

a 360 $m\mu$ band became evident. With 10% *sec*-butyl bromide, irradiation produced bands at 610 and 360 $m\mu$. Illumination caused the first to shift to 580 $m\mu$ but the second remained unchanged.

Discussion

The description of competitive electron attachment by two solutes according to eq. 1-4 requires that all electrons capable of attachment by solute molecules will, in fact, be attached by one solute or the other. As a matter of convenience the concentration of biphenyl, the reference solute, should be constant and sufficient to attach all electrons even when no second solute is present. Reference to Fig. 1 demonstrates that 0.2 mole % biphenyl fulfills this condition.

Analysis of data for the 680 $m\mu$ absorption in alkane-alkene systems indicates: (1) this band appears only when 2-methylpentene-1 is present; (2) it is enhanced by addition of known electron acceptors and increases in intensity when their concentration increases; (3) the presence of a substance of low ionization potential and high proton affinity, such as triethylamine, prevents the formation of this band even if large amounts of an electron acceptor, such as methyl chloride, are present. Consistent with these facts and with others is the assignment of the 680 $m\mu$ band to a cation of 2-methylpentene-1.

In systems containing iodine, hydrogen iodide, or organic iodides the band at 390 $m\mu$ can be assigned to I^- . The anionic character of the color center at 390 $m\mu$ is attested by its failure to appear when methyl chloride is present and by its enhancement when the electron band, in the run with diiodobenzene, was

optically bleached. Moreover it corresponds to an absorption threshold at 404 $m\mu$ for I^- in the gaseous state which has been reported recently.⁸

The marked effect of methyl iodide concentration upon the spectrum of radiation products, shown in Fig. 6, suggests an aggregation of permanent dipoles in the nonpolar medium which may be pronounced at low temperature. Single and dimeric (or higher) molecular aggregates of methyl iodide could give rise to various products with relative yields depending upon concentration.

The run with *p*-diiodobenzene tests this possibility since it is nonpolar, and extensive aggregation of molecules in glasses at -196° is less likely than for methyl iodide. Hence, products involving two or more atoms of iodine, *e.g.*, I_2 , I_2^- , or I_2^+ , are less likely. In fact, one band at 390 $m\mu$ was detected in the 350-800 $m\mu$ region.

The band at 430 $m\mu$ in glasses containing methyl iodide does not appear with other alkyl iodides. It is a cationic color center since addition of methyl chloride enhances O.D.₄₃₀ while toluene decreases it. The bands at 530 and 765 $m\mu$ appear to arise from different species since carbon tetrachloride did not enhance O.D.₅₃₀ and O.D.₇₆₅ proportionately. The species absorbing at 430 $m\mu$ both decomposes spontaneously and undergoes photolysis to form the other two color centers (Fig. 8 and 9).

Acknowledgment.—We are indebted to Mr. James B. Gallivan for gas chromatographic analyses.

(8) R. S. Berry, C. W. Reimann, and G. N. Spokes, *J. Chem. Phys.*, **37**, 2278 (1962).

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Gas Phase Radiolysis of Pentaborane-9¹

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Mass spectral analysis of the products produced by deuteron irradiation of pentaborane-9 shows that hydrogen, diborane, and decaborane-16 are formed in addition to polymeric materials. As a result of experiments involving the use of deuterium as a tracer, the rare gases as sensitizing agents, and iodine as a scavenging agent, a mechanism is proposed in which it is postulated that BH_3 , which is produced by the radiation fragmentation of B_5H_9 molecules, abstracts hydrogen in stepwise fashion from pentaborane-9, giving BH_3 and B_3H_3 radicals. BH_3 dimerizes to give diborane and two B_3H_3 radicals couple to give decaborane-16.

Introduction

In previous studies, Schmied and Koski³ and Hall and Koski⁴ reported that when certain boron hydrides are exposed to ionizing radiation such as protons or deuterons, new products are formed as a result of the coupling of hydride fragments. When pentaborane-9 is irradiated, decaborane-16 is produced, and when decaborane-14 is irradiated, icosaborane-26 ($B_{20}H_{26}$)⁴ is produced. These studies were limited to the synthetic aspect of the reactions and no details of the radiation and chemical processes involved were reported. In the present study, attention is primarily directed

to the radiation chemistry of the system. The *G*-values of the various products, the influence of iodine as a scavenging agent, and the effect of rare gas sensitization are reported and a mechanism is suggested.

Experimental

The irradiations were performed with 2-Mev. deuterons from an electrostatic generator. The irradiation cell was constructed of Pyrex tubing with a volume of about 125 cc. and it was attached by means of a Kovar seal to a brass flange which in turn was bolted to the accelerator. The cell window was 0.0001 in. thick nickel foil. The dose delivered to the sample was measured by ethylene dosimetry.⁵ *G* = 1.2 at 20 cm. pressure of ethylene was taken as a reference point.

The pentaborane-9 was purchased from the Callery Chemical Corp. and was purified by trap-to-trap distillation until mass spectroscopic analysis revealed no significant impurities. Matheson research grade rare gases were used. The deuterium (purity

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

(2) At present a postdoctoral fellow at the National Bureau of Standards.

(3) H. Schmied and W. S. Koski, Abstracts of Papers, 135th National Meeting of the American Chemical Society, 1959, p. 38M.

(4) L. H. Hall and W. S. Koski, *J. Am. Chem. Soc.*, **84**, 4205 (1962).

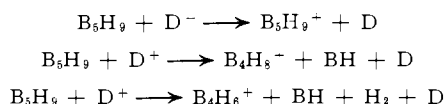
(5) M. C. Sauer and L. M. Dorfman, *J. Phys. Chem.*, **66**, 322 (1962).

>99.5%) was obtained from the Stewart Oxygen Co. and the iodine used for scavenging was Fisher certified reagent.

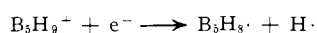
The irradiation cell was connected to a vacuum system. After irradiation the noncondensable products were removed from the cell by means of a Toepler pump. The condensable products were separated by distillation at low temperatures. The analysis of the products was made with a CEC 21-103 C mass spectrometer.

Results and Discussion

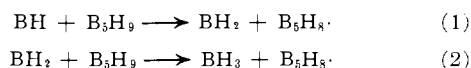
Typical results obtained when pentaborane-9 was irradiated with 2-Mev. deuterons are illustrated graphically in Fig. 1. The G -values rise with pressure, go through a maximum, and then level off in a pressure-independent region from 11 to 20 cm. of pentaborane-9. This behavior is not uncommon in radiation chemistry.^{5,6} Under these conditions, *i.e.*, at 15 cm. B_5H_9 pressure, only 5% of the pentaborane in the cell is destroyed on irradiation. It is clear from the nature of the products that the pentaborane-9 molecule has been fragmented and simpler boron hydrides such as diborane are produced. When energetic deuterons enter the cell, they are moderated by numerous collisions with the pentaborane-9 and, as a result of this exchange of kinetic energy, a certain, presumably small, amount of dissociation of the pentaborane-9 takes place to produce radicals such as $B_5H_8\cdot$. A more important interaction between the deuterons and pentaborane-9 molecules is charge exchange. Since the ionization potentials of atomic deuterium and B_5H_9 are 13.5 and 10.5 e.v., respectively, there is sufficient energy not only to ionize the B_5H_9 but also to produce a certain amount of fragmentation. Charge exchange reactions such as the following are reasonable ones.



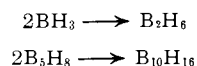
Such ionic species produced in this manner may undergo neutralization reactions such as



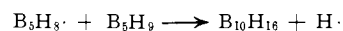
and the recombination of the $B_5H_8\cdot$ radicals may lead to one of the products, *i.e.*, decaborane-16. However, it is believed that radicals more important to the production of the observed products are produced by the abstraction of hydrogen from pentaborane-9 molecules as



The various free radicals and fragments can recombine giving their excess energy to the wall or to a molecule as



The process



is energetically less favorable.

This mechanism is consistent with the observed ratio of the G -values of diborane and decaborane-16. For every BH_3 produced there are two $B_5H_8\cdot$ units also produced according to eq. 1 and 2. Assuming, however,

(6) F. W. Lampe, *Radiation Res.*, **10**, 691 (1959).

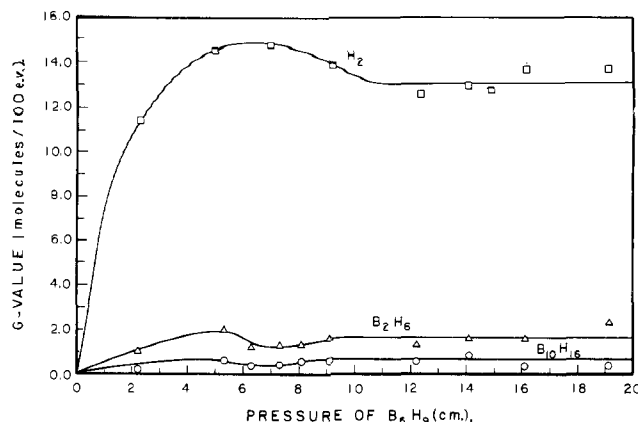


Fig. 1.—A plot of G -value vs. B_5H_9 pressure for H_2 , B_2H_6 , and $B_{10}H_{16}$. The pressure range includes pressures up to 19 cm. of B_5H_9 .

that there is equal probability for the removal of any one of the five terminal hydrogens in the pentaborane-9 molecule and since only hydrogen abstraction in the apical position can lead to decaborane-16, the calculated ratio of the diborane to decaborane-16 produced is 2.5. The observed ratio, $G(B_2H_6)/G(B_{10}H_{16}) = 2.8$ at 15.0 cm. B_5H_9 , compares well with the calculated one. This somewhat higher observed value may arise from abstraction of hydrogen by BH or BH_2 from molecules other than pentaborane-9.

The relatively high yield of hydrogen is not incompatible with this proposed mechanism. Polymeric boron hydrides are formed and since the hydrogen-to-boron ratio for such compounds is small and close to unity, H_2 may be a by-product of polymer formation. Such species as $B_4H_8^+$ and basal $B_5H_8\cdot$ radicals may be involved in the polymer formation.

Effect of Deuterium.—A mixture of 1 cm. of deuterium and 15 cm. of B_5H_9 was irradiated with deuterons and it was found that the $B_{10}H_{16}$ produced under these conditions contained no deuterium; however, deuterated diborane, HD , and very small amounts of B_5H_8D were observed in the products. The presence of deuterium in diborane is not particularly significant since D_2 will exchange with diborane⁷ at room temperature and under the radiation conditions the exchange rate could be further enhanced. The deuterated diborane can also arise from the reaction of BH with deuterium and HD can arise as a consequence of the above mechanism. On the other hand, the presence of B_5H_8D arises from the recombination of $B_5H_8\cdot$ and D since B_5H_9 and D_2 do not exchange⁸ under ordinary conditions.

Effect of Rare Gases.—Mixtures of 71 mole % of rare gas and 29 mole % of B_5H_9 on irradiation produced the results shown in Fig. 2. It is evident that the addition of a rare gas has a pronounced effect on the G -value of diborane. The yield of diborane is greatest in helium and steadily decreases as one proceeds through the rare gases to xenon. The $B_{10}H_{16}$ yield is not as greatly influenced but does go through a broad minimum as is apparent from Fig. 2.

When a rare gas-pentaborane-9 mixture is irradiated with deuterons, ionization and excitation of the rare gas takes place since the rare gas is present in excess. This is followed by energy transfer *via* charge exchange

(7) P. C. Maybury and W. S. Koski, *J. Chem. Phys.*, **21**, 742 (1953).

(8) J. J. Kaufman and W. S. Koski, *ibid.*, **24**, 403 (1956).

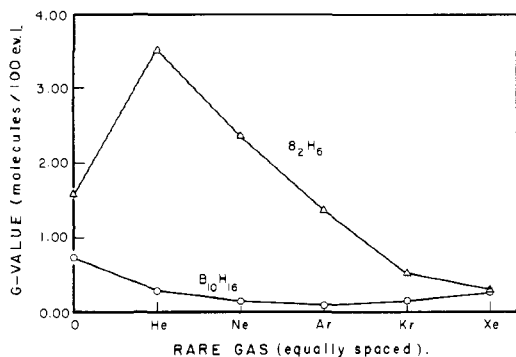
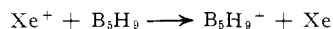
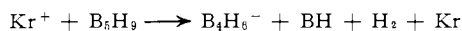
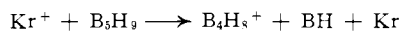
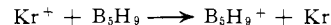


Fig. 2.—The effect of rare gas sensitization on G -values of B_2H_6 and $B_{10}H_{16}$. The rare gas symbols are placed at equal intervals along the abscissa; 71 mole % of rare gas at a total pressure of 65 cm. was used in each case. The point "0" on the abscissa refers to the experimental condition in which no rare gas was present.

to the B_5H_9 , leading to ionization and fragmentation of the molecule. In the case of Xe^+ one would expect mainly the ionization reaction



since the ionization potentials are 12.1 and 10.5 for xenon and pentaborane-9, respectively. The energy defect is too small to cause significant fragmentation of the B_5H_9 molecule and, as a result of the above mechanism, one would expect relatively small amounts of diborane. In the case of krypton the energy defect is somewhat larger and on the basis of the Massey-Burhop theory⁹ one would expect fragmentation of the molecule as

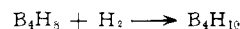


Here the presence of BH would increase the B_2H_6 yield over the case of xenon. With Ar^+ the fragmentation process may proceed still further, possibly to yield $B_3H_n^+$ ions in addition to $B_5H_n^+$ and $B_4H_n^+$ and since these would increase the yield of BH fragments, the diborane yield would be expected to be further enhanced. Thus, as one proceeds to the case of Ne^+ and He^+ , one would expect greater yields of the smaller ionic fragments such as $B_3H_5^+$ and correspondingly greater amounts of BH and, consequently, greater yields of diborane. This is observed as is evident from Fig. 2. With increased fragmentation, one would expect a lowering of the $B_{10}H_{16}$ yield because of competition of other reactions.

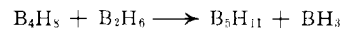
In the cases of He, Ne, and Ar sensitization, in addition to the above products small amounts of tetra-

(9) H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, Oxford, 1956.

borane-10 (B_4H_{10}) and hexaborane-10 (B_6H_{10}) were formed. These may arise by means of reactions such as



and



In the case where a 12 cm. B_5H_9 -53 cm. helium mixture was irradiated, the $G(B_4H_{10})$ was 0.14 and the $G(B_6H_{10})$ was 0.007. These reactions are in agreement with the observation of Fehner¹⁰ in his study of the shock tube pyrolysis of B_5H_9 .

Scavenger Effects of Iodine.—When 10^{-3} mole of iodine was added to 18 cm. of B_5H_9 on irradiation, the mixture contained no decaborane-16. The products consisted of H_2 , B_2H_6 , HI, and B_5H_8I . This observation was interpreted as being compatible with the proposed mechanism of radiolysis. The iodine effectively scavenged the $B_5H_8\cdot$ radicals to produce iodopentaborane and thus prevented the formation of decaborane-16. In a separate experiment we observed that no B_5H_8I is produced when B_5H_9 and I_2 are mixed at room temperature even after standing for several days.

In conclusion, therefore, it is shown that deuteron irradiation of B_5H_9 produces H_2 , B_2H_6 , and $B_{10}H_{16}$ with G -values of 13.1, 1.7, and 0.8, respectively, in the pressure-independent region around 15 cm. B_5H_9 . It is proposed that hydrogen is formed by molecular detachment from B_5H_9 as a damage product, as a result of hydrogen elimination in the polymer formation and from the recombination of hydrogen atoms. BH produced directly as a radiation damage product is proposed as a precursor to B_2H_6 ; BH abstracts hydrogen from pentaborane-9 in two steps to produce BH_3 which on recombination produces B_2H_6 . The decaborane-16 results mainly from the recombination of $B_5H_8\cdot$ (apical) radicals. Rare gases have a strong effect on the yield of diborane and this appears to be related to the energy defect, *i.e.*, the difference between the recombination energy of the bombarding ion and the energy required to produce the particular state of the boron hydride ion. The greater this energy defect, the greater is the fragmentation of the B_5H_9 molecule and the greater the diborane yield. The influence of iodine as a scavenger and deuterium as a tracer appear to be consistent with this picture.

Acknowledgment.—The mass spectrometer used in this study was obtained in part through a grant from the National Science Foundation. L. H. H. is indebted to the Lever Brothers Co. Foundation for its support through a graduate fellowship for 2 years.

(10) T. P. Fehner, Doctoral Dissertation, The Johns Hopkins University, 1963.