# THE RELATIVE ACCEPTOR POWER OF BORON TRIHALIDES AND BORANE TOWARD TRIMETHYLAMINE

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# THE RELATIVE ACCEPTOR POWER OF BORON TRIHALIDES AND BORANE TOWARD TRIMETHYLAMINE[1]

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Received July 15, 1963

## ABSTRACT

Gas phase displacement reactions of boron trihalides from their trimethylamine adducts show that the order of acceptor power is: $BBr_3 > BCl_3 > BF_3 > 1/2(B_2H_6)$. This order agrees with recent theoretical calculations and dipole moment, calorimetric, and infrared measurements on boron trihalide complexes with other reference bases.

## INTRODUCTION

On the basis of electronegativities and steric requirements of the halogens, the classically accepted order of acceptor power of the boron trihalides was $BF_3 > BCl_3 > BBr_3$ (1). Recent work, however, has indicated the reverse order to be correct. Calorimetric studies by Brown and Holmes (1) on the pyridine complexes of boron trihalides in nitrobenzene solution first revealed the new order. This order was confirmed by Bax, Katritzky, and Sutton (2), who measured dipole moments of boron trihalide and borane ($BH_3$) adducts of pyridine and trimethylamine. Lappert (3), using ethyl acetate as reference base and taking the shift of the carbonyl stretching frequency in the infrared as an indication of donor–acceptor bond strength, concluded that $BBr_3$ is a stronger acceptor than $BCl_3$. Similar studies by Cook (4) on boron trihalide–xanthone complexes also confirm the new order, as do the theoretical calculations of Cotton and Leto (5).

The same order, if correct, should be evident from a study of the displacements of boron trihalides from their molecular addition compounds. Displacement reactions, although complicated by lattice energy and volatility effects, are often used to determine qualitatively the relative stability of a series of closely related complexes in which lattice energies do not vary significantly (6). From such data the relative acceptor strengths of a series of related Lewis acids can be inferred. In all cases where this has been done, the conclusions have not had to be changed when quantitative data have subsequently been reported for gas phase dissociation of the same complexes (6).

Graham and Stone (7) using trimethylamine as reference base found no displacement of $BF_3$ from $(CH_3)_3N \cdot BF_3$ by $B_2H_6$ at 80° C. Dutton *et al.* (8) reported that $BCl_3$ almost quantitatively displaced $BF_3$ from $(CH_3)_3N \cdot BF_3$ at 205° C, and the reverse reaction was not detected. We have now extended this work by investigating gas phase displacements of $BH_3$, $BF_3$, $BCl_3$, and $BBr_3$ from their trimethylamine adducts.

## RESULTS AND DISCUSSION

It is evident from the results summarized in Table I that $BCl_3$ almost quantitatively displaced $BF_3$ from $(CH_3)_3N \cdot BF_3$ while the reverse reaction was not detected. Similarly, $BBr_3$ displaced $BCl_3$ and $BF_3$ from their trimethylamine adducts, while the reverse reaction occurred to a negligible extent. All three boron trihalides displaced $BH_3$ from

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[1] *This work was supported by a grant from The Defence Research Board of Canada (Grant number 9530-20, Project D46-95-30-20). Presented at the 46th Conference of the Chemical Institute of Canada, Toronto, Ontario, June 6–8, 1963.*

[2] *Holder of an N.R.C. Bursary, 1961–62, and N.R.C. Studentships, 1962–64.*

Canadian Journal of Chemistry. Volume 41 (1963)

TABLE I

Displacement data

| Reaction | Time (hr) | Temp | Average displacement (%) |
|---|---|---|---|
| $(CH_3)_3N \cdot BF_3 + BCl_3$ | 3 | 205 | 96.4[a] |
| $(CH_3)_3N \cdot BCl_3 + BF_3$ | 3 | 205 | 0.0[a] |
| $(CH_3)_3N \cdot BH_3 + BCl_3$ | 12 | 130 | 77.5 |
| $(CH_3)_3N \cdot BF_3 + BBr_3$ | 2/3 | 250–300 | 89.2 |
| $(CH_3)_3N \cdot BBr_3 + BF_3$ | 3/4 | 250–300 | 0.0 |
| $(CH_3)_3N \cdot BCl_3 + BBr_3$ | 1/2 | 250–300 | 72.6[b] |
| $(CH_3)_3N \cdot BCl_3 + BBr_3$ | 3/4 | 250–300 | 91.3[b] |
| $(CH_3)_3N \cdot BCl_3 + BBr_3$ | 3 | 263–265 | 95.6[b] |
| $(CH_3)_3N \cdot BBr_3 + BCl_3$ | 3/4 | 250–300 | 14.7[b] |
| $(CH_3)_3N \cdot BH_3 + BBr_3$ | 1 | 250–300 | 90.2 |
| $(CH_3)_3N \cdot BH_3 + BF_3$ | 3/4 | 130–140 | 83.3 |
| $(CH_3)_3N \cdot BF_3 + 1/2(B_2H_6)$ | 3/4 | 130–140 | 23.4 |

[a] Values in reference 8.
[b] Based on $BCl_3$.

$(CH_3)_3N \cdot BH_3$ with the evolution of diborane which decomposed at the temperatures used. The reverse reaction of $B_2H_6$ with $(CH_3)_3N \cdot BF_3$ occurred only to a small extent. These results lead us to conclude that the order of acceptor power of boron trihalides and diborane toward trimethylamine is: $BBr_3 > BCl_3 > BF_3 > 1/2(B_2H_6)$.

Brown and Holmes (1) suggested that the order of acceptor power of boron trihalides depends mainly on the extent of $p_\pi$—$p_\pi$ back bonding between the vacant $2p$-orbital of boron and a doubly occupied $p$-orbital of the halogen.

During adduct formation the hybridization of boron changes from $sp^2$ to $sp^3$ with resultant breaking of the $p_\pi$—$p_\pi$ bonds. Cotton and Leto (5) have shown that the strength of boron–halogen $p_\pi$—$p_\pi$ bonding decreases in the order $BF_3 > BCl_3 > BBr_3$, and that the reorganization energy required for adduct formation is also in the same order (48.3, 30.3, and 26.2 kcal $mole^{-1}$ respectively). These reorganization energies provide the most satisfactory explanation of the relative acceptor power of boron trihalides; the larger the reorganization energy, the weaker the acceptor power. The observation that $BBr_3$ displaced $BF_3$ to a greater extent than $BCl_3$ from their trimethylamine adducts may be due to the fact that the difference in reorganization energy between $BBr_3$ and $BF_3$ is much greater than that between $BBr_3$ and $BCl_3$. Similarly, the great difference between $BF_3$ and $BCl_3$ could account for the nearly quantitative displacement of $BF_3$ by $BCl_3$ and the absence of the reverse displacement. In the case of $BCl_3$ and $BBr_3$ where the difference in reorganization energy is small, the reverse reaction occurred to a significant extent (14.7%).

Since displacement reactions probably occur in the following two steps* (where X and would the heavier and presumably less volatile complex be formed in preference. However, the volatility of an adduct is not always determined by its molecular weight. For example, in trimethylamine complexes of germanium and silicon tetrahalides, $(CH_3)_3N \cdot GeF_4$ is more stable and less volatile than $(CH_3)_3N \cdot GeCl_4$ despite the latter's higher molecular weight (9). Similarly, $(CH_3)_3N \cdot SiF_4$ is more stable and less volatile than the heavier $(CH_3)_3N \cdot SiCl_4$ (9). Also, ammonia displaces tetrahydrofuran from its $BH_3$ complex forming a less volatile adduct (10), even though ammonia is lighter and more volatile than tetrahydrofuran.

Dipole moment measurements on trimethylamine and pyridine adducts (2) indicate that $BH_3$ is a slightly stronger acceptor than $BF_3$ but weaker than $BCl_3$. Although there is no possibility of supplementary $\pi$-bonding in the $BH_3$ group, there is the reorganization energy of $BH_3$ from $sp^2$ to $sp^3$ hybridization and the dissociation energy of diborane to be considered in displacement reactions involving diborane. No calculations have yet been made of the reorganization energy, but the dissociation energy of diborane is known to be $28.4 \pm 2$ kcal mole$^{-1}$ (11). Thus in displacement reactions involving the $BH_3$ group, additional energy (14.2 kcal mole$^{-1}$ of $BH_3$) is produced by dimerization of $BH_3$ groups. It appears that this extra energy makes the displacement of $BH_3$ by $BF_3$ energetically favorable even though $(CH_3)_3N \cdot BH_3$ is thermodynamically more stable than $(CH_3)_3N \cdot BF_3$. Thermochemical data (11) show that although the heat of reaction for $BF_3 + (CH_3)_3N$ is 26.6 kcal mole$^{-1}$ and 17.3 kcal mole$^{-1}$ for $1/2(B_2H_6) + (CH_3)_3N$, the calculated heat of reaction for $BH_3 + (CH_3)_3N$ is 31.5 kcal mole$^{-1}$. These values indicate that if $BH_3$ existed as a stable monomer it would be a stronger acceptor than $BF_3$ toward $(CH_3)_3N$ by about 5 kcal mole$^{-1}$ (11).

## EXPERIMENTAL

### *Methods and Apparatus*

Volatile substances were manipulated in a standard high vacuum apparatus made of Pyrex glass (12). Stopcocks and ground glass joints were lubricated with Kel-F 90 grease which is not appreciably attacked by boron trihalides. Molecular weights (M) were determined by vapor density. The purities of volatile components were checked by vapor pressure, molecular weight, and gas phase infrared spectra measurements. The purities of solid adducts were checked by melting point (m.p.) determinations.

The reaction vessel was a pyrex tube, 40 cm long and 4.1 cm diameter, which had at one end a capillary constriction and a magnetically operated break-seal. The other end of the reaction vessel was fused to 20 cm of 2.5 cm tubing through which the weighed solid was inserted in a fused solica boat. This end was then sealed off about 8 cm from the larger diameter tube. After the vessel and its contents were evacuated, a measured amount of the volatile component was condensed in, and the capillary constriction was sealed off. Reactions were carried out by heating the reaction vessel in a tube furnace so that one end of the reaction vessel projected slightly. When all the material had sublimed to this cool end, the reaction tube was pushed into the furnace so that the hot end emerged and cooled, and the sublimation process reversed. This procedure was repeated until the desired reaction time had elapsed. Several reactions were done by placing the entire reaction vessel in a closed oven, but there were no significant differences between these results and those obtained by the multiple pass procedure. On completion of a displacement reaction the vessel was cooled with liquid air and then opened to the vacuum system through the magnetic break seal. Volatile products were removed and analyzed in the vacuum apparatus. The reaction tube was then cut open and the solid material examined, usually by infrared spectroscopy.

Observations of the infrared spectra of solid complexes in KBr discs revealed that each complex had at least one unique peak; these were: 690 cm$^{-1}$ for $(CH_3)_3N \cdot BF_3$; 790 cm$^{-1}$ for $(CH_3)_3N \cdot BCl_3$; 730, 714, and 672 cm$^{-1}$ for $(CH_3)_3N \cdot BBr_3$ and 2357 cm$^{-1}$ for $(CH_3)_3N \cdot BH_3$.

### *Materials*

Diborane was prepared by the reaction of sodium borohydride with sulphuric acid (13). Commercial samples of boron trifluoride (Matheson), boron trichloride (Matheson), boron tribromide (Anderson), and trimethylamine (Matheson) were purified by several vacuum distillations and their purities were checked by vapor pressure, molecular weight, and infrared spectra measurements. Borane-trimethylamine (Callery) was purified by several vacuum sublimations (found m.p. 93–95°; lit. (14) m.p. 94°). Boron trifluoride-trimethylamine was prepared by bubbling trimethylamine and boron trifluoride into a flask of cooled dry benzene. This method proved to be more satisfactory than that described in Inorganic Syntheses (15). The crude product was recrystallized from pure ethanol and dried under vacuum (found m.p. 141°; lit. (15) m.p. 138°). Boron trichloride-trimethylamine was prepared from boron trichloride and trimethylamine as described in Inorganic Syntheses (15) (found m.p. 238–240°; lit. (15) m.p. 242–243°). Boron tribromide-trimethylamine was prepared by bubbling trimethylamine into boron tribromide in cooled dry benzene. The white precipitate was recrystallized from hot ethanol (found m.p. 239°; lit. (16) m.p. 238°). The infrared spectra of the trimethylamine complexes were identical to those of Katritzky (17).

*Reaction of $BBr_3$ with $(CH_3)_3N\cdot BF_3$*

The reaction of $(CH_3)_3N\cdot BF_3$ (4.85 mmole) with $BBr_3$ (10.21 mmole) at 250–300° for 40 minutes produced, after distillation at −130°, $BF_3$ (4.32 mmole) and $BBr_3$ (5.87 mmole), corresponding to 89.2% displacement. The solid product was shown by its infrared spectrum to be mainly $(CH_3)_3N\cdot BBr_3$, with only a trace of $(CH_3)_3N\cdot BF_3$. After recrystallization once from hot ethanol the solid melted at 234–239° (lit. (15) m.p. for $(CH_3)_3N\cdot BBr_3$: 238°).

*Reaction of $BF_3$ with $(CH_3)_3N\cdot BBr_3$*

When $(CH_3)_3N\cdot BBr_3$ (3.69 mmole) and $BF_3$ (9.24 mmole) were brought together for 45 minutes at 250–300°, the volatile products, separated by distillation at −120°, consisted of $BF_3$ (9.35 mmole) and $BBr_3$ (0.25 mmole), indicating that no significant reaction had occurred. The observed $BBr_3$ probably resulted from slight thermal decomposition of $(CH_3)_3N\cdot BBr_3$. The infrared spectrum of the solid was that of $(CH_3)_3N\cdot BBr_3$ with no sign of $(CH_3)_3N\cdot BF_3$.

*Reaction of $BBr_3$ with $(CH_3)_3N\cdot BCl_3$*

After 30 minutes at 250–300°, $(CH_3)_3N\cdot BCl_3$ (4.16 mmole) and $BBr_3$ (6.79 mmole) yielded a volatile product the infrared spectrum of which contained bands characteristic of $BBr_3$ and $BCl_3$ in addition to bands at 878, 916, 918, and 954 cm$^{-1}$. The first two bands are characteristic of $BCl_2Br$ and the last two of $BClBr_2$; both molecular species are present in a mixture of $BCl_3$ and $BBr_3$, and are impossible to isolate (18). Since it was not possible to separate the $BCl_3$–$BBr_3$ mixture quantitatively, its composition was estimated from the molecular weight of the gaseous mixture; the results were, $BCl_3$ (3.02 mmole) and $BBr_3$ (3.03 mmole). The $BCl_3$ value indicated 72.6% displacement, while the $BBr_3$ value indicated 90.0% displacement. The infrared spectrum of the solid showed $(CH_3)_3N\cdot BBr_3$ together with a small amount of $(CH_3)_3N\cdot BCl_3$. A mixed halide analysis of the solid indicated that 71.7% displacement had occurred, which is in excellent agreement with the value indicated by the $BCl_3$ recovery.

A second reaction of $(CH_3)_3N\cdot BCl_2$ (4.18 mmole) with $BBr_3$ (8.47 mmole) at 250–300° for 45 minutes produced $BCl_3$ (3.81 mmole), corresponding to 91.3% displacement.

The same reaction was repeated a third time with $(CH_3)_3N\cdot BCl_3$ (2.57 mmole) and $BBr_3$ (5.22 mmole) at 263–265° for 3 hours. In this case the reaction was carried out in an oven with more accurate temperature control. The amount of $BCl_3$ recovered (3.46 mole) indicated 95.6% displacement.

The three experiments show that displacement becomes almost quantitative as the reaction time is increased.

*Reaction of $BCl_3$ with $(CH_3)_3N\cdot BBr_3$*

The reaction of $(CH_3)_3N\cdot BBr_3$ (2.52 mmole) with $BCl_3$ (6.31 mmole) at 250–300° for 45 minutes produced $BBr_3$ (0.56 mmole) and unconsumed $BCl_3$ (5.94 mmole), corresponding to displacements of 22.2 and 14.7% based on $BBr_3$ produced and $BCl_3$ consumed, respectively.

The solid was mainly $(CH_3)_3N\cdot BBr_3$ as evident from its infrared spectrum which also indicated a small amount of $(CH_3)_3N\cdot BCl_3$.

*Reaction of $BF_3$ with $(CH_3)_3N\cdot BH_3$*

Boron trifluoride (6.18 mmole) and $(CH_3)_3N\cdot BH_3$ (3.32 mmole) reacted at 130–150° for 45 minutes to yield a yellow non-volatile oil which solidified on cooling. This solid was probably polymeric $(BH)_x$ produced by thermal decomposition of diborane formed from the displaced $BH_3$: $xB_2H_6 \rightarrow 2xH_2 + 2(BH)_x$. This decomposition, if quantitative, should yield 1 mole of hydrogen per mole of $(CH_3)_3N\cdot BH_3$ decomposed. The volatile products from the displacement and simultaneous decomposition were hydrogen (2.78 mmol) and $BF_3$ (3.58 mmole). On the basis of $BF_3$ consumed, displacement had occurred to 80.5%, while, on the basis of hydrogen produced, the displacement reaction was 86% complete. The infrared spectrum of the solid showed $(CH_3)_3N\cdot BF_3$ with a small amount of $(CH_3)_3N\cdot BH_3$.

*Reaction of $B_2H_6$ with $(CH_3)_3N\cdot BF_3$*

Diborane (3.90 mmole, i.e. 7.80 mmole $BH_3$) and $(CH_3)_3N\cdot BF_3$ (2.64 mmole) were kept at 130–140° for 45 minutes. Then, while all the solid material was at one end of the reaction vessel, the other end was heated to 200° for 1 hour to decompose excess $B_2H_6$. This procedure was adopted because $B_2H_6$ cannot be easily separated quantitatively from $BF_3$ by vacuum distillation. The volatile products consisted of hydrogen (6.84 mmole), boron trifluoride (0.84 mmole), and diborane (0.42 mmole). The displacement based on the amount of $BF_3$ recovered was 31.8%, and 14.9% based on hydrogen produced. The infrared spectrum of the solid showed it to be mainly $(CH_3)_3N\cdot BF_3$ with a small amount of $(CH_3)_3N\cdot BH_3$.

### *Reaction of* $BCl_3$ *with* $(CH_3)_3N \cdot BH_3$

The reaction of $(CH_3)_3N \cdot BH_3$ (5.82 mmole) with $BCl_3$ (6.38 mmole) in an oven at 130° for 12 hours produced hydrogen (4.46 mmole) and $BCl_3$ (1.84 mmole) as the only volatile products. The percentage displacement was 76.9 calculated on the amount of hydrogen produced, and 78.0 on the basis of $BCl_3$ produced. Infrared measurements revealed that the solid was $(CH_3)_3N \cdot BCl_3$ contaminated with some $(CH_3)_3N \cdot BH_3$.

### *Reaction of* $BBr_3$ *with* $(CH_3)_3N \cdot BH_3$

Boron tribromide (6.12 mmole) reacted with $(CH_3)_3N \cdot BH_3$ (4.18 mmole) at 250–300° for 60 minutes to produce hydrogen (3.85 mmole) and $BBr_3$ (2.42 mmole). The $BBr_3$ consumed indicated 88.5% displacement while the hydrogen produced indicated 92%. The solid was almost entirely $(CH_3)_3N \cdot BBr_3$, as evident from its infrared spectrum.

### *Effect of Heat on the Trimethylamine Adducts*

The pure complexes were heated separately under the same conditions used in the displacement reactions. In the case of $(CH_3)_3N \cdot BF_3$, $(CH_3)_3N \cdot BCl_3$, and $(CH_3)_3N \cdot BBr_3$ there was no detectable decomposition in 45 minutes at 250–300°, and the infrared spectra of each was unchanged. However, $(CH_3)_3N \cdot BH_3$ decomposed, with formation of hydrogen and $(CH_3)_3N$, to an extent of 30.0% based on the amount of hydrogen evolved.

## ACKNOWLEDGMENTS

We are grateful to the Defence Research Board for financial assistance and to the National Research Council for the award of scholarships to one of us (J. M. M.).

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