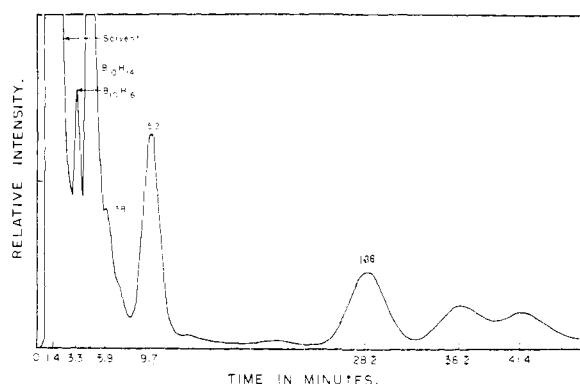


Fig. 3.—Vapor phase chromatogram of the mixture of solid products produced by deuteron irradiation of a mixture of B_2H_6 , B_4H_{10} , and B_5H_9 ; the argon flow rate is 60 ml./min. and the column temperature is 157°.

solid decaborane or with mixtures of the various volatile hydrides under a total pressure of 20 to 30 cm. A typical mixture of volatile hydrides under a total pressure of 25 cm. is 70% B_2H_6 , 25% B_4H_{10} , and 5% B_5H_9 .

In the case of the irradiation of $B_{10}H_{14}$, the cell was maintained at 100° so that the $B_{10}H_{14}$ was in the molten state. Following the irradiation, the remaining volatile hydrides and H_2 were pumped off and the solid hydrides analyzed in the mass spectrometer by methods described above.

Results and Discussion

When gaseous pentaborane-9 was irradiated with ionizing radiation such as protons or deuterons, solid boron hydrides were deposited on the walls of the reaction vessel. This material was subjected to a gas chromatographic separation, and the compound causing the single large peak in the chromatogram was collected from the exit flow and analyzed in a mass spectrometer. The high mass cut-off was found to be 126. Larger amounts of this material were purified by sublimation and its complete mass spectrum is illustrated graphically in Fig. 1. No observable amount of decaborane-14 was detected. Undoubtedly, other higher boron hydrides were present but presumably their volatility was sufficiently low to preclude observation under the experimental conditions. The boron hydride with molecular weight 126 is decaborane-16, a hydride formed by coupling of two pentaborane-9 units as proposed by Schmied and Koski,³ and whose structure was recently determined by Lipscomb and co-workers.⁴ The latter investigators produced the material by an electrical discharge process and have demonstrated that decaborane-16 does indeed correspond to two pentaborane-9 tetragonal pyramids connected by a B-B bond through the apical borons.

The idea that at least some of the higher hydrides of boron were made up of simpler boron hydride polyhedral units bonded through a boron-boron (or hydrogen bridge) linkage is an attractive one. Consequently, a search is being made to see if such coupling reactions may be more general.

Another experiment that was performed and which has some further bearing on this subject was the deuteron irradiation of molten decaborane-14. Mass spectroscopic analysis of the resulting

(4) Russell Grimes, F. E. Wang, Ruth Lewin and W. N. Lipscomb, *Proc. Natl. Acad. Sci. (U. S.)*, No. 7, July (1961).

products showed that the high mass cut-off point was 246 corresponding to icosaborane-26 or $B_{10}H_{13}$ - $B_{10}H_{13}$, two decaborane units coupled by a B-B bond. A typical mass spectrum is shown in Fig. 2. No mass peaks higher than 246 were observed although one might expect such coupling reactions to continue further. However, the volatility of the products presumably would be too low to observe mass spectroscopically under our conditions.

During the course of these studies, it was found that if a mixture containing diborane-6, tetraborane-10 and pentaborane-9 was irradiated with deuterons, both liquids and solids of low volatility were formed in the cell. The volatile hydrides remaining after irradiation contain small amounts of hexaborane-10 in addition to the starting materials. When the resulting solids or solutions of the solids were introduced into the gas chromatograph, results such as the ones in Fig. 3 were obtained. Mass spectroscopic measurements showed several groups of peaks displaying shapes characteristic of boron hydrides. The m/e values ranged from 10 to 246 and included decaborane-14. It was possible to collect some of the individual separated materials by trapping them from the exit flow gas and then to analyze them mass spectroscopically. The identity of the peaks or their

mass cut-offs are indicated in the figure. In addition to the m/e 's indicated above, 226 has also been observed. It therefore appears that there is a host of boron hydrides with molecular weights greater than decaborane which appear to possess reasonable stabilities and which are amenable to study by modern techniques.

In conclusion, therefore, just as it is possible under appropriate conditions to couple two pentaborane-9 molecules to form decaborane-16, two decaborane-14 molecules can be combined to give icosaborane-26. In addition, some of the hydrides with molecular weights between 126 and 246 also show some indication of this type of coupling behavior. For example, mass 138 could correspond to a pentaborane-9 and hexaborane-10 joined by a B-B bond across the apical borons, and 186 may result from a decaborane-14 and a pentaborane-9 combination. The evidence in the latter cases, of course, is not as convincing as in the former cases; however, it is suggestive. It is planned to explore these indications further by irradiation of other purified boron hydrides and by studies of some of the purified crystalline products.

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The Photoöxidation of 2,2'-Azoisobutane at 25°

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A rate study of the photoöxidation of 2,2'-azoisobutane has been made in an oxygen-rich atmosphere at 25°. Long-path infrared spectrophotometry was used to identify the major products of the *tert*-butyl free radical-oxygen reaction as acetone, formaldehyde, *tert*-butyl hydroperoxide and *tert*-butyl alcohol; methanol and carbon dioxide were minor products. Reasonably good mass balances were obtained. From a consideration of the initial rates of product formation and azoisobutane disappearance, a detailed mechanism was proposed. The results suggested that for this oxygen-rich system at 25° the radical-radical disproportionation reactions are the origin of hydroperoxide and alcohol products, and that H-abstraction from azoisobutane, formaldehyde or other H-containing products in the system was unimportant here. The rate data are consistent with a value of about 5 sec.⁻¹ for the first-order rate constant for the decomposition of the *tert*-butoxy radical at 25°.

Our knowledge of the nature of the products and the reactions of alkyl free radicals in an oxygen-rich atmosphere at 25° is very limited today. Air pollution workers and health authorities are particularly concerned with this information as it bears on the light-initiated free radical oxidations in auto-exhaust-polluted atmospheres. It is not uncommon for an investigator to suggest mechanisms for the oxidation of alkyl free radicals for the low temperature, oxygen-rich systems by extrapolation of high temperature oxidation results obtained from the combustion of near stoichiometric mixtures of hydrocarbons and oxygen. Results obtained with the simple methyl radical show that this procedure may lead to the incorrect mechanism choice.¹⁻³ For example, the methyl peroxy

radical formed in the oxidation of methyl radicals at 25° in oxygen-rich media does not take part in the H-abstrating reactions generalized by 1, although reactions of this sort are often suggested as dominant chain-propagating reactions in high temperature combustions. The hydroperoxide

$$CH_3O_2 + RH \longrightarrow CH_3OH + R \quad (1)$$

formed in this system is derived from radical-radical interactions.

The mechanism of oxidation of the higher alkyl free radicals in oxygen-rich media at 25° has received little attention. Quantitative studies are very difficult since the complex mixture of reaction products may contain many compounds of high reactivity so that the conventional analytical procedures cannot be used. The success of the long-path infrared techniques in the previous studies of the methyl radical reactions¹⁻³ encouraged us to extend the method to the more complicated *tert*-butyl radical system. A very complex mixture of reaction products is expected

(1) N. R. Subbaratnam and J. G. Calvert, Chapter 7, "Chemical Reactions in the Lower and Upper Atmosphere," Interscience Publishers, Inc., New York, N. Y., 1961, p. 109.

(2) N. R. Subbaratnam and J. G. Calvert, *J. Am. Chem. Soc.*, **84**, 1113 (1962).

(3) D. F. Dever and J. G. Calvert, *ibid.*, **84**, 1362 (1962).