

Bromine Oxides

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Introduction

The atomic combination of bromine and oxygen is possibly the most unfavorable one in nonmetal chemistry. From the little we know about the system Br–O it remains sure that all compounds are thermally unstable, and if accumulated in larger quantities, explosive. So why should we deal with these unfortunate compounds? First, we want to know why this is so and what the parallels to and differences from the quite well understood systems Cl–O and I–O are. Second, and very important in these days of need for application of research, ozone is often used in bromine oxide syntheses, and it is well established that the ozone depletion potential of bromine compounds (Br₂, HBr) is very high.^{1–3} For illustration the reciprocal concentrations of bromine and ozone in the atmosphere, as established in 1988, are shown in Figure 1.³

Before embarking on the progress report on bromine oxides, some definitions about stability and the existence of a compound should be tried. Certainly all bromine oxides are metastable with respect to decomposition, ultimately into Br₂ and O₂. A few of these compounds are at least stable enough to be held in a condensed phase without a diluent, the ultimate characterization goal of a (meta)stable compound so that the routine physical characterizations can be made. Some seem to exist only in the dilute gaseous phase and have been studied therein, and finally there are those that have so far been observed only under matrix conditions at cryogenic temperatures. We will call progress not only the finding of a new compound, but also the moving up in the ladder of a more complete description. And we will not deal with bromine oxides that have been claimed only once and have not been successfully traced back later.

While the interest in this field remained largely dormant after the detection of the first bromine oxides in the late 1920s and 1930s, in the last few years there has been an outbreak of new work. This was not only caused by the interest in the man-made ozone depletion problem, but also by the advent of more and more sophisticated methods of preparing, handling, and analyzing highly unstable compounds. M. W. Chase gives a possibly

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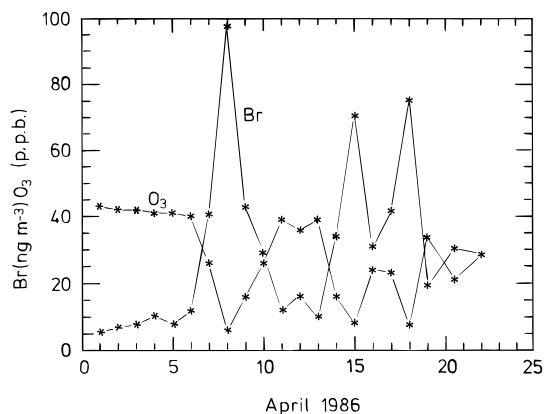


FIGURE 1. Daily mean ground level of O₃ and filterable Br concentration at Alert, Canada, in April 1986. Reprinted with permission from ref 1. Copyright 1988 Macmillan Magazines Limited.

complete survey of the literature on bromine oxides in his thermodynamic table collection.⁴

BrO

It always seems possible to detect diatomic species in the gas phase, but as the first observers note, BrO is one of the short-lived ones.^{5,6} Its microwave spectra,⁵ its ionization energy,⁷ and the kinetics of its possible self-reaction⁸ have been measured, and the quadrupole coupling constant has been calculated.⁹ However, there remains the impression that this free radical will always remain a transient in gas phase reactions.

BrO₂

Bromine dioxide is one of the mystery molecules. There are many physical and chemical parameters known about it, but the compound has never been obtained in even close to a pure state, if at all. In 1937 a BrO₂ was reported as a yellow solid, formed from Br₂ and O₂ in a glow discharge,¹⁰ or by the reaction of Br₂ and ozone in 1959.¹¹ We now have shown that the bulk of this material is not BrO₂, but rather a mixture of Br₂O₃ and Br₂O₅; see below. Of course the BrO₂ molecule can be identified by optical absorption in the gas phase reaction of Br₂/O₂ under flash photolysis¹² or in the Br₂/O₃ reactions.¹³ ESR spectra at cryogenic temperature have been assigned to the BrO₂ free radical,^{14,15} and it is assumed to play an intermediate part in the famous Belousov–Zhabotinsky oscillating reac-

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tion.¹⁶ Microwave discharge of O₂/Br₂ gas mixtures at -20 °C gives a solid product of nuclear composition, which has a vapor pressure of ~0.1 Pa of BrO₂. Its microwave spectrum was analyzed for a bent molecule with Br-O (164.91(15) pm) and O-Br-O (114.44(25)°). Even the asymmetric stretching frequency has been observed in the gas IR.¹⁷ From all this it must be concluded that it should exist as a pure compound in the condensed state. What could the structure be? There are proposals for O₂Br-BrO₂,¹⁸ OBr-O-BrO₂,¹⁹ and Br-O-BrO₃.²⁰ The first two structures are based on Raman spectroscopy, and the latter structure is based on bromine K α -edge EXAFS, however on materials that are now known not to be uniform. Br-O-BrO₃ might be prepared systematically; after all ClOClO₃ and BrOClO₃ are well-described compounds.²¹ However, this isomer would not be the one found in the gas phase and inert matrix state.

Ar/Br₂/O₂ codeposition under discharge at 10 K gave the first indication of the Br-O-O isomer,²² which was very recently more fully described in a flash pyrolysis experiment.²³ This rearranges upon irradiation into "normal" BrO₂.

The reasons why an isolation of pure BrO₂ has not been met with success may become obvious by comparison with ClO₂, SO₂, and SeO₂. If the equilibrium 2BrO₂ \rightleftharpoons (BrO₂)₂ exists, it may be shifted very much to the right-hand side, in contrast to ClO₂, where electron pairing is observed only in the solid state below -93 °C, resulting in a weak oxygen double bridged dimer.²⁴ Even if it does not dimerize to an electron-paired system, it may be an oxygen-bridged polymer like SeO₂, in contrast to SO₂, and therefore only slightly volatile and difficult to obtain in solution or even pure.

BrO₃

The situation for BrO₃ is particularly sad. Except for the detection by ESR in various irradiated ionic crystals at cryogenic temperatures,²⁵⁻²⁷ there is no sure report on this radical in spite of over 20 original papers over the years.

Br₂O

Only with Br₂O do we find safer ground. Known since the 1930s it is prepared either from the HgO/Br₂ reaction or by decomposing higher bromine oxides. The solid is described as dark brown,²⁸⁻³⁰ whereas the gas shows only

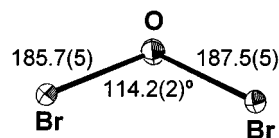


FIGURE 2. Structure of Br₂O in the crystal. Vibrational ellipsoids represent 50% probability. Numeric values are in picometers and degrees.

a weak absorption in the blue coming from the tail of a medium strong UV band,³¹ and in CCl₄ solution a green color is reported. The shape of the molecule is symmetrical and bent according to its microwave spectrum with Br-O (184.20(20) pm) and Br-O-Br (112.24(20)°).¹⁷ This agrees with IR²⁸ and recent bromine K-edge EXAFS²⁹ measurements. A single-crystal structure determination of Br₂O is also available;³⁰ see Figure 2. In the course of the single-crystal structure determination, it was found that the synthetic route HgO/Br₂ is not a convenient source for Br₂O. With the controlled hydrolysis reaction 2BrOTeF₅ + H₂O \rightarrow 2HOTeF₃ + Br₂O a reliable alternative was established; Br₂O appears as yellow needle-shaped crystals, which, if thicker, appear brown, even black.³⁰

The present interest in Br₂O arises from the fact that it seems to be the first (comparable) stable oxidation product of Br₂, but what are the real first oxidation products? Cocondensation of Br₂ and O₃ in argon gives evidence for a weak Br₂/O₃ complex that is assumed to have a nonsymmetric structure,³² which then relaxes into Br-Br=O, and further into Br-O-Br.^{29,32} An *ab initio* study of these two molecules with a very large atomic natural orbital (ANO) basis set level and CCSD(T) electron correlation showed that Br-Br=O is 14.6 \pm 0.8 kcal higher in energy than Br-O-Br. The calculated IR frequencies agree with the measured ones.³³

The mechanism Br₂ + O₃ \rightarrow Br₂·O₃ \rightarrow Br-BrO \rightarrow BrOBr seems to be the keystone of the bromine ozone reaction.

Br₂O₃ and Br₂O₅

The reaction of Br₂ and O₃ in CFCl₃ or other inert solvents gives reproducibly a lemon yellow powder, the nature of which has been the source of much speculation. Only very recently it was shown that this is a mixture of two compounds, and from the total amounts found it can be stated that other compounds are formed only in very minor quantities, if at all. The orange-yellow, CH₂Cl₂ soluble Br₂O₃ could be crystallized out and found to be bromine bromate, Br-OBrO₂; see Figure 3.³⁴ In the solid state there is a weak Br···Br interaction between the two Br(I) atoms at angles close to 90° and 180°, something which is similarly found even in solid Br₂. On the basis of Raman data such a compound has been proposed among others in the primary product.^{19,35} The Raman spectrum of BrOBrO₂ is so similar to that of BrOBrO₃

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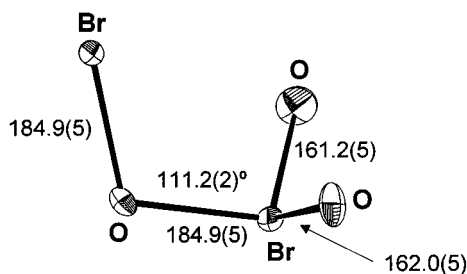


FIGURE 3. Structure of BrOBrO_2 in the solid state. Vibrational ellipsoids represent 50% probability. Numeric values are in picometers and degrees. Reprinted with permission from ref 34. Copyright 1993 VCH Verlag.

(generated by Br_2/O_2 discharge, no purification, bromine $\text{K}\alpha$ -edge EXAFS method) that the latter compound may well be only BrOBrO_2 , but it also cannot be excluded that the similarity in the Raman spectra is accidental. The colorless, CH_2Cl_2 insoluble, but $\text{C}_2\text{H}_5\text{CN}$ soluble bromine oxide turned out to be Br_2O_5 ; see Figure 4,³⁶ with a structure analog to I_2O_5 , except that the terminal oxygen atoms are close to being eclipsed in Br_2O_5 . Intermolecular contacts are not observed, in contrast to I_2O_5 , but the role of weak additional contacts is taken by $\text{C}_2\text{H}_5\text{CN}$ solvent molecules. Br_2O_5 has also previously been mentioned, but the evidence by Raman spectroscopy remains scarce.³⁷ The fact that “ BrO_2 ” turned out to be largely or totally a

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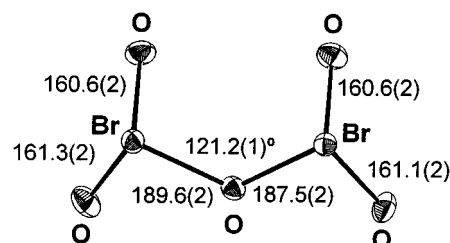


FIGURE 4. Structure of $\text{O}_2\text{Br}-\text{O}-\text{BrO}_2$ in the solid state. Vibrational ellipsoids represent 50% probability. Numeric values are in picometers and degrees. Reprinted with permission from ref 36. Copyright 1994 VCH Verlag.

mixture of Br_2O_3 and Br_2O_5 explains the confusion in the discussion of higher bromine oxides.

Conclusion

Three well-characterized bromine oxides, $\text{Br}-\text{O}-\text{Br}$, $\text{Br}-\text{O}-\text{BrO}_2$, and $\text{O}_2\text{Br}-\text{O}-\text{BrO}_2$, are made up of only two building principles, namely, terminal $-\text{OBr}$ and pyramidal $-\text{O}-\text{BrO}_2$. No further possibilities with these building blocks can be constructed. Other bromine oxides, if they become more fully characterized, will therefore show other building principles, but will most likely be even less stable. At least the most recent development of the structural chemistry of bromine oxides has laid the foundation of further chemical work, and still much needs to be done before a high level of knowledge of the chlorine oxides and iodine oxides is reached.

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