Perhaps an explanation for this behavior can be sought in the polar character of the tin–halogen bond in organotin halides, in which tin carries a positive charge.[15] The presence of the positive charge may contract the vacant *d*-orbitals of tin enough to permit conjugation with an organo-group, provided the organo-group has electrons in π-orbitals. Because greater electron delocalization would be involved, a phenyl group should conjugate with a tin atom more effectively than a perfluorovinyl group, so that the tin–phenyl bond in phenyltin halides would be strengthened over that in the neutral $(C_6H_5)_2SnR_2$ derivatives.

(three forms)

It is interesting to note in passing that resonance of this type in phenyltin halides has been postulated to account for their spectroscopic properties.[16] The situation with tin may be somewhat analogous to that in phosphorus chemistry. In neutral tetracoördinate phosphorus compounds *d*-orbital resonance does not appear to be important.[17a,b] However, if in a tetracoördinate phosphorus compound the phosphorus atom carries a positive charge, the idea that phosphorus *d*-orbitals are used in bonding accounts for certain properties.[17c] In neutral tetracoördinate tin compounds the tin *d*-orbitals may be too diffuse to be involved in bonding, at least in the ground state.

A subsequent paper will describe how perfluorovinyltin compounds can be used to prepare perfluorovinylboron halides such as $(CF_2{:}CF)_2BCl$ (b.p. extrap. 100.5°).

[16] V. S. Griffiths and G. A. W. Derwish, *J. Molec. Spectroscopy*, **3**, 165 (1959).

[17] (a) J. R. Van Wazer, THIS JOURNAL, **78**, 5709 (1956). (b) H. D. Kaesz and F. G. A. Stone, *ibid.*, **82**, 6213 (1960). (c) W. von E. Doering and A. K. Hoffmann, *ibid.*, **77**, 521 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

Organoboron Halides. IV. Exchange Reactions with Boron Trihalides[1,2]

BY F. E. BRINCKMAN[3] AND F. G. A. STONE

RECEIVED MAY 20, 1960

A mass spectrometric study has been made of a series of exchange reactions between boron trifluoride and organoboron halides, RBX_2 or R_2BX (X = Cl, Br). By using isotopically enriched boron trifluoride in these reactions, it was established that the mechanism does not involve rupture of boron–carbon bonds. Mass spectrometric evidence was obtained for the existence of species RB(F)X (X = Cl, Br).

Binary mixtures of boron trihalides equilibrate to form mixed boron halides such as BF_2Cl, $BBrCl_2$, *etc.*, establishing that halogen exchange between boron atoms readily occurs.[4] Organo-groups in unsymmetrical triorganoborines are also very labile, and compounds such as Me_2BEt have only a transitory existence even at low temperatures.[5] Disproportionation reactions also occur reversibly in organoboron halides.[6] However, these exchange reactions, involving both halogen and organo-group transfer from one boron atom to another, usually require the action of heat for their occurrence. Related to the disproportionation of organoboron halides, in the sense that exchange reactions occur, is the preparation of these compounds by heating mixtures of boron trihalides with triorganoboron compounds.[6,7]

The work described above prompted us to study reactions between organoboron halides and boron trihalides at temperatures below those which would normally bring about disproportionation of organoboron halides. Exchange processes would be expected to occur, but it was not possible to predict whether the reactions would be readily reversed or whether the exchange mechanism would involve halogen transfer only or whether organo-group transfer followed by halogen transfer would take place. Reactions such as

$$3EtBF_2 + 2BCl_3 = 3EtBCl_2 + 2BF_3$$

$$3Me_2BCl + BF_3 = 3Me_2BF + BCl_3$$

proved to be readily reversible, but the equilibria were not too labile to prevent isolation by fractional distillation of the compounds indicated in the equations. This is in contrast to the very labile equilibria involved in binary mixtures of boron trihalides. A mass spectrometric study of the reactions was made both to determine what kinds of atoms or groups were involved in the exchange and to obtain evidence for the existence of mixed species of the type RB(Cl)F.

Experimental

1. **Apparatus and Starting Materials.**—The organoboron halides used in this work were prepared from organotin compounds as previously described.[8] Boron trihalides were commercial samples purified by standard techniques. Boron trifluoride enriched in ^{10}B isotope was obtained by

---

[1] Previous paper, T. D. Coyle and F. G. A. Stone, THIS JOURNAL, **82**, 6223 (1960).

[2] The work described in this paper was made possible by the award of a Grant (G5106) from the National Science Foundation.

[3] Public Health Predoctoral Fellow of the National Cancer Institute.

[4] (a) L. P. Lindemann and M. K. Wilson, *J. Chem. Phys.*, **24**, 242 (1956); (b) R. E. Nightingale and B. Crawford, *ibid.*, **22**, 1468 (1954); T. H. S. Higgins, E. C. Leisegang, C. J. G. Raw and A. J. Rossouw, *ibid.*, **23**, 1544 (1955); (c) T. D. Coyle and F. G. A. Stone, *ibid.*, **32**, 1892 (1960); (d) L. H. Long and D. Dollimore, *J. Chem. Soc.*, 4457 (1954); (e) J. Goubeau, D. E. Richter and H. J. Becher, *Z. anorg. Chem.*, **278**, 12 (1955).

[5] T. D. Parsons, M. B. Silverman and D. M. Ritter, THIS JOURNAL, **79**, 5091 (1957), and references cited therein.

[6] P. A. McCusker, G. F. Hennion and E. C. Ashby, *ibid.*, **79**, 5192 (1957).

[7] V. W. Buls, O. L. Davis and R. I. Thomas, *ibid.*, **79**, 337 (1957).

[8] F. E. Brinckman and F. G. A. Stone, *ibid.*, **82**, 6218 (1960).

heating the complex $CaF_2 \cdot {}^{10}BF_3$.[9] Prior to every mass spectral study of an exchange reaction the $^{11}B/^{10}B$ isotope ratio (q^*) in the isotopically enriched boron trifluoride ($^*BF_3$) was assayed by mass spectrometry in order to take into account the previous history of the sample.[10]

Much of the work described was carried out with the aid of a conventional high-vacuum system. Infrared spectra, taken in the gas phase, were recorded employing a Model 21 Perkin–Elmer double-beam spectrometer with sodium chloride optics, using 4 cm. cells. The mass spectrometer was a Consolidated Electrodynamics Corporation Model 21-103C. All mass spectral data were obtained under the standardized operating conditions: ionizing voltage 70 e.v., ionizing current 10 μamp., peak sensitivities obtained with a precision micromanometer.

2. **Exchange Reactions.** (a) **Reaction between Isotopically Enriched BF_3 and Organodihaloborines.**—As an example of an exchange reaction studied, that between vinyldichloroborine and ^{10}B-enriched BF_3 is described. A 43.4 cc.[11] sample of spectroscopically pure vinyldichloroborine and 44.4 cc. of $^*BF_3$ ($q^* = 0.089$) were condensed into a 300 cc. Pyrex reaction bulb. The reaction vessel was sealed off from the vacuum line and heated at 90° for 20 hr. The bulb then was attached to the vacuum line through a tube opener and the products (83.7 cc.) identified by their infrared spectra as boron trifluoride, vinyldifluoroborine, boron trichloride and vinyldichloroborine. Fractionation of the mixture afforded samples of boron trifluoride and vinyldifluoroborine sufficiently pure for mass analysis. The boron isotopic ratio ($q_{obsd.}$) in recovered boron trifluoride was determined from the BF_2^+ peaks $m/e = 48$ and 49, and the BF_3^+ peaks $m/e = 67$ and 68. Similarly, the isotopic content of recovered vinyldifluoroborine was evaluated from the BF_2^+ ions produced in its mass spectrum (Table I). In this manner, by taking the average of several determinations, the boron isotopic ratios given in Table II for this reaction were obtained.

TABLE I

FRAGMENTATION PATTERNS FOR SOME PURE BORON FLUORIDES[a]

m/e	Ion	Pattern, %	m/e	Ion	Pattern, %
	BF_3			$^*BF_3$	
29	$^{10}BF^+$	1.4	29	$^{10}BF^+$	1.9
30	$^{11}BF^+$	3.3	30	$^{11}BF^+$	0.2
48	$^{10}BF_2^+$	24.3	48	$^{10}BF_2^+$	100
49	$^{11}BF_2^+$	100	49	$^{11}BF_2^+$	9.3
67	$^{10}BF_3^+$	1.2	67	$^{10}BF_3^+$	4.7
68	$^{11}BF_3^+$	4.4	68	$^{11}BF_3^+$	0.4
	$MeBF_2$[b]			Me_2BF[b]	
26	MeB^+	0.2	26	MeB^+	1.9
30	BF^+	4.4	30	BF^+	2.5
45	$MeBF^+$	20.6	41	Me_2B^+	4.1
48	$^{10}BF_2^+$	25.6	44	$Me^{10}BF^+$	34.6
49	$^{11}BF_2^+$	100	45	$Me^{11}BF^+$	100
63	$Me^{10}BF_2^+$	11.7			
64	$Me^{11}BF_2^+$	15.4	60	Me_2BF^+	9.0
	$EtBF_2$[b]			$ViBF_2$[b,c]	
28	$C_2H_4^+$	100	27	$C_2H_3^+$	69.3
30	BF^+	4.4	30	BF^+	16.5
40	EtB^+	~0	38	$C_2H_3B^+$	0.3
48	$^{10}BF_2^+$	5.1	48	$^{10}BF_2^+$	18.6
49	$^{11}BF_2^+$	20.4	49	$^{11}BF_2^+$	73.8
59	$EtBF^+$	10.3	57	$C_2H_3BF^+$	37.2
78	$EtBF_2^+$	4.6	76	$C_2H_3BF_2^+$	100

[a] Only peaks pertinent to the exchange study shown. [b] Ions assigned on the basis of predominant ^{11}B isotope. [c] Vi = $CH_2{:}CH$ group.

(b) **Reaction between Isotopically Enriched BF_3, and Diorganohaloborines, Boron Trichloride or Boron Tribromide.**—Using a procedure similar to that described above, a variety of other boron halide exchange reactions was investigated. Fragmentation patterns for the various pure fluorides, required for calibration purposes, are given in Table I. Boron isotopic ratios observed in the various boron fluoride reaction products are summarized in Table II.

The boron trifluoride–boron trihalide exchange reaction was studied in this work in order to establish that dilution in this system is statistical.

The complexity of the mass spectrum of dimethylfluoroborine[12] made it necessary to search for changes in the boron isotopic ratio by comparing selected peaks in the mass spectrum of dimethylfluoroborine recovered from an exchange reaction with corresponding peaks in the mass spectrum of pure dimethylfluoroborine having a normal boron isotopic ratio (Table I).

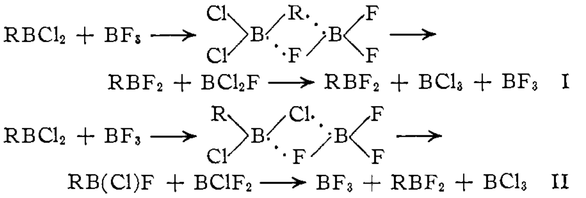
3. **Equilibrium Studies.**—In order to establish that the reactions described in the previous section between boron trifluoride and organoboron halides are reversible, reactions between organoboron fluorides and boron trichloride or boron tribromide were studied. For example, a 74.6-cc. sample of ethyldifluoroborine was heated with 75.0 cc. of boron trichloride at 90° for 18 hr. An infrared study was made on the recovered mixture (152 cc.). The spectrum showed bands attributable to the starting materials and, in addition, bands attributable to boron trifluoride were observed at 691 cm.$^{-1}$ and to ethyldichloroborine at 898 cm.$^{-1}$.

Direct evidence for the presence of species of the type RBXF (X = Cl, Br) in the equilibrium reactions was obtained by mass spectrometry. For example, mass analysis (Fig. 1) of the equilibrium mixture resulting from treatment of vinyldichloroborine with boron trifluoride indicated presence of these various species, with m/e values as indicated: BF_3 (67–68), $ViBF_2$ (~73–76), $BClF_2$ (83–86), ViBClF (~91–94), BCl_2F (99–104), $ViBCl_2$ (~106–112), BCl_3 (115–122).

In other exchange reactions the mixed species MeB(Cl)F (m/e, ~77–82), MeB(Br)F (m/e, ~121–126) and EtB(Cl)F (m/e, ~90–96) were observed.

Discussion

As suggested elsewhere,[4a,b,13,14] rearrangements of trivalent boron compounds probably proceed *via* bridge-bonded dimers. Similar four-centered transition states have been suggested for the disproportionation of certain halo- and alkylsilanes, as well as for some organoaluminum and mercury compounds.[14] In the organodihaloborine reactions described in this paper two mechanisms were possible, depending on whether R (alkyl, vinyl) groups or halogen atoms function as the bridge in the initial exchange step.



Use of ^{10}B enriched boron trifluoride in these exchange reactions permitted an unequivocal determination of whether process I or process II was operating. In mechanism I, involving organogroup exchange, dilution of the isotopically en-

---

(9) Supplied by Stable Isotope Research and Production Division, Oak Ridge, Tenn.

(10) T. Matsuura, *Bull. Chem. Soc. Japan*, **31**, 999 (1958).

(11) Throughout this paper the abbreviation "cc." refers to gases at standard conditions.

(12) The most abundant species in the mass spectrum of dimethylfluoroborine are the ions $Me^{10}BF^+$ and $Me^{11}BF^+$. However, species, such as $CH_2{}^{11}BF^+$ contribute, along with $Me^{10}BF^+$, to the 44 peak. This clearly affects the observed $^{11}B/^{10}B$ ratio (Table II).

(13) T. D. Parsons and D. M. Ritter, THIS JOURNAL, **76**, 1710 (1954); G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, *ibid.*, **79**, 5190 (1957).

(14) For a useful summary of reactions of this type see G. A. Russell *ibid.*, **81**, 4815 (1959).

TABLE II

STUDY OF BORON HALIDE EXCHANGE REACTIONS BY MASS SPECTROMETRY

Reaction[a]	R	X	$^*BF_3$, q^*, starting material	$q_{(obsd.)}$,[b] products		$q_{calcd.}$[c] for mechanism X exchange only		R & X exchange	
					BF_3		BF_3		
I	...	Cl	0.089		0.704		0.802		....
	...	Br	0.093		0.828		0.808		....
				RBF_2	BF_3	RBF_2	BF_3	RBF_2	BF_3
	CH_3	Br	0.158	1.32	0.180	1.33	0.158	...	0.877
			.128	1.34	.187	1.32	.128	...	.837
II	C_2H_5	Cl	.090	3.74	.089	4.03	.089	0.783	.783
	$CH_2{:}CH$	Cl	.089	4.05	.132	3.97	.089	.776	.776
				R_2BF	BF_3	R_2BF	BF_3	R_2BF	BF_3
III	CH_3	Cl	0.093	2.99	0.091	2.89	0.093	...	0.901

[a] (I) $BX_3 + {}^*BF_3 \rightleftarrows BX_2F + BXF_2$; (II) $3RBX_2 + 2{}^*BF_3 \rightleftarrows 3RBF_2 + 2BX_3$; (III) $3R_2BX + {}^*BF_3 \rightleftarrows 3R_2BF + BX_3$. [b] $q = {}^{11}B/{}^{10}B$ ratio. [c] q taken as 4.00 for normal boron.

riched boron trifluoride would occur, accompanied by an increase in the ^{10}B content of the organoboron fluoride. In the mechanism involving halogen exchange only, no change in the $^{11}B/^{10}B$ ratio in recovered boron trifluoride or organoboron fluoride should occur. The results summarized in Table II show that only halogen exchange occurs in reactions between boron trihalides and organodihaloborines, under conditions where disproportionation of the organoboron halides by themselves would not occur.

In reactions between boron trifluoride and diorganohaloborines no organodifluoroborines were produced. Thus dimethylchloroborine and boron trifluoride gave dimethylfluoroborine, no methyldifluoroborine being formed. The absence of organodifluoroborines as products in exchanges involving diorganohaloborines shows that organo-group transfer is not taking place. This is further confirmed by the isotopic study (Table II).

As indicated in the Experimental section, during the course of the mass spectrometric work several mixed species of the type RBXY (X = F, Y = Cl, Br) were observed.[15] The existence of these unstable mixed species strongly supports the four-center bimolecular mechanism for exchange discussed earlier.

Finally it is worth noting that the exchange reactions described in this paper provide the basis of a method for the quantitative replacement of halogen X in an RBX_2 or an R_2BX compound by a halogen Y, provided the desired organoboron halide RBY_2 or R_2BY is a weaker Lewis acid than RBX_2 or R_2BX.[16] This quantitative exchange may be brought about by addition of a suitable deficiency of trimethylamine to the boron trihalide-organoboron halide equilibrium mixture so that the stronger Lewis acids are removed. Alternatively, a preformed amine-adduct may be heated with a suitably chosen boron trihalide whereupon an exchange takes place such as

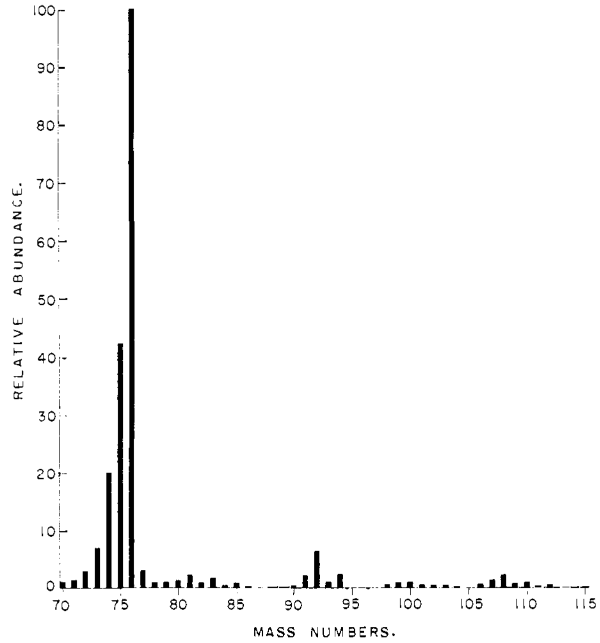


Fig. 1.—Fragmentation pattern for the equilibrium mixture resulting from reaction of vinyldichloroborine with boron trifluoride.

$$Me_3N{\cdot}BX_2R \xrightarrow{BY_3} RBY_2 + Me_3N{\cdot}BX_2Y^{17}$$

---

[15] To our knowledge the only attempt to verify the existence of moieties RBXY is the work of Buls, Davis and Thomas.[7] These workers obtained evidence for the transitory existence of $C_4H_9B(F)Cl$.

[16] F. E. Brinckman and F. G. A. Stone, *Chem. and Ind.* (*London*), 254 (1959).

[17] Solids obtained in these reactions may be mixtures of $Me_3N{\cdot}BX_3$ and $Me_3N{\cdot}BY_3$ rather than as formulated.