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NOTE

POSSIBLE INTERMEDIATES IN THE DISCHARGE SYNTHESIS OF DIBORON TETRAHALIDES

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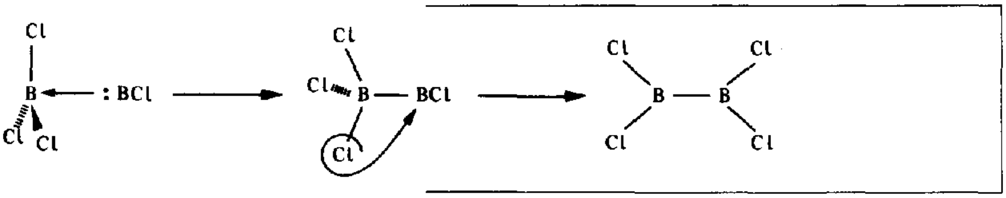
Abstract—When boron trichloride and tribromide are passed through a radiofrequency discharge to prepare the corresponding sub-halides, BCl and BBr can be detected spectroscopically. It is suggested that they are intermediates in the formation of B_2Cl_4, B_4Cl_4 and B_2Br_4. By the same technique, good yields of B_2I_4 are obtained from BI_3, although no BI could be detected because of the presence of much free I_2. Using a microwave discharge, although no known BI bands were observed, four new bands assigned to BI were found in an emission spectrum once again largely dominated by I_2.

Schlesinger first prepared B_2Cl_4 by passing BCl_3 vapour through a mercury discharge and assumed the product arose by dimerization of BCl_2 radicals formed by chlorine atom abstraction from BCl_3 by excited mercury atoms.[1] It was shown much later[2] that the spectrum of such discharges contains no bands of BCl_2 whereas strong emission from BCl was present. Similarly, the spectrum of BCl was observed during the microwave excitation of BCl_3 vapour a system which also produced B_2Cl_4 (and chlorine[3]). These results suggest that BCl is a precursor in the formation of B_2Cl_4. Thermodynamically, the reaction:

$$\begin{array}{llll} & BCl_3 + & BCl \rightarrow & B_2Cl_4 \\ \Delta G_f^{\circ} & -388.7 & 120.9 & -460.7\,\mathrm{kJ\,mol^{-1}}\ \text{(Ref. 4)} \end{array}$$

is favoured ($\Delta G^{\circ} = -192.9\,\mathrm{kJ\,mol^{-1}}$) and presumably proceeds via the donation of a lone pair of electrons on BCl into the empty 2p orbital of BCl_3:



Urry[5] has objected to this mechanism for the mercury discharge system, mainly because mercury(I) chloride is a by-product (he presumably thought mercury(II) chloride would be a more obvious product of stripping two chlorine atoms from a BCl_3 molecule) but also because he observed no mixed chlorides when BCl_3 and $SiCl_4$ were passed through the discharge (BCl might be expected to insert into $SiCl_4$; viz. $BCl + SiCl_4 \rightarrow Cl_2BSiCl_3$).

However, it is known[6] that mercury(II) chloride reacts with mercury to form Hg_2Cl_2. Furthermore, Cl_2BSiCl_3 has indeed been isolated as a by-product in the discharge-preparation of B_2Cl_4, probably arising from $SiCl_4$ impurity[7] in the BCl_3. Thus, two of Urry's initially plausible objections can now be discounted. His other cognate objection was that no Cl_2BPCl_2 was detected when a mixture of boron and phosphorus trichlorides was passed through the mercury discharge;[8] perhaps this experiment ought to be repeated.

Whether or not BCl reacts with BCl_3 will depend of course on the prevailing conditions. For example, Timms and Maddren[9] have shown that BCl and BCl_3 do not form B_2Cl_4 when they are co-

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condensed at −196°C (under similar extreme conditions BF does insert into BF_3 to give diboron tetrafluoride[10], $\Delta G_f^\circ = -140.2$ kJ mol^{-1}). More recently,[11] it was found that BCl_3, when passed at low pressure through a radiofrequency discharge in the presence of mercury, produces B_2Cl_4 and B_4Cl_4.

Diener and Pflugmacher[12] prepared B_2Br_4 by passing BBr_3 through an electrical discharge maintained between nickel electrodes. Previously, an almost identical system had been used to study the emission spectrum of BBr in the discharge zone.[13] Again, when BBr_3 is passed at low pressure through a radiofrequency glow discharge, B_2Br_4 is formed.[14] Now for the reaction:

$$BBr_3 + BBr \rightarrow B_2Br_4$$
$$\Delta G_f^\circ:\ -232.5 + 195.4\ \text{—kJ mol}^{-1}$$

the value of $\Delta G_f^\circ(B_2Br_4)$ is unknown, but the high positive value of $\Delta G_f^\circ(BBr)$ ensures that ΔG° (reaction), given by $\Delta G_f^\circ(B_2Br_4) - (-232.5 + 195.4)$, will be highly negative for any plausible value assigned to $\Delta G_f^\circ(B_2Br_4)$. It is therefore, reasonable to suggest BBr as a possible intermediate in the formation of B_2Br_4 from BBr_3.

In this paper, we report the result of radio frequency and microwave discharges in BI_3 vapour, and of additional studies on BCl_3 and BBr_3.

EXPERIMENTAL

The radiofrequency generator (30 MHz) was similar to that of Schumb[16]. The pyrex discharge cell was about 30 cm long by 7.5 cm dia. and had a silica window fused onto one end, using a graded seal. R. F. power was applied to seven turns of 1 mm dia. copper wire wrapped round one end of the tube. A boron halide under study (mixed with carrier gas when necessary) was evaporated in a high vacuum system, from a U-tube on one side of the cell into a U-tube at −196°C on the other side. The discharge produced in the vapour was photographed through the silica window using a Hilger medium quartz spectrograph, type E498. The R. F. generator was replaced by an Evans Electro-medical Supplies Microtron 200 microwave generator, operating at 2.450 GHz, for the microwave excitation studies. Boron trihalide vapour was flowed through a quartz tube which passed through a tuned cavity. Argon and helium gases (B.O.C.) were taken direct from the cylinders without further treatment.

RESULTS AND DISCUSSION

It was found that the emission spectrum resulting from the radiofrequency discharge through BCl_3, in the presence of liquid mercury, contained not only the expected mercury atomic lines but also the (0,0), (1,0), (0,1), (1,1), (2,0), (2,1), (2,2), (0,3), (4,4), and (5,5) bands of the A $^1\Pi \rightarrow$ X $^1\Sigma^+$ system of BCl[18]. This species has therefore been shown to be present with up to five quanta of vibrational energy (53.4 kJ mol^{-1}), and once again one is led to the conclusion that the production of the two subchlorides, B_2Cl_4 and B_4Cl_4, occurs via the BCl intermediate. The well-known doublet of atomic boron (249.7, 249.8 nm) was also detected, the longer wavelength line being relatively less intense than its calculated Boltzmann value. Analogous results were obtained for the effect of the radiofrequency discharge on pure BBr_3 vapour. An intense A→X band system[18] of BBr was observed in which the longest wavelength band was the (3,5), corresponding to a vibrational excitation energy of 43.7 kJ mol^{-1}. On the addition of liquid mercury to the system, the only observed change was the appearance of mercury lines in the spectrum.

Only in the case of BI_3 were any problems experienced due to the spectrum of free halogen. It was found that molecular iodine dominated the spectrum emitted by the radiofrequency discharge through pure BI_3 vapour, and no bands were observed which could be assigned to BI or any other molecule containing boron. Once more, atomic boron in a non-equilibrium state was detected. About 25 cm^3 of mercury were added to the discharge cell to diminish the intensity of the iodine spectrum, but it still proved impossible to detect any bands of the BI spectrum corresponding to those reported by either Briggs and Piercy[17] or Lebreton.[15] The only other molecule to be detected was HgI, for which bands of the B $^2\Sigma^+ \rightarrow$ X $^2\Sigma$ and C $^2\Pi_{\frac{1}{2}} \rightarrow$ X $^2\Sigma^+$ systems were present. Following Lebreton[15] who used the gas to suppress the iodine spectrum in his studies on BI (produced using a Schüler type discharge), argon was flowed through the discharge cell. The pressure was such as just to sustain the glow, but in spite of this iodine emission was still relatively intense.

In a further series of experiments, BI_3 vapour, mixed with argon or helium, was subjected to microwave discharge. Four bands, degrading to the red, were observed at 349.8, 350.8, 351.2 and 352.5 nm. None of these corresponds to bands reported for I_2 or B_2, and they are not present in the spectra of discharges in He, Ar or I_2, in the absence of BI_3. It seems reasonable to conclude that the new bands relate to BI, although once more neither the BI bands[17] at 349.1 and 349.3 nm, nor the system belonging to the semi-forbidden transition[15] $a^3\Pi_{0+} \rightarrow X^1\Sigma^+$ near 600 nm, was observed. This result is perhaps not unexpected, since the former bands were obtained following the flash photolysis of BI_3, and the latter constitute a weak system overlaid in the present instance by iodine emission. Other spectral features in the BI_3 discharge were an intense atomic iodine line at 206.2 nm and two intense atomic boron doublets at 208.9 and 209.0, and at 249.7 and 249.8 nm.

It may be concluded reasonably that the available data are consistent with the hypothesis that the formation of boron subhalides in radiofrequency or microwave discharge systems does occur via the donation of BX lone pair electrons into the empty $2p$ orbital of BX_3 ($X = Cl$, Br or I).

REFERENCES

1. G. Urry, T. Wartik, R. E. Moore and H. I. Schlesinger, *J. Am. Chem. Soc.* 1954, **76**, 5293.
2. A. G. Briggs, M. S. Reason and A. G. Massey, *J. Inorg. Nucl. Chem.* 1975, **37**, 313.
3. R. T. Holzmann and W. F. Morris, *J. Chem. Phys.* 1958, **29**, 677.
4. D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey and R. H. Schumb, *N. B. S. Technical Note* 270–3 (1968).
5. G. Urry, In *The Chemistry of Boron and its Compounds* (Edited by E. L. Muetterties), p. 325. Wiley, New York (1967).
6. A. G. Sharpe, *Inorganic Chemistry*, p. 641. Longman, London (1981).
7. A. G. Massey and D. S. Urch, *Proc. Chem. Soc.* 1964, 284.
8. A. G. Garrett and G. Urry, *Inorg. Chem.*, 1963, **2**, 400.
9. P. L. Timms, In *Cryochemistry* (Edited by M. Moskovits and G. A. Ozin), p. 61. Wiley–Interscience, New York (1976).
10. P. L. Timms, *J. Am. Chem. Soc.* 1967, **89**, 1629.
11. T. Davan and J. A. Morrison, *Inorg. Chem.* 1979, **18**, 3194.
12. W. Diener and A. Pflugmacher, *Angew. Chem.* 1957, **69**, 777.
13. E. Rosenthaler, *Helv. Phys. Acta* 1940, **13**, 355.
14. N. A. Kutz and J. A. Morrison, *Inorg. Chem.* 1980, **19**, 3295.
15. J. Lebreton, J. Ferran, A. Chatalic, D. Iacocca and L. Marsigny, *J. Chim. Phys. Physicochim. Biol.* 1974, **71**, 587.
16. W. C. Schumb, E. L. Gamble and M. D. Banus, *J. Am. Chem. Soc.* 1949, **71**, 3225.
17. A. G. Briggs and R. Piercy. *Spectrochim. Acta* 1973, **A29**, 851.
18. K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure—IV. Constants of Diatomic Molecules*, p. 74. Van Nostrand, New York (1979).