Spectroscopic Studies of Bromine Oxides: the Infrared Spectrum of Solid Bromide Monoxide

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OF the possible halogen oxides of formula XOX (X = halogen), OF_2 and Cl_2O have accurately known structures and spectral properties,[1,2] I_2O is unknown and Br_2O, although characterised by analysis,[3] has had no structural properties established. We report some preliminary i.r. data on solid Br_2O.

The oxide $(BrO_2)_x$ was prepared by passing a high voltage electrical discharge (1600 v, 50 mA) through a bromine–oxygen gas mixture ($Br_2 : O_2 \sim 1 : 5$) at about 1 torr pressure in a Pyrex vessel at −196°. Ozone and bromine were removed by pumping as the sample warmed to −50°; the $(BrO_2)_x$ was then allowed to decompose slowly by warming and the products pumped through a trap at −196°; the mixture obtained was purified by pumping off the bromine and the other oxides at −63·5° leaving pure Br_2O.[3,4] This was then allowed to distil on to a cold (−196°) caesium iodide or Polythene window in a conventional glass cold cell. Considerable decomposition occurred even with a minimum path length; hence our inability to obtain any gas-phase spectra. The spectra obtained are of solid Br_2O–Br_2 mixtures since it is not possible to control the temperature of the window sufficiently accurately to distil off the bromine. The spectra shown in the Figure were recorded on Perkin–Elmer 521 and FS 720 spectrometers, and the samples were annealed by allowing them to warm up in the i.r. beam while monitoring the spectra, and then re-cooling to −196°. Figure 1c shows an expanded spectrum obtained in the high frequency region using ~25% $^{18}O_2$ in the preparation—it was not practicable to study the low frequency region using $^{18}O_2$ because of the low intensity of the low frequency bands and the great expense of $^{18}O_2$.

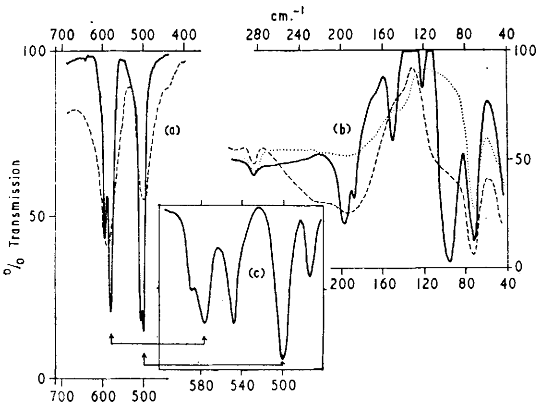

FIGURE. *The infrared spectra of solid* Br_2O *obtained on Perkin-Elmer* 521 (a) *and R.I.I.C.* FS 720 (b) *spectrometers*: · · · *background*; - - - *solid spectrum before annealing*; (c) *the expanded spectrum of* Br_2O *prepared with oxygen containing* ~ 25% $^{18}O_2$.

The spectra are most satisfactorily explained as the vibrations of a bent triatomic molecule of symmetry C_{2v} as follows: ν_3 (asymmetric stretch) 587 cm.$^{-1}$, ν_1 (symmetric stretch) 504 cm.$^{-1}$, ν_2 (bend) 197 cm.$^{-1}$; the bands at 150, 121, and 95 cm.$^{-1}$ are almost certainly lattice modes. This assignment follows from the experimental facts: (i) there are three readily assigned vibrations in the regions expected (*cf.* OF_2 and Cl_2O[1,2]), ν_3 at 821 and 671, ν_1 at 925 and 631, and ν_2 at 461 and 296 cm.$^{-1}$; (ii) the isotopic shifts (for $Br_2\,^{18}O$, $\nu_3 \approx 553$, $\nu_1 \approx 476$ cm.$^{-1}$) agree with predictions for a harmonic simple valence force field; (iii) the vibrations at 150, 121, and 95 cm.$^{-1}$ are resolved only after annealing, and are in the regions expected for librational and translational lattice modes; (iv) the splittings of the fundamentals can be ascribed to correlation field splitting.†

In principle, assuming a value of 113° for the Br–O–Br angle (*cf.* OF_2, 103°; Cl_2O, 110°), the three fundamental frequencies with the additional data from isotopic substitution provide enough information to evaluate the four force constants of a general valence force field:

$$2V = K[(\delta r_1)^2 + (\delta r_2)^2] + K_{2\theta}(r\delta_{2\theta})^2 + 2K_1\delta r_1\delta r_2 + 2K_2(\delta r_1 + \delta r_2)r\delta_{2\theta}.$$

In practice the isotopic shifts are not very helpful. A variety of methods of calculating the force constants (*e.g.* minimising K_2, setting $K_1 = 0$, isotopic frequencies, Lehmann's average rule[5]) result in the most likely set: $K = 2{\cdot}4 \pm 0{\cdot}2$. $K_{2\theta} = 0{\cdot}4 \pm 0{\cdot}1$, $K_1 = 0{\cdot}4 \pm 0{\cdot}2$, $K_2 = 0{\cdot}2 \pm 0{\cdot}1$ mdyne/Å. The force constant $K = 2{\cdot}4$ mdyne/Å is the value for the prototype single Br–O bond; Rochkind and Pimentel[2b] have predicted $K = 2{\cdot}1$ mdyne/Å from data on OF_2, Cl_2O, and other halogen compounds. That the value of 2·4 is reasonable is seen from the Table. The force constants all refer to nominal X–O single bonds; the reason for the variation for chlorine and bromine oxygen compounds is not yet understood.

Force constants of a number of halogen–oxygen species, (*values in mdynes/Å.*)

X		F	Cl	Br
OX_2	..	3·95[a]	2·75[b]	2·4[e]
OX^-	..		3·3[c]	3·0[f]
HOX	..		3·98[d]	3·59[d]

[a] Ref. 1; [b] ref. 2b; [c] ref. 6; [d] ref. 7; [e] this work; [f] ref. 8.

This research was supported by a grant from the S.R.C.

(*Received, May 9th,* 1968; *Com.* 581.)

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† This is based partly on simple matrix isolation experiments and also on the analysis of the variation of the splitting with $^{16}O/^{18}O$ ratio. Details will be published elsewhere.

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