THE RELATIVE ACCEPTOR POWER OF BORON TRIHALIDES AND BORANE TOWARD TRIMETHYLAMINE

J. M. Miller and M. Onyszchuk
THE RELATIVE ACCEPTOR POWER OF BORON TRIHALIDES AND BORANE TOWARD TRIMETHYLAMINE

J. M. MILLER and M. ONYSCHUK
Inorganic Chemistry Laboratory, McGill University, Montreal, Quebec
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·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·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·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

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.


Canadian Journal of Chemistry. Volume 41 (1963) 2898
reorganization energy is small, the reverse reaction occurred to a significant extent. In the absence of the reverse displacement, in the case of BCb and BBra where the difference in reorganization energy between BBra and BF3 is much greater than that between BBra and BCb. Similarly, the great difference between BF3 and BBr3 could account for the nearly quantitative displacement of BF3 by BBr3 and the absence of the reverse displacement. In the case of BC13 and BBr3, 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

\[(\text{CH}_3)_3N \cdot \text{BF}_3 + \text{BCl}_3 \rightarrow \text{BF}_3 + \text{BCl}_3 \]

\[(\text{CH}_3)_3N \cdot \text{BH}_3 + \text{BBra} \rightarrow \text{BH}_3 + \text{BBra} \]

\[(\text{CH}_3)_3N \cdot \text{BF}_3 + \text{BBra} \rightarrow \text{BF}_3 + \text{BBra} \]

\[(\text{CH}_3)_3N \cdot \text{BCl}_3 + \text{BBra} \rightarrow \text{BCl}_3 + \text{BBra} \]

\[(\text{CH}_3)_3N \cdot \text{BH}_3 + \text{BBr}_3 \rightarrow \text{BH}_3 + \text{BBr}_3 \]

\[(\text{CH}_3)_3N \cdot \text{BF}_3 + 1/2(\text{B}_2\text{H}_6) \rightarrow \text{BF}_3 + 1/2(\text{B}_2\text{H}_6) \]

Brown and Holmes (1) suggested that the order of acceptor power of boron trihalides depends mainly on the extent of \(p_r-p_r\) 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 \(p_r-p_r\) bonds. Cotton and Leto (5) have shown that the strength of boron-halogen \(p_r-p_r\) bonding decreases in the order BF3 > BBr3 > BBr3, 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 BBr3 displaced BF3 to a greater extent than BCl3 from their trimethylamine adducts may be due to the fact that the difference in reorganization energy between BBr3 and BF3 is much greater than that between BBr3 and BCl3. Similarly, the great difference between BF3 and BCl3 could account for the nearly quantitative displacement of BF3 by BCl3 and the absence of the reverse displacement. In the case of BCl3 and BBr3, 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

\[\begin{align*}
\text{Reaction} & \quad \text{Time} & \quad \text{Temp} & \quad \text{Average} \\
(\text{CH}_3)_3N \cdot \text{BF}_3 + \text{BCl}_3 & \quad 3 & \quad 205 & \quad 96.4^a \\
(\text{CH}_3)_3N \cdot \text{BCl}_3 + \text{BF}_3 & \quad 3 & \quad 205 & \quad 0.0^a \\
(\text{CH}_3)_3N \cdot \text{BH}_3 + \text{BCl}_3 & \quad 1 & \quad 130 & \quad 77.5 \\
(\text{CH}_3)_3N \cdot \text{BF}_3 + \text{BBr}_3 & \quad 2/3 & \quad 250-300 & \quad 89.2 \\
(\text{CH}_3)_3N \cdot \text{BBr}_3 + \text{BF}_3 & \quad 3/4 & \quad 250-300 & \quad 0.0 \\
(\text{CH}_3)_3N \cdot \text{BCl}_3 + \text{BBr}_3 & \quad 1/2 & \quad 250-300 & \quad 72.6^a \\
(\text{CH}_3)_3N \cdot \text{BCl}_3 + \text{BBr}_3 & \quad 3/4 & \quad 250-300 & \quad 91.3^a \\
(\text{CH}_3)_3N \cdot \text{BCl}_3 + \text{BBr}_3 & \quad 3 & \quad 263-265 & \quad 95.6^a \\
(\text{CH}_3)_3N \cdot \text{BBr}_3 + \text{BCl}_3 & \quad 3/4 & \quad 250-300 & \quad 14.7^b \\
(\text{CH}_3)_3N \cdot \text{BH}_3 + \text{BBr}_3 & \quad 1 & \quad 250-300 & \quad 90.2 \\
(\text{CH}_3)_3N \cdot \text{BH}_3 + \text{BF}_3 & \quad 3/4 & \quad 130-140 & \quad 83.3 \\
(\text{CH}_3)_3N \cdot \text{BF}_3 + 1/2(\text{B}_2\text{H}_6) & \quad 3/4 & \quad 130-140 & \quad 23.4 \\
\end{align*}\]

\(^a\)Values in reference 8.

\(^b\)Based on BCI3.
would the heavier and presumably less volatile complex be formed in preference. However, the volatilitly of an adduct is not always determined by its molecular weight. For example, in trimethylamine complexes of germanium and silicon tetrahalides, \((\text{CH}_3)_3\text{N} \cdot \text{GeF}_4\) is more stable and less volatile than \((\text{CH}_3)_3\text{N} \cdot \text{GeCl}_4\) despite the latter's higher molecular weight (9). Similarly, \((\text{CH}_3)_3\text{N} \cdot \text{SiF}_4\) is more stable and less volatile than the heavier \((\text{CH}_3)_3\text{N} \cdot \text{SiCl}_4\) (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 \(sp^3\) to \(sp^2\) 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 ± 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 \((\text{CH}_3)_3\text{N} \cdot \text{BH}_3\) is thermodynamically more stable than \((\text{CH}_3)_3\text{N} \cdot \text{BF}_3\) .

Thermochemical data (11) show that although the heat of reaction for \(\text{BF}_3 + (\text{CH}_3)_3\text{N}\) is 26.6 kcal mole\(^{-1}\) and 17.3 kcal mole\(^{-1}\) for \(1/2(\text{B}_2\text{H}_6) + (\text{CH}_3)_3\text{N}\), the calculated heat of reaction for \(\text{BH}_3 + (\text{CH}_3)_3\text{N}\) 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 \((\text{CH}_3)_3\text{N}\) 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 silica 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 \((\text{CH}_3)_3\text{N} \cdot \text{BF}_3\), 790 cm\(^{-1}\) for \((\text{CH}_3)_3\text{N} \cdot \text{BCl}_3\); 730, 714, and 672 cm\(^{-1}\) for \((\text{CH}_3)_3\text{N} \cdot \text{BBF}_2\) and 2357 cm\(^{-1}\) for \((\text{CH}_3)_3\text{N} \cdot \text{BH}_3\).

**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 trifluoride-trimethylamine was prepared by reaction of boron trifluoride 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. 16 m.p. 238°). The infrared spectra of the trimethylamine complexes were identical to those of Katritzky (17).

**Reaction of BBra with (CH₃)₃N·BF₃**

The reaction of (CH₃)₃N·BF₃ (4.83 mmole) with BBra (10.21 mmole) at 250–300° for 40 minutes produced, after distillation at −130°, BF₃ (4.32 mmole) and BBra (5.87 mmole), corresponding to 89.2% displacement. The solid product was shown by its infrared spectrum to be mainly (CH₃)₃N·BBra, with only a trace of (CH₃)₃N·BF₃. After recrystallization from hot ethanol the solid melted at 234–239° (lit. (15) m.p. for (CH₃)₃N·BBra: 238°).

**Reaction of BF₃ with (CH₃)₃N·BBra**

When (CH₃)₃N·BBra (3.69 mmole) and BF₃ (9.24 mmole) were brought together for 45 minutes at 250–300°, the volatile products, separated by distillation at −120°, consisted of BF₃ (9.35 mmole) and BBra (0.25 mmole), indicating that no significant reaction had occurred. The observed BBra probably resulted from slight thermal decomposition of (CH₃)₃N·BBra. The infrared spectrum of the solid was that of (CH₃)₃N·BBra, with no significant displacement.

**Reaction of BBra with (CH₃)₃N·BBr₃**

The reaction of (CH₃)₃N·BBr₃ (4.16 mmole) and BBra (6.79 mmole) yielded a volatile product, to be separated by distillation at −120°. The first two bands are characteristic of BBr₃ and the last two of BCl₃. Both molecular species are present in a mixture of BCl₃ and BBra, and are impossible to isolate (18). Since it was not possible to separate the BCl₃-BBra mixture quantitatively, its composition was estimated from the molecular weight of the gaseous mixture; the results were, BCl₃ (3.02 mmole) and BBra (3.05 mmole). The BCl₃ value indicated 72.8% displacement, while the BBr₃ value indicated 90.0% displacement. The infrared spectrum of the solid showed that 73.7% displacement had occurred, which is in excellent agreement with the value indicated by the BCl₃ recovery.

**Reaction of BCl₃ with (CH₃)₃N·BBra**

After 30 minutes at 250–300°, (CH₃)₃N·BCl₃ (4.16 mmole) and BBra (8.47 mmole) were brought together for 45 minutes produced BBr₃ (3.81 mmole), corresponding to 91.3% displacement.

**Reaction of BCl₃ with (CH₃)₃N·BBr₃**

The reaction of (CH₃)₃N·BBra (2.52 mmole) with BCl₃ (6.31 mmole) at 250–300° for 45 minutes produced BBr₃ (0.56 mmole) and unconsumed BCl₃ (5.94 mmole), corresponding to 72.2% displacement. The infrared spectrum of the solid was that of (CH₃)₃N·BBra, together with a small amount of (CH₃)₃N·BCl₃. A mixed halide analysis of the solid indicated that 76.6% displacement had occurred, which is in excellent agreement with the value indicated by the BCl₃ recovery.

**Reaction of BBr₃ with (CH₃)₃N·BCl₃**

A second reaction of (CH₃)₃N·BCl₃ (4.16 mmole) with BBra (8.47 mmole) at 250–300° for 45 minutes produced BBr₃ (3.81 mmole) and unconsumed BCl₃ (5.94 mmole), corresponding to 91.3% displacement.

**Reaction of BBr₃ with (CH₃)₃N·BBr₃**

The reaction of (CH₃)₃N·BBr₃ (2.52 mmole) with BBra (6.31 mmole) at 250–300° for 45 minutes produced BBr₃ (0.56 mmole) and unconsumed BCl₃ (5.94 mmole), corresponding to 72.2% displacement. The infrared spectrum of the solid showed that 76.6% displacement had occurred, which is in excellent agreement with the value indicated by the BCl₃ recovery.

**Reaction of BBr₃ with (CH₃)₃N·BCl₃**

The reaction of (CH₃)₃N·BCl₃ (4.16 mmole) with BBra (6.79 mmole) at 250–300° for 45 minutes produced BBr₃ (3.81 mmole) and unconsumed BCl₃ (5.94 mmole), corresponding to 72.2% displacement.

**Reaction of BCl₃ with (CH₃)₃N·BBr₃**

The reaction of (CH₃)₃N·BBr₃ (3.69 mmole) and BF₃ (9.24 mmole) was carried out in an oven with more accurate temperature control. The amount of BCl₃ recovered (3.46 mmole) indicated 95.6% displacement.

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

**Reaction of BCIBr with (CH₃)₃N·BBra**

The reaction of (CH₃)₃N·BCl₃ (4.16 mmole) and BBra (8.47 mmole) was carried out in an oven with more accurate temperature control.

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

**Reaction of BCIBr with (CH₃)₃N·BBra**

When BBra (10.21 mmole) and BF₃ (6.18 mmole) were brought together for 45 minutes at 263–265° for 3 hours, the mixture was inhomogeneous, and the mixture was re-run for 30 minutes at 250–300°, (CH₃)₃N·BBra (4.16 mmole) and BBra (8.47 mmole) were brought together for 45 minutes produced BBra (3.81 mmole) and unconsumed BCl₃ (5.94 mmole), corresponding to 72.2% displacement.

**Reaction of BCl₃ with (CH₃)₃N·BBr₃**

The reaction of (CH₃)₃N·BBr₃ (2.52 mmole) with BCl₃ (6.31 mmole) at 250–300° for 45 minutes produced BBr₃ (0.56 mmole) and unconsumed BCl₃ (5.94 mmole), corresponding to 72.2% displacement.

**Reaction of BBr₃ with (CH₃)₃N·BCl₃**

The reaction of (CH₃)₃N·BCl₃ (4.16 mmole) with BBra (6.79 mmole) at 250–300° for 45 minutes produced BBr₃ (3.81 mmole) and unconsumed BCl₃ (5.94 mmole), corresponding to 72.2% displacement.

**Reaction of BCl₃ with (CH₃)₃N·BBr₃**

The reaction of (CH₃)₃N·BBr₃ (3.69 mmole) and BF₃ (9.24 mmole) at 250–300° for 45 minutes produced BBra (0.25 mmole) and unconsumed BCl₃ (5.94 mmole), corresponding to 72.2% displacement.

**Reaction of BBr₃ with (CH₃)₃N·BCl₃**

The reaction of (CH₃)₃N·BCl₃ (4.16 mmole) with BBra (6.79 mmole) at 250–300° for 45 minutes produced BBr₃ (3.81 mmole) and unconsumed BCl₃ (5.94 mmole), corresponding to 72.2% displacement.

**Reaction of BCl₃ with (CH₃)₃N·BBr₃**

The reaction of (CH₃)₃N·BBr₃ (2.52 mmole) with BCl₃ (6.31 mmole) at 250–300° for 45 minutes produced BBr₃ (0.56 mmole) and unconsumed BCl₃ (5.94 mmole), corresponding to 72.2% displacement. The infrared spectrum of the solid showed that 76.6% displacement had occurred, which is in excellent agreement with the value indicated by the BCl₃ recovery.

**Reaction of BBr₃ with (CH₃)₃N·BCl₃**

The reaction of (CH₃)₃N·BCl₃ (4.16 mmole) with BBra (6.79 mmole) at 250–300° for 45 minutes produced BBr₃ (3.81 mmole) and unconsumed BCl₃ (5.94 mmole), corresponding to 72.2% displacement.
The reaction of BCl₃ with (CH₃)₃N·BH₃ evolved.
composed, with formation of hydrogen and (CH₃)₃N, to an extent of 30.0% based on the amount of hydrogen produced. Infrared measurements revealed that the solid was (CH₃)₃N·BCl₃ contaminated with some (CH₃)₃N·BH₃.

The reaction of BB₃ with (CH₃)₃N·BH₃ produced hydrogen (3.85 mmole) and BB₃ (2.42 mmole). The BB₃ consumed indicated 88.5% displacement while the hydrogen produced indicated 92%. The solid was almost entirely (CH₃)₃N·BB₃, as evident from its infrared spectrum.

Effect of Heat on the Trimethylamine Adducts

In the case of (CH₃)₃N·BF₃, (CH₃)₃N·BCl₃, and (CH₃)₃N·BB₃ there was no detectable decomposition in 45 minutes at 250-300°, and the infrared spectra of each was unchanged. However, (CH₃)₃N·BH₃ decomposed, with formation of hydrogen and (CH₃)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.).

REFERENCES
