1022. *Flash Photolysis of Boron Chlorides.*

By A. G. Massey and J. J. Zwolenik.

Flash photolysis of boron trichloride, diboron tetrachloride, or tetraboron tetrachloride produces only those absorption bands attributable to BCl radicals; the implications of this are briefly discussed.

Microwave discharges in boron trichloride at pressures less than 4 mm. Hg produce diboron tetrachloride, $Cl_2B{\cdot}BCl_2$, and molecular chlorine.[1] In the conditions of synthesis, the emission spectrum from the electrodeless discharge consisted only of bands due to the $A^1\Pi - X^1\Sigma$ system for BCl and atomic lines of boron and chlorine.[2] When diboron tetrachloride decomposes spontaneously at room temperature, approximately one mol. of boron trichloride is formed with certain amounts of tetraboron tetrachloride, B_4Cl_4, and octaboron octachloride, B_8Cl_8 [3] (later work [4] shows that the free radical $B_{12}Cl_{11}$, and not octaboron octachloride, is the main product arising from thermal decomposition of diboron tetrachloride). The formation of these less volatile residues of over-all composition $(BCl_n)_x$, where n approaches unity, suggests that the decomposition of diboron tetrachloride occurs with the production of BCl radicals and that the reversibility prevails under certain conditions.[4,5]

$$BCl_3 + BCl \longrightarrow B_2Cl_4 \qquad (1)$$

$$B_2Cl_4 \longrightarrow BCl_3 + BCl \qquad (2)$$

Experimental

Flash photolysis decomposes absorbing parent molecules in a few microseconds, the short-lived intermediates being observed spectroscopically as a function of time after the photolysis flash.[6] In the experiments reported here, a 2000 *J* flash of 30 microseconds' duration partially photolysed the contents of a quartz reaction vessel 50 cm. in length and 2 cm. in diameter. Transient absorption spectra were photographed by using a Hilger and Watts medium quartz spectrograph and a 100 *J* spectroscopic background flash of 7 microseconds' duration.

Diboron tetrachloride was prepared by passing boron trichloride, at low pressure, through a mercury discharge; boron trichloride was an unavoidable impurity in the sample. Tetraboron tetrachloride (1—2 mg.) also resulted from the discharge decomposition of boron trichloride and was freed from the other chlorides by fractional condensation *in vacuo*. Boron trichloride (B.D.H. sample) was similarly purified. The photolysis tube was thoroughly flamed and flushed several times with the appropriate boron chloride before introduction of the photolysis sample.

Results and Discussion

The photolysis of diboron tetrachloride was studied at 1 mm. pressure both in the presence and in the absence of oxygen-free, dry nitrogen to elucidate the mechanism of the decomposition and to search for the absorption spectrum of the triatomic radical BCl_2.

Only the absorption bands corresponding to the $A^1\Pi - X^1\Sigma$ system of BCl radicals appeared.[7,8] From available bond energies [9] one might expect that the boron–boron bond in diboron tetrachloride would be cleaved readily under these conditions; however, no new spectral lines attributable to BCl_2 radicals were to be observed. Under isothermal conditions, with 370 mm. pressure of nitrogen present, the maximum concentration of BCl radicals occurred about 15 microseconds after the photolysis flash, the absorption spectrum

---

[1] Frazer and Holzman, *J. Amer. Chem. Soc.*, 1958, **80**, 2907.

[2] Holzman and Morris, *J. Chem. Phys.*, 1958, **29**, 677.

[3] Urry, Wartik, Moore, and Schlesinger, *J. Amer. Chem. Soc.*, 1954, **76**, 5293.

[4] Urry and Schram, *J. Amer. Chem. Soc.*, 1962, **84**, 2654.

[5] Holliday and Massey, *Chem. Rev.*, 1962, **62**, 303.

[6] Porter, " Flash Photolysis " in " Techniques of Organic Chemistry, Vol. VIII," Interscience Publ. Inc., New York, 1963.

[7] Pearse and Gaydon, " Identification of Molecular Spectra," Chapman and Hall, London, 1950.

[8] Miescher, *Helv. Phys. Acta*, 1935, **8**, 279.

[9] Gunn, Green, and von Egidy, *J. Phys. Chem.*, 1959, **63**, 1787.

being detectable for almost 100 microseconds. At maximum intensity the BCl bands corresponding to $\Delta v = v' - v'' = 0$ for $v' = v'' \leqslant 4$ and to $\Delta v = 1$ for $0 \leqslant v'' \leqslant 2$ appear. As the maximum intensity decays only those $\Delta v = 0$ bands near 2720 Å persist. In the absence of added nitrogen, the BCl absorption is most intense at 250 microseconds. In addition to increased intensity of the bands found in the isothermal case there are bands corresponding to $|\Delta v| = 1$ for $1 \leqslant v'' \leqslant 4$. In the build-up and decay of the BCl spectrum the latter bands are the last to appear and the first to disappear, since they represent transitions from high vibrational levels of the ground state which would be appreciably populated only at maximum adiabatic heating. At delays greater than 850 microseconds only the $\Delta v = 0$ bands near 2720 Å are observed.

The radicals formed under these adiabatic conditions are in the main due to thermal decomposition, as opposed to photolysis, of the diboron tetrachloride sample. This provides the first direct evidence in support of equation (2).

It is known from Meader's work,[10] that high-voltage discharges through boron trichloride produce BCl radicals in abundance. Attempts to produce BCl radicals by flash photolysis of boron trichloride failed in the presence of added nitrogen, but succeeded in experiments with boron trichloride alone at a pressure of 1 mm. A weak BCl absorption at 2720 Å can be seen for delays up to 30 microseconds. This spectrum was not due to $(BCl)_x$ wall deposits, as was shown by blank experiments, and, further, the boron trichloride was of high purity. In the light of these modes for BCl formation from boron trichloride and the absence of any new spectrum attributable to BCl_2 radicals, a suitable scheme for the production of diboron tetrachloride in a high-voltage mercury discharge is:

$$BCl_3 \xrightarrow[\text{discharge}]{\text{Mercury}} BCl + Hg_2Cl_2 \quad \ldots\ldots\ldots\ldots \quad (3)$$

$$BCl + BCl_3 \longrightarrow B_2Cl_4 \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$xBCl \longrightarrow (BCl)_x \quad \ldots\ldots\ldots\ldots \quad (4)$$

Formerly, reduction of the boron trichloride by mercury to give BCl_2 radicals with subsequent dimerization was postulated.[3]

The low yield of diboron tetrachloride in such a discharge preparation may be explained in part by the competition of reactions (4) and (1) since the BCl radicals may combine with the excess of boron trichloride to yield diboron tetrachloride or may polymerize on the tubes leading from the discharge to give the familiar yellow monochloride, $(BCl)_x$.

Experiments with the limited amount of tetraboron tetrachloride available showed that the vapour-phase absorption maximum occurs at 2450 Å and that about 35% of the parent material is destroyed by a single flash. Photographically the ultraviolet region down to 2150 Å could be easily observed; presumably the absorption maxima for boron trichloride, diboron tetrachloride, and tetraboron tetrachloride approach the higher ultraviolet region in the order listed.

Isothermal flash photolysis of tetraboron tetrachloride (1 mm. pressure) in the presence of a large excess of nitrogen yielded the same BCl absorption bands as were obtained from diboron tetrachloride under similar conditions. However, under adiabatic conditions the absorption due to BCl radicals is very intense. Bands appear from 2600 to 2915 Å and involve vibrational levels $0 \leqslant v'' \leqslant 9$ and $0 \leqslant v' \leqslant 7$ where $\Delta v = 0$, 1, 2, and 3. No bands appeared which could not be fitted into the BCl vibrational schemes of refs. 7 and 8, nor, in particular, did the radical B_2 appear.[11]

We thank the National Science Foundation, U.S.A., and Imperial Chemical Industries Limited for Fellowships.

DEPARTMENTS OF INORGANIC CHEMISTRY AND OF PHYSICAL CHEMISTRY,
THE UNIVERSITY, LENSFIELD ROAD, CAMBRIDGE.
[*Received, June 22nd*, 1963.]

[10] Maeder, *Helv. Phys. Acta*, 1943, **16**, 503.

[11] Douglas and Herzberg, *Canad. J. Res.*, 1940, **18**, *A*, 165.