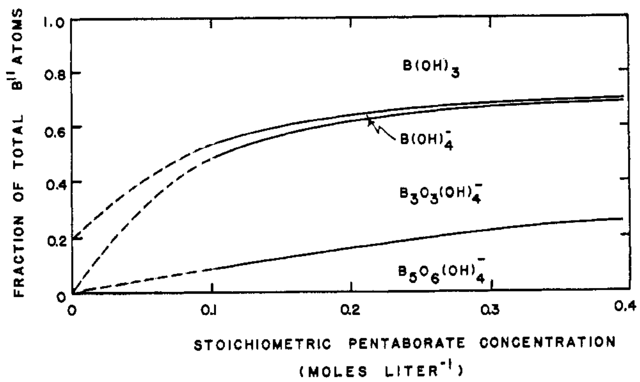


Figure 1.—Distribution of B^{11} atoms among borate species in aqueous sodium pentaborate solutions.

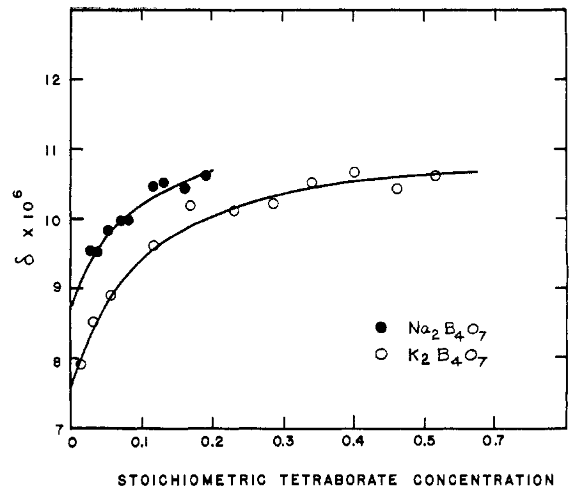


Figure 2.—B^{11} chemical shifts in alkali tetraborate solutions.

to infinite dilution is to the mean of the chemical shifts of boric acid and monoborate ion. We conclude from this that dissociation into these species is complete at low stoichiometric tetraborate concentrations

$$B_4O_7^{2-} + 7H_2O = 2B(OH)_3 + 2B(OH)_4^-$$

This is not a simple equilibrium, however. Fairly rapid exchange of boron atoms must be occurring between at least two distinct sites. That these sites might be only monomeric boric acid and monoborate ion is excluded because the chemical shift is concentration-dependent while the pOH of tetraborate solutions is essentially independent of concentration.[1] That is to say, the $[B(OH)_4^-]/[B(OH)_3]$ ratio is fixed over the whole concentration range by the equilibrium expression $[B(OH)_4^-]/[B(OH)_3] = K_1[OH^-] =$ constant. It has the value of unity at all concentrations, evaluated from the chemical shift at $c = 0$. From the chemical shift at $c = 0$ ($\delta_{Na_2B_4O_7}$ 8.7×10^{-6}) we obtain $K_1 = 1.0 \times 10^5$, in good agreement with Ingri's value,[4] $K_1 = 1.86 \times 10^5$.

More than one polyborate species must be present at all finite tetraborate concentrations, however, because the data of Figure 2 cannot be fitted to equilibria involving boric acid, monoborate ion, and only *one* polyborate species, such as $B_2O(OH)_5^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$, or $B_5O_6(OH)_4^-$. The upfield trend of the chemical shift with increasing concentration makes it appear highly probable that tetramers and/or pentamers may be present. Because there is no resolution of the single B^{11} resonance into its components, however, it is not possible to identify all the polyborate species and to determine their distribution uniquely.

Acknowledgment.—We wish to thank the Air Force Office of Scientific Research for its support of this research under grant No. AF-AFOSR-1086-66 with The University of Chicago and the Advanced Research Projects Agency for its assistance under contract No. SD-89. We also thank the American Potash and Chemical Corp. for its gift of alkali borates.

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York

Gaseous Boroxine: Mechanism of Reaction with Boron Trihalides[1]

By M. Nadler and Richard F. Porter

Received September 26, 1966

Low-pressure reactions of gaseous boroxine ($H_3B_3O_3$) with boron trihalides to produce dihaloborane and boric oxide have been studied by infrared absorption techniques. Kinetic data indicate that the reaction is close to first order in boroxine pressure. The pressure dependence of BF_3 in the BF_3–$H_3B_3O_3$ reaction is close to zero order for BF_3 pressures above 10 mm but tends toward a higher order at lower pressures. Reactions are accelerated in cells coated with B_2O_3(s). Reaction rates increase in the order $BF_3 < BCl_3 < BBr_3$. Spectra of products of the reaction of ^{10}B-labeled compounds show that the boron atoms in $H_3B_3O_3$ appear in HBX_2 and the boron atom in BX_3 appears in B_2O_3(s). A surface mechanism which accounts for the ^{10}B distribution in the products is proposed.

Introduction

Studies of the chemical behavior of boroxine ($H_3B_3O_3$) have shown that the compound is reactive with a number of reagents including oxygen, carbon monoxide,[2] and the boron trihalides.[3] The kinetic behavior of gaseous boroxine may be investigated provided its

(1) Work supported by the U. S. Army Research Office (Durham) and the Advanced Research Projects Agency.

(2) G. H. Lee II and R. F. Porter, *Inorg. Chem.*, **5**, 1329 (1966).

(3) R. F. Porter and S. K. Wason, *J. Phys. Chem.*, **69**, 2208 (1965).

reactions with other reagents are faster than its decomposition to B_2H_6 and B_2O_3. Results of a kinetic investigation of the $H_3B_3O_3(g)$–O_2 and $H_3B_3O_3(g)$–CO reactions have been presented earlier.[2] The experimental work described in this paper was designed to answer fundamental questions regarding the mechanism of the $H_3B_3O_3(g)$–BX_3 reactions.

Experimental Section

Gaseous boroxine was prepared by exploding low-pressure mixtures of diborane and oxygen.[4] In these experiments extreme caution should always be exercised. Reaction vessels should be taped and all mixing operations should be performed behind a safety shield. Diborane was prepared from sodium borohydride by the method of Jeffers.[5] Matheson reagent grade oxygen was used. The experimental procedure was to prepare $H_3B_3O_3$ and then immediately transfer the product into an infrared cell containing a known quantity of BX_3. The reaction vessel was a 125-ml Pyrex bulb joined to a vacuum stopcock and a taper joint for connection to an infrared cell. The best yields of boroxine were obtained with an equal molar mixture of B_2H_6 and O_2 at a total pressure of about 20 mm. Gases were mixed by first adding diborane to the reaction vessel and then slowly adding the appropriate quantity of oxygen from a reservoir at sufficient backing pressure to prevent flow of diborane into the oxygen source. The reaction vessel was then joined to the infrared cell and the cell and connecting tubing were evacuated before introducing BX_3. Reaction between B_2H_6 and O_2 was initiated by touching the wall of the reaction vessel with the point of a Tesla coil discharge: (reaction is evident by a flash of light; *note safety precautions*). The gaseous products were then transferred to the cell and allowed to mix with BX_3. The $H_3B_3O_3$–BX_3 reaction was followed by measuring the change in absorbance of the 918 cm^{-1} band on $H_3{}^{11}B_3O_3$ with time. Measurements were made with a Perkin-Elmer Model 337 Infracord. Initial cell pressures of $H_3B_3O_3$ were obtained from the initial absorbance and an absorbance–pressure calibration curve obtained by a procedure described earlier.[2,6]

To note the effect of surface conditioning on the reaction, rate experiments were conducted in cells precoated with $B_2O_3(s)$. The coating was obtained by flashing a low-pressure mixture of B_2H_6 and O_2 in the cell before making experimental observations.

In a series of experiments $H_3B_3O_3$ and BF_3 labeled with ^{10}B were used in place of compounds containing the natural ^{10}B and ^{11}B abundance (subsequently referred to as ^{n}B). The $H_3{}^{10}B_3O_3$ was prepared from $^{10}B_2H_6$ and O_2 by the same procedure as described above. The $^{10}B_2H_6$ was obtained by heating a small quantity of $CaF_2 \cdot {}^{10}BF_3$[7] with an excess of $LiAlH_4$ in a copper crucible *in vacuo*. This reaction is characterized by a rapid evolution of gas when the solid mixture is heated above 100°. The products, including $^{10}B_2H_6$, $H^{10}BF_2$, and $^{10}BF_3$, were collected in a trap at −196°. Impurities of $H^{10}BF_2$ and $^{10}BF_3$ were removed by adding a small quantity of diethyl ether to the mixture. Samples of $^{10}BF_3$ were obtained by decomposing solid $CaF_2 \cdot {}^{10}BF_3$, *in vacuo*, on heating to about 250°.

Results

Stoichiometry.—Infrared spectra showed that the products of the BX_3–$H_3B_3O_3$ reaction were mainly $HBX_2(g)$ and $B_2O_3(s)$. Analyses of the infrared spectra of HBF_2,[3] $HBCl_2$,[8–10] and $HBBr_2$[11,12] have been published. For the BF_3–$H_3B_3O_3$ reaction it was possible to obtain an approximate check on the stoichiometry

$$2BF_3(g) + H_3B_3O_3(g) = 3HBF_2(g) + B_2O_3(s) \qquad (1)$$

In a series of experiments BF_3 was allowed to react with $H_3B_3O_3$, and the products, including B_2H_6, HBF_2, and unreacted BF_3, were collected in a trap at −196°. The partial pressures of B_2H_6 and BF_3 in the products were obtained from absorbance measurements, and the yield of HBF_2 was obtained by difference from the total sample pressure. From six determinations the moles of HBF_2 produced per mole of BF_3 reacted was found to be 1.33 ± 0.18. It was generally noted, however, that only about 95% of the initial BF_3 could be recovered as products. Correction for this loss gives a ratio of 1.43 ± 0.19, which is fair agreement with the theoretical value of 1.50 for eq 1. A certain fraction of the diborane observed in the products is produced by the decomposition of $H_3B_3O_3$, and thus it was not possible from these measurements to establish a reliable stoichiometric relationship between BF_3 and $H_3B_3O_3$. This relationship was determined by comparison of decrements in BF_3 and $H_3B_3O_3$ pressures as the reaction proceeded. From a series of five pressure–time plots (see Figure 2) the ratio $\Delta P_{BF_3}/\Delta P_{H_3B_3O_3}$ at the onset of the reaction was found to be in the range 1.8 ± 0.2. This is reasonable agreement with the value of 2.0 from eq 1.

Kinetic Measurements.—Results of kinetic studies of the BF_3–$H_3B_3O_3$ reaction over a range of initial pressures of BF_3 are illustrated in Figure 1. The data show that when BF_3 is in excess ($P_{BF_3}{}^0 > 10$ mm) a plot of log $P_{H_3B_3O_3}$ *vs.* time is linear. This indicates a first-order pressure dependence on $H_3B_3O_3$. In Table I are given experimental values for the half-life based on first-order rate constants. For BF_3 pressures between 10 and 20 mm, the half-life varies only slightly, suggesting that the reaction is close to zero order in BF_3 under these conditions. The data in Figure 1 also show that when the initial pressure of BF_3 is reduced below about 10 mm, the rate falls off and a pressure dependence on BF_3 is observed. The kinetic data (Table I) are not sufficiently quantitative to establish a unique pressure dependence on BF_3 in the lower pressure range. From data for the rate of disappearance of both $H_3B_3O_3$ and BF_3 it was possible to construct plots of the integrated form of $1/P_{H_3B_3O_3} \int dP_{BF_3}/P_{BF_3}{}^b$ *vs.* time for various values of b. The results, using the data in Figure 2 and data from plots with $P_{BF_3}{}^0$ = 2.3 and 1.5 mm, indicate that b is definitely less than unity and is probably intermediate between zero and 0.5.

Kinetic results from a series of measurements on the BCl_3–$H_3B_3O_3$ and BBr_3–$H_3B_3O_3$ reactions are summarized in Table I.

Isotope Tracer Studies.—Infrared spectra of products of the reactions $^{n}BF_3 + H_3{}^{n}B_3O_3$, $^{n}BF_3 + H_3{}^{10}B_3O_3$, and $^{10}BF_3 + H_3{}^{n}B_3O_3$ are compared in Figure 3.

(4) L. Barton, F. A. Grimm, and R. F. Porter, *Inorg. Chem.*, **5**, 2076 (1966).
(5) W. Jeffers, *Chem. Ind.* (London), 431 (1961).
(6) L. Barton, C. Perrin, and R. F. Porter, *Inorg. Chem.*, **5**, 1446 (1966).
(7) Obtained from Oak Ridge National Laboratory, Oak Ridge, Tenn. (starting material 96% ^{10}B).
(8) C. D. Bass, L. Lynds, T. Wolfram, and R. E. de Wames, *Inorg. Chem.*, **3**, 1063 (1964).
(9) H. W. Myers and R. F. Putnam, *ibid.*, **2**, 655 (1963).
(10) L. Lynds and C. D. Bass, *ibid.*, **3**, 1147 (1964).
(11) S. K. Wason and R. F. Porter, *J. Phys. Chem.*, **69**, 2461 (1965).
(12) L. Lynds, T. Wolfram, and C. D. Bass, *J. Chem. Phys.*, **43**, 3775 (1965).

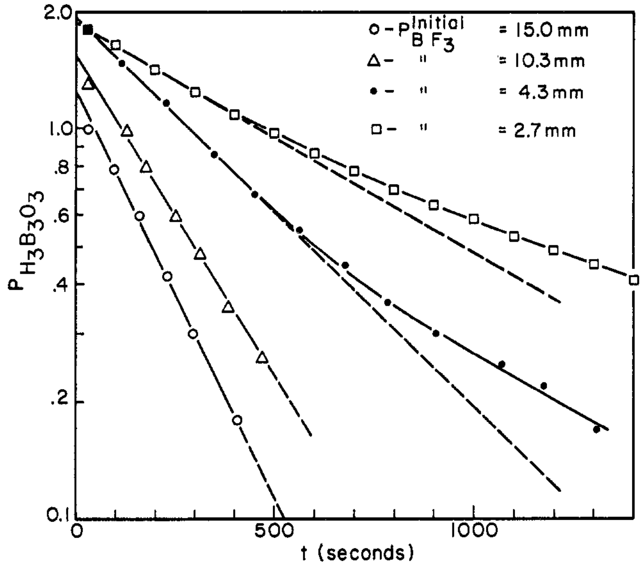


Figure 1.—Plots of log $P_{H_3B_3O_3}$ *vs.* time for various initial pressures of BF_3.

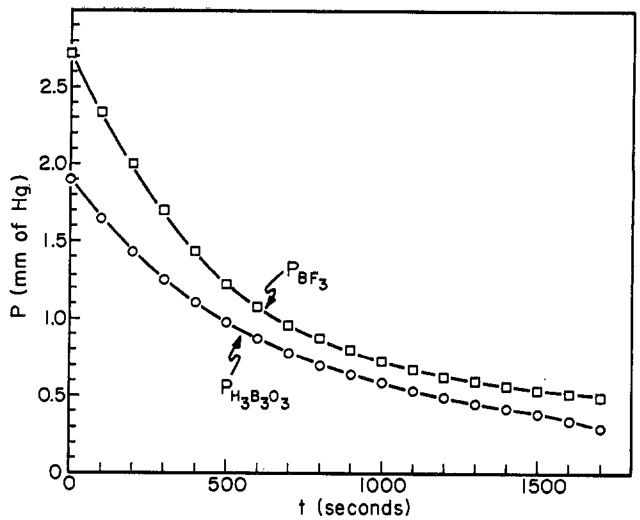


Figure 2.—Pressure *vs.* time plot for low-pressure reaction of $H_3B_3O_3$ and BF_3; $P_{H_3B_3O_3}{}^0$ 1.9 mm, $P_{BF_3}{}^0$ 2.7 mm.

Table I

Kinetic Data for the Reaction of $H_3B_3O_3$ with BX_3 ($T = 30°$)

Reactant halide	Cell surface	Initial P_{BX_3}, mm	Initial $P_{H_3B_3O_3}$, mm	Half-life,[b] sec
BF_3	Uncoated	19.7	1.4	183
		18.3	1.8	140
		14.1	1.3	145
		11.9	2.2	145
		10.5	1.6	168
		10.3	1.6	181
		4.3	1.9	(272)
		2.7	1.9	(530)
		2.3	1.6	(346)
		1.5	1.7	(630)
	B_2O_3 coated	10.9	2.0	63.2
		10.9	1.5	47.8
		10.5	1.4	45.8
		5.3	1.8	(80.0)
		4.0	2.0	(95.5)
		2.5	2.0	(142)
BCl_3	Uncoated	13.9	0.5	61.3
		11.8	0.8	51.4
		9.5	1.1–1.3	55.4 ± 5.4[a]
		4.0	1.6	(131)
		2.0	1.5	(491)
	B_2O_3 coated	10.0	1.0	38.5
		10.0	0.6	35.9
BBr_3	Uncoated	14.5	0.7	10.0
		9.6	1.1	16.9
		9.5	1.0	11.3
		7.8	1.1	(22.1)
		2.8	0.9	(45.5)
	B_2O_3 coated	10.0	. . .	<5

[a] An average of five determinations. [b] Values in parentheses were obtained from initial slopes of log $P_{H_3B_3O_3}$ *vs.* time curves and are intended only for comparison purposes.

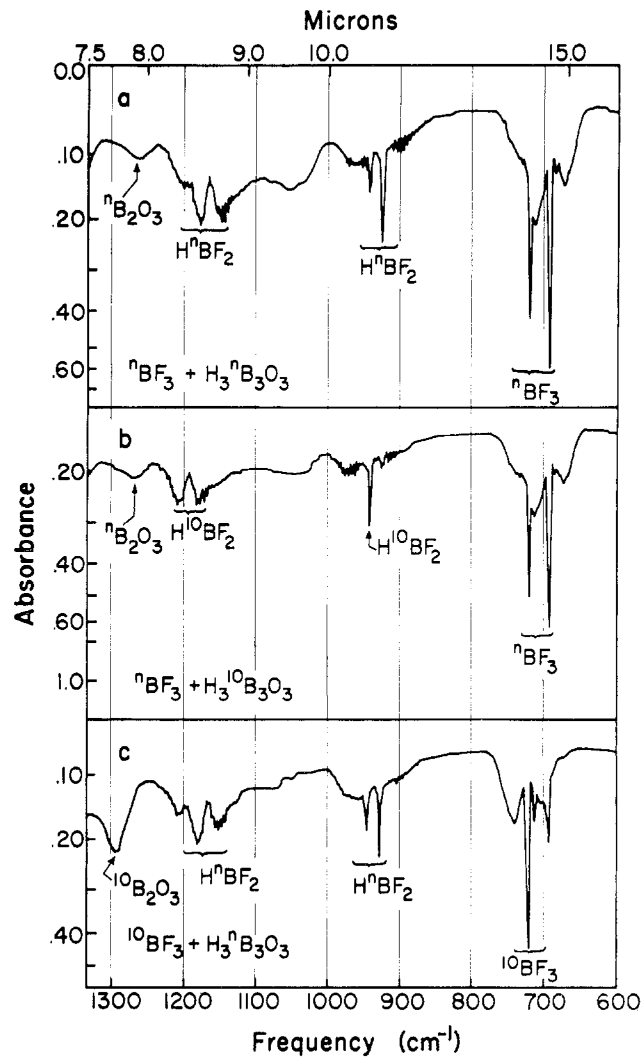


Figure 3.—Portion of infrared spectra of products for the reaction $H_3B_3O_3$ + BF_3 with different isotopic labeling: a, $P_{BF_3}{}^0$ 10 mm; b, $P_{BF_3}{}^0$ 12 mm; c, $P_{^{10}BF_3}{}^0$ 6 mm.

From the appearance of ^{10}B in the products it is interesting to note that HBF_2 contains the boron atom from $H_3B_3O_3$, while B_2O_3 contains the boron atom from BF_3. The isotopic composition of products in these reactions did not depend markedly on the initial pressure of BF_3. However, several hours after the reaction between $H_3{}^{10}B_3O_3$ + $^nBF_3$ was complete, the concentration of $^{10}BF_3$ in the products gradually increased. This can be accounted for by H–F exchange subsequent to the initial reaction and/or disproportionation of $H^{10}BF_2$ according to the equilibrium $3HBF_2 \rightleftharpoons 2BF_3 + {}^1/_2B_2H_6$. Figures 4 and 5 show infrared spectra of products of the reactions of $^nBCl_3$ and $^nBBr_3$ with ^{10}B-labeled boroxine. In these figures the dependence of isotopic composition of the products on initial pressure of BX_3 is illustrated.

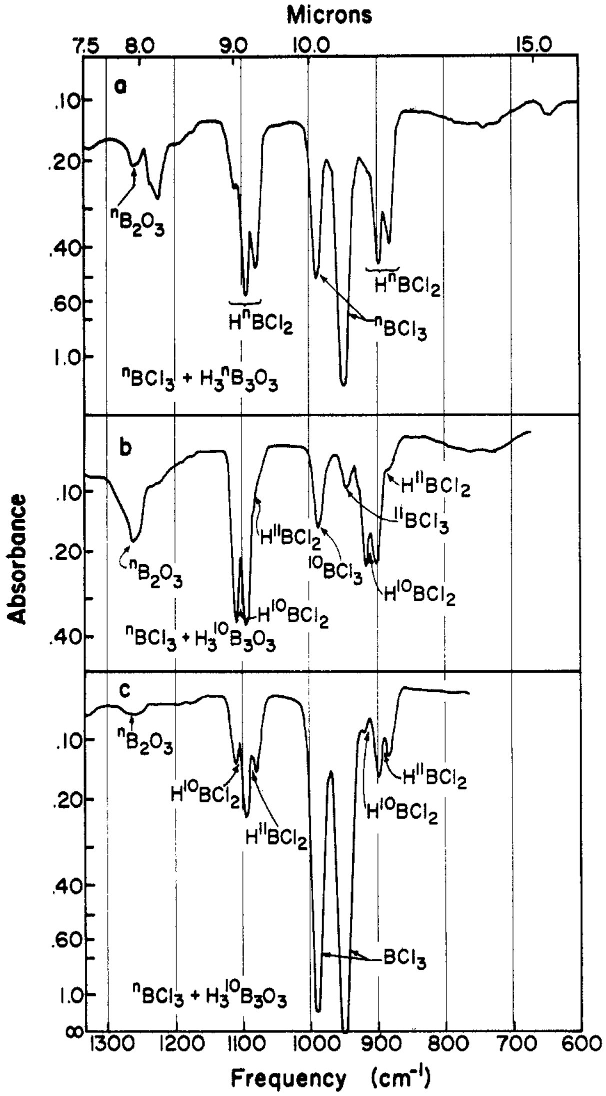


Figure 4.—Portion of infrared spectra of products for the reaction $H_3B_3O_3 + BCl_3$ with different isotopic labeling: a, $P_{BCl_3}{}^0$ 4 mm; b, $P_{BCl_3}{}^0$ 3 mm; c, $P_{BCl_3}{}^0$ 8 mm.

Discussion

The foregoing observations strongly indicate that the BF_3–$H_3B_3O_3$ reaction follows a heterogeneous path under the experimental conditions employed in these studies. The effect of change of surface conditions is noted by a marked increase in reaction rate in cells precoated with a layer of solid B_2O_3 (see Table I). Since B_2O_3 is produced in the BF_3–$H_3B_3O_3$ reaction we cannot rule out the possibility that some catalytic effect due to the B_2O_3 formed is also operating in cells initially free from B_2O_3 (termed "uncoated" in Table I).

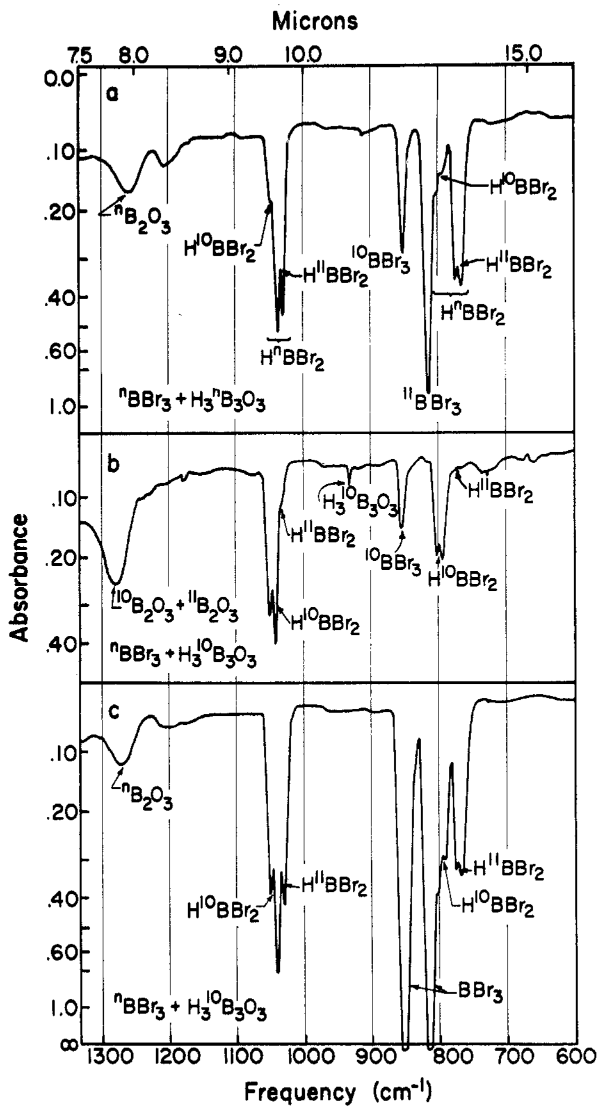


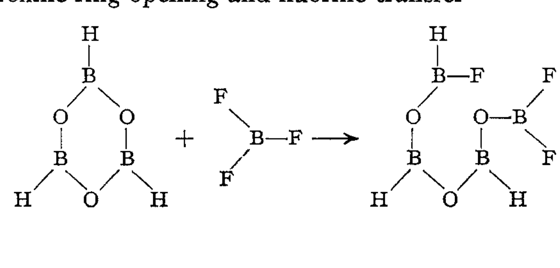
Figure 5.—Portion of infrared spectra of products for the reaction $H_3B_3O_3 + BBr_3$ with different isotopic labeling: a, $P_{BBr_3}{}^0$ 4 mm; b, $P_{BBr_3}{}^0$ 2 mm; c, $P_{BBr_3}{}^0$ 8 mm.

The kinetic data are generally consistent with a rate law of the form

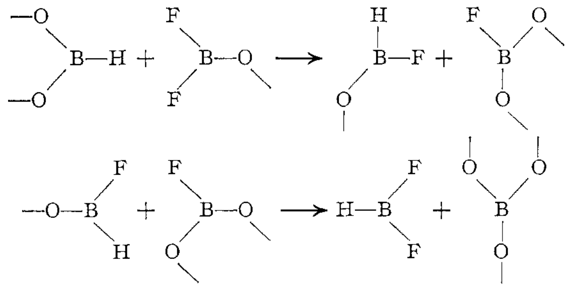
$$\frac{dP_{H_3B_3O_3}}{dt} = \text{constant} \times P_{H_3B_3O_3}\theta_{BF_3}$$

where θ_{BF_3} is the fraction of active sites occupied by BF_3 molecules. With this expression we can account for a zero-order dependence on BF_3 as θ_{BF_3} approaches unity at high BF_3 pressures, and the increase in kinetic order with respect to BF_3 at low BF_3 pressures when θ_{BF_3} is dependent on pressure.

A mechanism allowing for the boron isotope distribution in the products is proposed as follows: (1) Surface accommodation of $H_3B_3O_3$ and BF_3 followed by boroxine ring opening and fluorine transfer



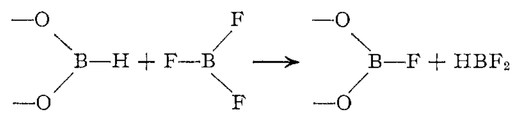
(2) Further rapid fluorine transfer from BF_3 or $-O-B<^{F}_{F}$ and $-O-B<^{O}_{F}$ groups to $^{-O}_{-O}>B-H$ or $-O-B<^{H}_{F}$ groups as exemplified by the following



In this mechanism boron atoms in BF_3 become coordinated by oxygen atoms in B_2O_3 and boron atoms in $H_3B_3O_3$ become coordinated by fluorine atoms originally in BF_3. For every B–F or B–O bond broken a new bond is formed. Thermochemical data indicate the reaction

$$2BF_3(g) + H_3B_3O_3(g) = 3HBF_2(g) + B_2O_3(s)$$

is about 1.4 kcal/mole, exothermic.[3,13] The slow decomposition of $H_3B_3O_3$ to $B_2H_6 + B_2O_3$ implies a mechanism involving transfer of H atoms from one boron to another. However, in the faster BF_3–$H_3B_3O_3$ reaction a fluorine atom is apparently transferred more rapidly than a hydrogen atom. The absence of $H^{11}BF_2$ in the products of the reaction of $H_3{}^{10}B_3O_3 + {}^{n}BF_3$ shows that the mechanism is not a simple exchange of the type



as was suggested earlier.[3]

Infrared spectra in Figures 4 and 5 suggest that the mechanism for the reaction of BCl_3 or BBr_3 with boroxine is substantially the same as that for the BF_3 reaction. However, the effect of hydrogen–halogen exchange and/or disproportionation of HBX_2 subsequent to this initial reaction is much more evident in the reaction with BCl_3 or BBr_3. The kinetic data in Table I show that the reaction rates increase in the order $BF_3 < BCl_3 < BBr_3$ and that the catalytic effect of B_2O_3 is general for all of the reactions.

Although one is tempted to correlate the reaction rate of the $H_3B_3O_3$–BX_3 reaction with the acidity of the boron atom in BX_3, it should be noted that in postulating a donor–acceptor intermediate we should consider the acceptor strength of boron atoms in both of the reacting molecules. The increase in reaction rates from the fluoride to the bromide may simply reflect the relative decrease in B–X bond strength.

(13) L. Barton, S. K. Wason, and R. F. Porter, *J. Phys. Chem.*, **69**, 3160 (1965).

CONTRIBUTION FROM CALLERY CHEMICAL COMPANY,
RESEARCH AND DEVELOPMENT DIVISION, CALLERY, PENNSYLVANIA 16024

Practical Synthesis for Decahydrodecaborates

BY JOSEPH M. MAKHLOUF, WILLIAM V. HOUGH, AND GERALD T. HEFFERAN

Received July 15, 1966

High-yield synthesis of the decahydrodecaborate(2–) anion was achieved from the thermolysis of tetraethylammonium tetrahydroborate(1–), $(C_2H_5)_4NBH_4$, and tetraethylammonium octahydrotriborate(1–), $(C_2H_5)_4NB_3H_8$, at atmospheric pressure and 185°. The thermolysis of tetramethylammonium tetrahydroborate(1–), $(CH_3)_4NBH_4$, under similar conditions gives only trimethylamine borane, $(CH_3)_3NBH_3$, and methane, while a near equimolar mixture of $[(CH_3)_4N]_2B_{10}H_{10}$ and $[(CH_3)_4N]_2B_{12}H_{12}$ was the major product obtained from pyrolysis of tetramethylammonium octahydrotriborate(1–), $(CH_3)_4NB_3H_8$. Although $B_{10}H_{10}^{2-}$ was a major product, complex mixtures of products containing the BH_4^-, $B_{10}H_{10}^{2-}$, $B_{11}H_{14}^-$, and $B_{12}H_{12}^{2-}$ anions were obtained from the 185° pyrolysis of potassium and cesium octahydrotriborates(1–), KB_3H_8 and CsB_3H_8, respectively. No evidence was obtained for $B_9H_9^{2-}$ or $B_{11}H_{11}^{2-}$ when the pyrolysis temperatures were maintained at 185°.

Introduction

The absence of an economical method for synthesis of salts of decahydrodecaborate(2–) from diborane or hydroborates has been conspicuous.[1] Preparation of these salts can be accomplished using decaborane as a starting material[2] with nearly quantitative conversion of decaborane to $B_{10}H_{10}^{2-}$, but formation of $B_{10}H_{10}^{2-}$ from lower boron hydride derivatives has been observed only in small quantities while other species (B_9, B_{11}, B_{12}) were major products.[3] The dodecahydrododecaborate(2–) ion ($B_{12}H_{12}^{2-}$), on the other hand, is easily derived from nonboron–boron-bonded parents.[4,5]

The requirement for decaborane as a starting material has been a limiting factor in consideration of deca-

(1) E. L. Muetterties and W. H. Knoth, *Chem. Eng. News*, **44** (19), 88 (1966).

(2) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **81**, 5519 (1959).

(3) F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **5**, 1955 (1966).

(4) I. A. Ellis, D. F. Gaines, and R. Schaeffer, *J. Am. Chem. Soc.*, **85**, 3885 (1963).

(5) H. C. Miller, N. E. Miller, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1456 (1964).