

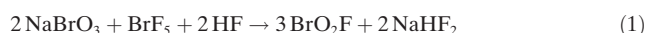
Mixed-Valent Compounds

International Edition: DOI: 10.1002/anie.201912271
German Edition: DOI: 10.1002/ange.201912271Reactions of Bromine Fluoride Dioxide, BrO₂F, for the Generation of the Mixed-Valent Bromine Oxygen Cations Br₃O₄⁺ and Br₃O₆⁺

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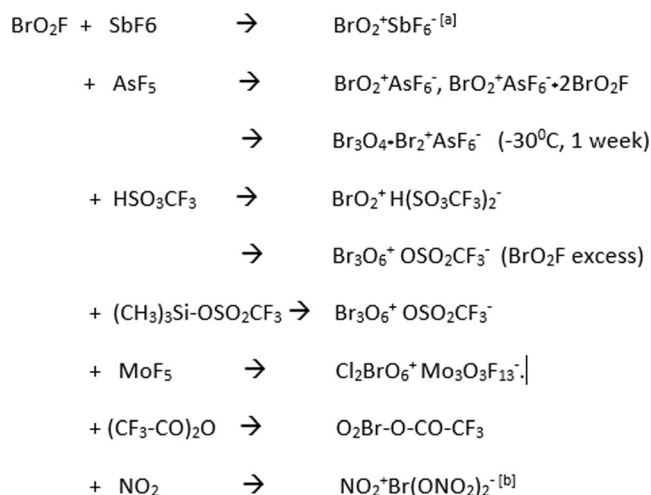
Abstract: A reliable synthesis of unstable and highly reactive BrO₂F is reported. This compound can be converted into BrO₂⁺SbF₆⁻, BrO₂⁺AsF₆⁻, and BrO₂⁺AsF₆⁻·2BrO₂F. The latter decomposes into mixed-valent Br₃O₄⁺Br₂⁺AsF₆⁻ with five-, three-, one-, and zero-valent bromine. BrO₂⁺H(SO₃CF₃)₂⁻ is formed with HSO₃CF₃. Excess BrO₂F yields mixed-valent Br₃O₆⁺OSO₂CF₃⁻ with five- and three-valent bromine. Reactions of BrO₂F and MoF₅ in SO₂ClF or CH₂ClF result in Cl₂BrO₆⁺Mo₃O₃F₁₃⁻. The reaction of BrO₂F with (CF₃CO)₂O and NO₂ produces O₂Br-O-CO-CF₃ and the known NO₂⁺Br(ONO₂)₂⁻. All of these compounds are thermodynamically unstable.

Bromine fluoride dioxide (bromyl fluoride) has long been known,^[1] and its pyramidal structure has been established by spectroscopic methods.^[2] It is a very reactive and unstable species that decomposes above 10°C, often with explosion. Herein, we present a reliable and safe procedure for its high-yielding preparation in a PFA tube system between -78° and -10°C in amounts of 100–200 mg [Eq. (1)].



A previous single-crystal determination had suffered from O/F disorder.^[3] However, recrystallization from acetone at low temperatures produced several adducts. In the adduct 3BrO₂F·4acetone, the bond lengths are undisturbed by disorder: $r_{\text{Br-O}} = 1.587\text{--}1.620(2)$ and $r_{\text{Br-F}} = 1.781\text{--}1.822(2)$ Å. Solutions in SO₂ClF or CH₂ClF are stable at low temperature if all reductive reagents (H₂O!) are excluded. Even in anhydrous HF slow decomposition occurs (Scheme 1).

SbF₅ and BrO₂F form BrO₂⁺SbF₆⁻. This product is identical to the one that has been obtained recently in the reaction of BrO₃F with SbF₅ under loss of oxygen.^[4] AsF₅ works in the same way as SbF₅, giving BrO₂⁺AsF₆⁻. This compound can be sublimed with some decomposition in vacuum at 10°C. This indicates that the fluoride ion affinity of



Scheme 1. Reactions of BrO₂F. [a] See Ref. [4]. [b] See Ref. [5].

AsF₅ is just large enough for the formation of this ionic species. AsF₅ as a gas can easily be applied in various amounts relative to BrO₂F: In a reaction with excess BrO₂F, crystals of BrO₂⁺AsF₆⁻·2BrO₂F are formed. These turned into dark-red Br₃O₄⁺Br₂⁺AsF₆⁻ under loss of oxygen after standing for days at -30°C.

The cation Br₃O₄⁺·Br₂ of this salt is shown in Figure 1. The Br₂ part of the cation can be described as a Br₂ molecule attached to the Br-O part of the cation: The Br-Br bond length of 2.280(1) Å, the Br-Br...Br bond angle of 104.8(1)°, and the corresponding Raman line of 297.5 cm⁻¹ are typical for molecular bromine bonded through halogen bonding. The Br₃O₄⁺ cation can be viewed as a combination of BrO₂⁺ and neutral O=Br-O-Br or as O₂Br-O-Br⁺-O-Br. In each description, it contains one-, three-, and five-valent bromine (in addition to the zero-valent Br₂).

HSO₃CF₃ dissolves BrO₂F under formation of BrO₂⁺H(SO₃CF₃)₂⁻. The anion H(SO₃CF₃)₂⁻ has only occasionally

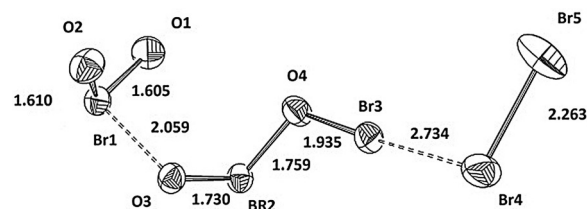


Figure 1. Cation 1 in Br₃O₄⁺·Br₂AsF₆⁻. Cation 2 (almost identical) and anions are omitted. Displacement parameters (also in all figures below) set at 50%. Distances given in Å. Angles: O1-Br1-O2 110.6°, O3-Br2-O4 103.5°, O4-Br3...Br4 177.0°.

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been observed;^[6] the non-symmetric O–H···O bridge here is 2.515 Å long, as compared to 2.410 Å in Ref. [6].

When an excess of BrO_2F relative to HSO_3CF_3 was applied, brown crystals of $\text{Br}_3\text{O}_6^+\text{SO}_3\text{CF}_3^-$ were obtained. The cation of $\text{Br}_3\text{O}_6^+\text{SO}_3\text{CF}_3^-$ can be described as a combination of two BrO_2^+ units and one BrO_2^- that weakly interact. The geometries of the two BrO_2^+ units are very similar to those observed in the neat BrO_2^+ compounds. Little is known about bromite, BrO_2^- : The preparation of NaBrO_2 is quite tedious.^[7] A crystal structure determination on $\text{NaBrO}_2 \cdot 3\text{H}_2\text{O}$ reveals $r_{\text{Br-O}} = 1.701(2)$, $1.731(2)$ Å, and $\delta_{\text{O-Br-O}} = 105.3(1)^\circ$.^[8] For our BrO_2^- unit, these data are $r_{\text{Br-O}} = 1.733(1)$, $1.739(1)$ Å, and $\delta_{\text{O-Br-O}} = 102.7(1)^\circ$. The Br_3O_6^+ cation is overall close to C_2 symmetry. Aside from the description as $\text{BrO}_2^+ \cdot \text{BrO}_2^- \cdot \text{BrO}_2^+$, this cation could also be described as a Br^{III} -dibromate(V) cation, albeit with two extreme long central bromine–oxygen bonds (Figure 2).

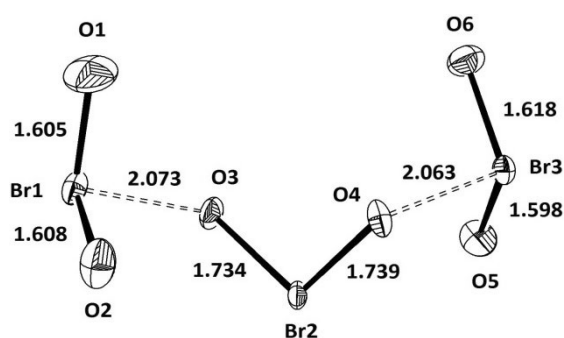


Figure 2. The cation Br_3O_6^+ in $\text{Br}_3\text{O}_6^+ \text{OSO}_2\text{CF}_3^-$; distances in Å. Angles: O1–Br1–O2 110.3°, O3–Br2–O4 102.8°, O5–Br3–O6 108.9°.

BrO_2F and $(\text{CH}_3)_3\text{Si-OSO}_2\text{CF}_3$ in SO_2ClF also react to $\text{Br}_3\text{O}_6^+\text{SO}_3\text{CF}_3^-$, now in the form of a yellow fine powder, as confirmed by its identical Raman spectrum (see the Supporting Information).

In speculations about the formation of these mixed-valent cations, the intermediacy of the free radical $\cdot\text{BrO}_2$ could be considered. In contrast to long-known $\cdot\text{ClO}_2$, it has never been isolated. It has been detected in matrices,^[9] by microwave,^[10] and UV/Vis spectroscopy,^[11] and it has been postulated as a central intermediate in the Belousov–Zhabotinsky oscillating reaction.^[12] We often observed violet solutions in our reactions, although always for only a short period of time. This species seems to dimerize at low temperature, similar to $\cdot\text{ClO}_2$.^[13] A dimer Br_2O_4 might dissociate into $\text{BrO}_2^+ \cdot \text{BrO}_2^-$, which in turn could react with BrO_2^+ to Br_3O_6^+ . Obviously not many cases of such a radical dimer dissociation into an ion pair are known; the dissociation of N_2O_4 into solid $\text{NO}^+ \cdot \text{NO}_3^-$ in the presence of IF_5 is one example.^[14]

The reaction of BrO_2F with MoF_5 in SO_2ClF or CH_2ClF offers another surprise: Aside from an ochre-colored powder and colorless crystals, a red-brown crop of crystals was always obtained, with the composition $\text{Cl}_2\text{BrO}_6^+ \text{Mo}_3\text{O}_3\text{F}_{13}^-$. The cation can be formulated as $\text{ClO}_2^+ \cdot \text{BrO}_2^- \cdot \text{ClO}_2^+$, similar to $\text{BrO}_2^+ \cdot \text{BrO}_2^- \cdot \text{BrO}_2^+$. Because of the extreme oxidation power of BrO_2F , a lot of atom scrambling has obviously occurred with the solvents (Figure 3).

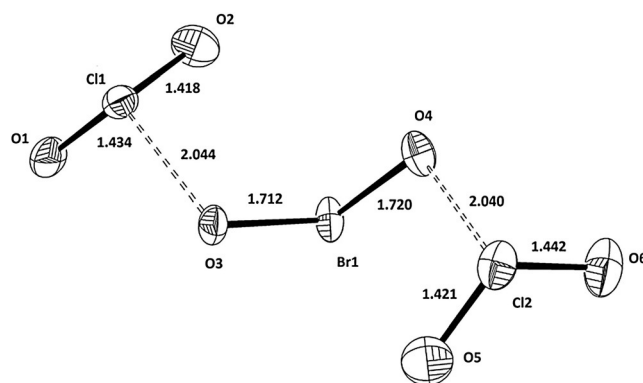


Figure 3. The cation $\text{BrCl}_2\text{O}_6^+$ in $\text{BrCl}_2\text{O}_6^+ \text{OSO}_2\text{CF}_3^-$; distances in Å. Angles: O1–Cl1–O2 116.0°, O3–Br1–O4 105.1°, O5–Cl2–O6 115.7°.

The reaction of BrO_2F with neat $(\text{CF}_3\text{-CO})_2\text{O}$ affords $\text{O}_2\text{Br-O-CO-CF}_3$ as a pale-yellow solid that melts at -12°C , and inevitably explodes upon further warming (Figure 4).

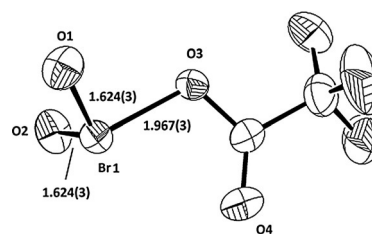


Figure 4. Molecule 1 in the crystal structure of $\text{O}_2\text{Br-O-CO-CF}_3$; distances in Å. Angles: O1–Br1–O2 110.3°, O1–Br1–O3 98.5°, O2–Br1–O3 97.3°. The three independent molecules in the unit cell differ mainly only in the torsion of the CF_3 group.

The reaction of BrO_2F with NO_2 gives the known compound $\text{NO}_2^+ \text{Br}(\text{ONO}_2)_2^-$ in quantitative yield as a colorless crystalline solid, formerly made from N_2O_5 and Br-ONO_2 .^[5] The central Br^{I} is linearly bonded to two oxygen atoms, as expected, and the overall structure is centrosymmetric (Figure 5).

The structures of the cations Br_3O_4^+ , Br_3O_6^+ , $\text{BrCl}_2\text{O}_6^-$, of the compound $\text{O}_2\text{Br-OCO-CF}_3$, and of the anion $\text{Br}(\text{NO}_3)_2^-$ have been calculated by the methods B3LYP, MP2, and B97D.

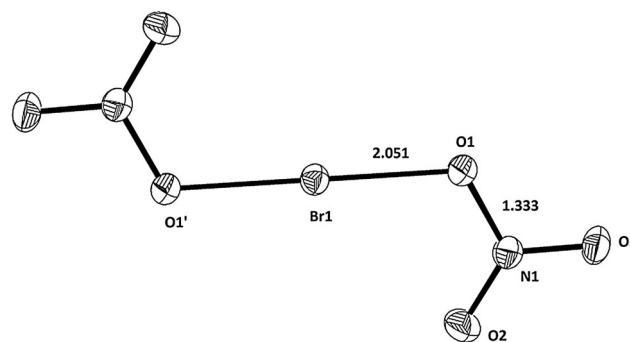


Figure 5. The anion $\text{Br}(\text{NO}_3)_2^-$ in $\text{NO}_2^+ \text{Br}(\text{NO}_3)_2^-$; distances in Å. Angles: Br1–O1–N1 116.2°; sum of angles at N1: 360.0°.

Whereas the direct bonds and angles were satisfactorily reproduced, the contact lengths between the units in Br_3O_4^+ , Br_3O_6^+ , and $\text{BrCl}_2\text{O}_6^+$ were too long. The B3LYP method gives the best results among the three methods. However, the long-distance interactions are still so far off from the experimental values that the calculations of the vibrational spectra are unreliable (see the Supporting Information).

The generation of a thus far non-reproducible by-product $\text{Cl}_2\text{BrO}_6^+ \text{ClO}_4^-$ in a reaction of $\text{BrO}_2\text{F}/\text{HSO}_3\text{CF}_3^-/\text{SO}_2\text{ClF}$ is reported in the Supporting Information, only to show that more of these compounds can exist. Long ago, a compound described as $\text{BrO}_2^+\text{ClO}_4^-$ was made by ozonization of BrOClO_3 in CFCl_3 , but solely characterized by Cl/Br analysis.^[15]

Experimental Section

The generation of BrO_2F from NaBrO_3 , BrF_5 , and HF is most easily performed on a metal vacuum line in a PFA tube (poly(perfluoroethylene perfluorovinyl ether) co-polymer) at -78°C , and subsequent sublimation at -10°C into a second PFA trap cooled to -78°C . The product obtained is completely colorless. The same reaction without a metal vacuum line is described in detail in the Supporting Information, as are the reactions of BrO_2F with SbF_5 , AsF_5 , HSO_3CF_3 , $(\text{CH}_3)_3\text{Si-OSO}_2\text{CF}_3$, MoF_5 , $(\text{CF}_3\text{-CO})_2\text{O}$, and NO_2 .

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Conflict of interest

The authors declare no conflict of interest.

Keywords: bromyl fluoride · bromine oxygen compounds · crystal structures · mixed-valent compounds

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