Activation of Dioxygen by Halocarbon Ions

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Tandem mass spectrometry is used to show that low energy collisions of ionized halocarbenes, including $CBr_2^{\bullet+}$ and $CBrCl^{\bullet+}$, with molecular oxygen lead to (i) decarbonation with formation of the dihalogen molecular cation and (ii) oxygenolysis yielding $BrCO^+$. Both reactions may occur via the same ion−molecule addition product of molecular oxygen and the ionized carbene. Reaction is favored at low collision energies, such as are encountered in an ion trap. Insights into the energetics of the reactions of $CBr_2^{\bullet+}$ with O_2 are obtained from ab initio molecular orbital theory. Other aspects of the positive ion chemistry of dioxygen with various halogen-containing ions are also discussed. Dioxygen activation by halocarbon ions suggests additional channels that might affect the fate of halocarbons and the ozone balance in the atmosphere.

Introduction

The atmospheric chemistry of halogens, in particular their role in ozone depletion, is increasingly well-documented.[1] Although attention has focused on the chemistry in the troposphere and lower stratosphere, the long lifetimes[2] of organohalogen species such as $CC1_2F_2$ (Freon CFC-12, lifetime 110 ± 20 years), CF_4 (Freon CFC-4, lifetime > 50 000 years), and $CBrF_3$ (Halon 1301, lifetime 65 years) make transport of these compounds to the upper regions of the atmosphere probable. There, single- and multiphoton excitation by visible and near-UV photons might result in dissociative photoionization of chloro-, fluoro- and bromocarbons to yield halocarbon ions and open-shell neutral fragments,[3] although the data on this point are still inconclusive.

The reactivity of organohalogen ions with oxygen is unexplored. We now show that dioxygen is readily activated by various halocarbon cations and conclude that the formation of XCO^+ and XO^+ ($X = F$, Cl, and Br), with the simultaneous generation of atomic oxygen, is likely in the upper atmosphere. This result suggests a possible regeneration channel of ozone in the meso- and ionospheres. We also show that ionized dihalocarbenes react with dioxygen to form the dihalogen radical cation, a process that converts organic bromides to inorganic bromine.

The mass spectrometric experiments described here reveal two new types of ion−molecule reactions of molecular oxygen. Both are exemplified by the ionized carbene $CBr_2^{\bullet+}/O_2$ system. One is an unprecedented type of low energy reaction channel, formal elimination of atomic C, with generation of molecular bromine ions upon collision of $CBr_2^{\bullet+}$ with dioxygen. In the second reaction, formal atomic oxygen addition occurs to give $BrCO^+$ and, competitively, BrO^+. The scope of the first reaction seems to be rather narrow, while the second process is found to occur for a variety of reactant ions, although all do not necessarily react by the same type of mechanism. Evidence is presented in the $CBr_2^{\bullet+}$ case that both reactions, formal elimination of atomic C and formal atomic oxygen addition, may occur from the same ion−molecule intermediate.

In addition to the possible implications of the reactions of halocarbon-derived cations for the chemistry of the atmosphere, oxygen ion chemistry is of intrinsic interest and potential relevance to various combustion and plasma processes. Despite this, the subject is little explored, and information on the cation chemistry is particularly sparse. Reactions of C $^{4+}$ and C_{60}^{5+} with O_2 are representative of earlier studies on cationic ion−molecule reactions with O_2. It is also known that dioxygen can be activated using N^+ and N_2^+ cations.[6] In recent work of atmospheric significance, Cacace et al.[7] show that $C1_2^{\bullet+}$ reacts with dioxygen to yield $Cl{-}O{-}Cl^+{-}O^\bullet$. They also show that neutral halocarbons can undergo dissociative charge exchange with O_2^+ to yield halocarbon ions.[8] This reaction might be an alternative to photolysis as a route to produce halocarbon ions which then could be involved in the oxygenolysis reactions that form the topic of this paper.

Experimental Section

Gas-phase ion−molecule reactions were carried out using a Finnigan TSQ 700 triple-quadrupole mass spectrometer[9] (Finnigan MAT, San Jose, CA). The source temperature was maintained at 150 °C, and the manifold, at 70 °C. The precursor ions were generated by 70 eV electron impact on CBr_4, $CHBr_3$, CH_2Br_2, $CC1_4$ (Aldrich Chemical Co., Milwaukee, WI), and C_6F_{14} (Lancaster, Windham, NH). The neutral precursors were evaporated into the source via a leak valve (Granville Phillips Co., Boulder, CO). Product ion mass spectra were recorded by selecting the precursor ion of interest using the first quadrupole mass analyzer (Q1) and passing it into the collision cell, Q2, to collide with the target gas at laboratory kinetic energies varying between 2 and 100 eV, and scanning the second analyzer, Q3. Most of the experiments were performed under single-collision conditions achieved by maintaining ion beam attenuation under 15%, which corresponded to a collision cell pressure of ∼0.4 mTorr. Pressure dependences were studied by varying the pressure of the collision gases O_2, N_2, NH_3, and SF_6 at fixed collision energy. The gas pressures were corrected by appropri-

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ate calibration procedures.[10] For all experiments, there was a small residual concentration of ~1% O_2 in the collision cell due to leaks in the plumbing lines which could not be eliminated.

Rate constants were obtained by calibrating the collision gas concentration using the known rate constants[11] of the proton–transfer reaction, $NH_3^{\bullet+} + NH_3 \rightarrow NH_4^+ + NH_2^{\bullet}$. The calculated concentration was corrected for the gauge response for the gases concerned and used in the equation, $\ln(I_s/I_p) = \sigma nl$, where σ is the reaction cross section, n is the number density of target molecules in molecules per cubic centimeter and l is the path length in centimeters (18 cm). I_s and I_p are the secondary and primary ion currents. The rate constant, k, was calculated from the relation $k = \sigma v$, where v is the ion velocity.

Ion trap experiments employed a prototype Finnigan ion trap mass spectrometer which has been described previously.[12] Carbon tetrabromide was admitted to the vacuum manifold through a heated variable leak valve (Granville Phillips Co., Boulder, CO) to a pressure of 6×10^{-7} Torr (uncorrected). Oxygen and helium were admitted through independent leak valves to uncorrected gauge pressures of 1×10^{-5} and 1×10^{-4} Torr, respectively. Internal electron ionization was used, and the $C^{79}Br^{81}Br^{\bullet+}$ fragment at m/z 172 was isolated by the rf/dc apex isolation procedure. After isolation, the dc voltage was turned off and the rf trapping voltage was adjusted so as to place m/z 172 at a q_z value of 0.3 for a reaction period of 60 ms. Mass spectra were recorded by scanning the rf trapping voltage with an auxiliary ac potential of 530 kHz and 1.1 V applied to the end cap electrodes for axial modulation.

The ion/surface scattering experiments[13] were conducted in a four-analyzer BEEQ mass spectrometer described previously.[14] A mass and energy analyzed ion beam was directed to the surface held in an ultrahigh vacuum scattering chamber. Ion beams were selected with unit mass resolution and with a kinetic energy half width of 1 eV. The beam was decelerated to the desired energy prior to collision with the fluorinated self-assembled monolayer surface. The mass spectrum of the scattered product ions was recorded using the quadrupole mass analyzer. The scattering angle was set at 90°, and the collision energy range investigated was 10–90 eV. The experiments were conducted at a base pressure of 2×10^{-9} Torr. Primary ions were generated by 70 eV electron impact of CBr_4, $CHBr_3$, CH_2Br_2, $CC1_4$ (Aldrich Chemical Co., Milwaukee, WI), and C_6F_{14} (Lancaster, Windham, NH).

The target surface, a fluorocarbon self-assembled monolayer, $CF_3(CF_2)_7CH_2CH_2S{-}Au$, was prepared[15] by exposing a 1 mM solution of the corresponding thiol in ethyl alcohol to a clean gold surface for 24 h. The gold surface was prepared by thermal evaporation of Au (2000 Å) on a (111) polished Si surface (with a 50 Å buffer layer of Cr). The X-ray diffractogram of the gold surface prepared this way showed only (111) reflections. The surfaces after monolayer growth were sonicated in ethanol for 1 min and washed repeatedly with the same solvent and dried in a stream of nitrogen before introduction into the scattering chamber.

Results and Discussion

In the course of investigating ion/surface reactions and surface-induced dissociation (SID)[13] pathways of molecular ions derived from CBr_4, we examined the corresponding gas-phase events by collision-induced dissociation (CID) in a triple-quadrupole mass spectrometer.[9] When the $CBr_2^{\bullet+}$ ion of m/z 172 ($C^{79}Br^{81}Br^{\bullet+}$) was mass-selected and collided with oxygen under single-collision conditions[16] at 2 ± 1 eV laboratory translational energy, the spectrum shown in Figure 1 was recorded. Experiments with different isotopic forms of the projectile ion confirmed the identity of the product ions. The doublets at m/z 91/93 and 79/81, due to CBr^+ and Br^+, are simply due to dissociation following an inelastic collision.[17] The peak at m/z 160, due to $Br_2^{\bullet+}$, is formally the product of loss of atomic carbon, which would be an unprecedented fragmentation process.[18,19]

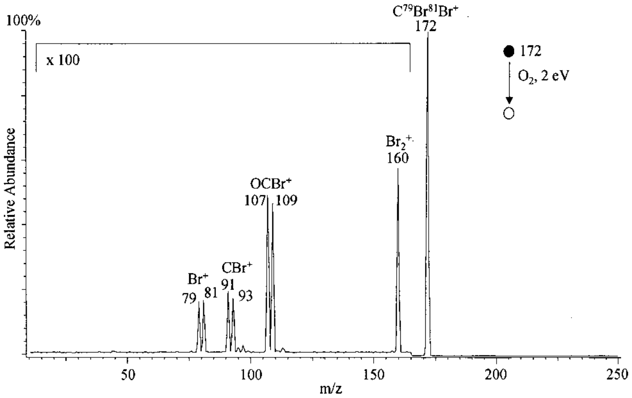


Figure 1. Mass spectrum showing product ions arising from collisions of mass-selected $CBr_2^{\bullet+}$ with dioxygen in a triple-quadrupole mass spectrometer. The kinetic energy of the ions was nominally 2 eV, and the target gas was 1% dioxygen in argon at a nominal pressure of 0.2 mTorr, corresponding to attenuation of the parent ion beam by <10%.

Formation of the molecular halogen ion, $Br_2^{\bullet+}$, is most efficient at low collision energies, a fact which suggests that an ion-molecule reaction rather than an inelastic collision is involved. The ion abundance ratio $[CBr_2^{\bullet+}]/[Br_2^{\bullet+}]$ is at a maximum at a nominal 2 eV collision energy. The efficiency was estimated by calibrating the target gas pressure and path length in the triple quadrupole using the reaction ($NH_3^{\bullet+} + NH_3 \rightarrow NH_4^+ + NH_2^{\bullet}$) of known cross section and measuring the extent of product formation as a function of oxygen pressure. This procedure yielded an approximate measure of the rate constant for $Br_2^{\bullet+}$ formation as 8×10^{-10} cm^3 molecule^{-1} s^{-1}.

Figure 2 shows the collision energy dependence of the reaction under single-collision conditions, as well as showing, for all the major product ions, the response to changes in oxygen pressure. Direct collisional activation of $CBr_2^{\bullet+}$ and subsequent fragmentation, $CBr_2^{\bullet+} \rightarrow Br_2^{\bullet+} + C$, is expected to be highly endothermic (the corresponding reaction of $CC1_2^{\bullet+}$ is estimated from literature data to be 158 kcal/mol endothermic). Collision-induced dissociation might occur to form $Br_2^{\bullet+}$ at the higher collision energies but not at lower energy. This conclusion is reinforced by the ion/surface collision data (Figure 3) which show no $Br_2^{\bullet+}$ in the range of lab collision energies from 3 to 30 eV. Detailed comments on the ion/surface processes are not the subject of this paper, but inspection of Figure 3 reveals a number of ion/surface reactions leading to bond formation, as well as the expected inelastic dissociation process, known as surface- induced dissocation, which yields predominantly CBr^+. Similarly, the precursor ion $CH_2Br_2^{\bullet+}$ yields $Br_2^{\bullet+}$ in collisions at a fluorinated self-assembled monolayer only at energies above 30 eV, and the same ion at a threshold collision energy of 50 eV in argon collisions (Supporting Information).

The CID and SID data exclude the formation of $Br_2^{\bullet+}$ by simple fragmentation of $CBr_2^{\bullet+}$, as does the fact that substitution of oxygen by argon as the target gas fails to display this product.[20] This possibility is also removed by the low collision energy threshold observed and the fact that the thermochemistry for the direct dissociation of $CBr_2^{\bullet+}$ to give C and $Br_2^{\bullet+}$ is estimated[21] to be 128.3 kcal/mol endothermic. These consid-

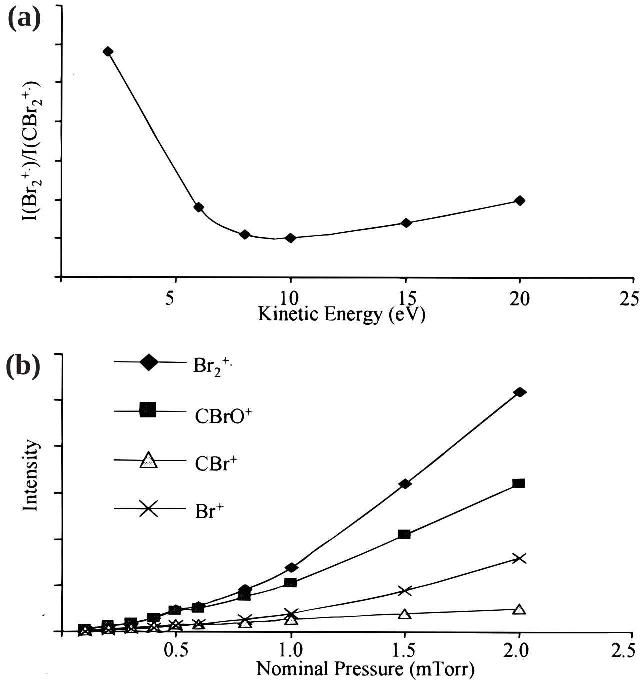


Figure 2. (a) Variation of $Br_2^{\bullet +}$ intensity with $CBr_2^{\bullet +}$ collision energy at 0.4 mTorr O_2 collision gas pressure. (b) Variation of product ion intensities with collision gas pressure at the same collision energy.

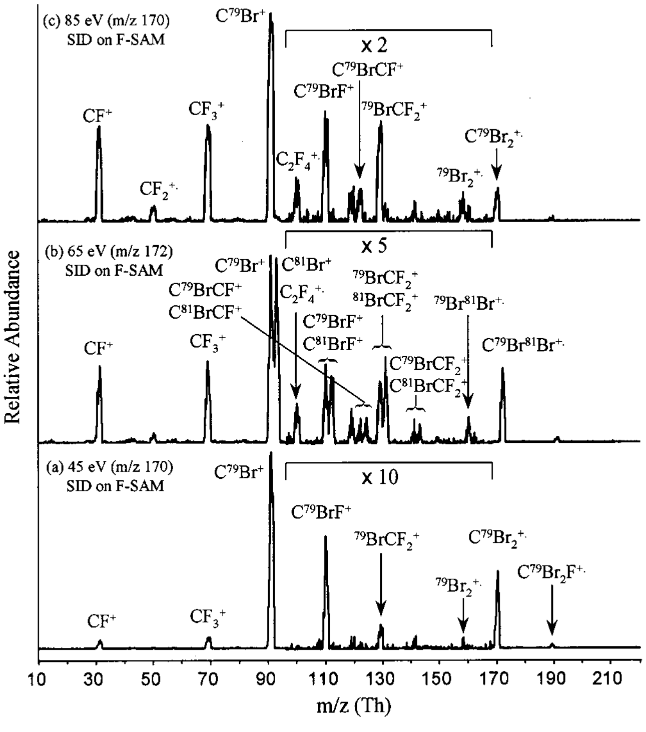


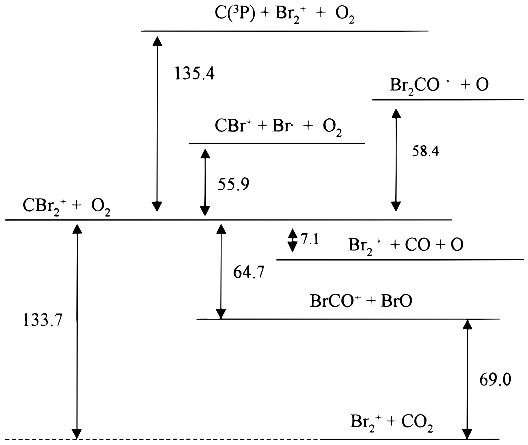
Figure 3. Mass spectra recorded upon collision of $C^{81}Br_2^{+}$ (*m/z* 174) and $C^{79}Br^{81}Br^{+}$ (*m/z* 172) at a fluorocarbon self-assembled monolayer surface at different collision energies. Note that the spectra show characteristic fluorine abstraction products. At collision energies above 45 eV, $Br_2^{\bullet +}$ is observed.

erations strongly suggest the occurrence of the ion−molecule reaction (eq 1). Energies for species involved in the $CX_2^{\bullet +}$

$$CBr_2^{+} + O_2 \rightarrow [CBr_2O_2^{\bullet +}] \rightarrow Br_2^{\bullet +} + CO_2 \qquad \Delta H_{rxn} = -133.7 \text{ kcal/mol} \quad (1)$$

reactions (eqs 1−3) were calculated using Gaussian-2 (G2)

SCHEME 1. Energy Diagram for the $CBr_2^{\bullet +} + O_2$ System Showing Several Possible Ion−Molecule Reaction Products, Including Those Leading to Formation of $Br_2^{\bullet +}$ and $BrCO^{+}$ as Well as the High Energy Dissociation Channels Leading to Br_2^{+} and CBr^{+}[a]



[a] The indicated values are obtained from G2 calculations. The intact adduct does not correspond to a stable minimum.

theory.[21] G2 energies for CBr^{+}, $CBr_2^{\bullet +}$, $BrCO^{+}$, $BrCOO^{+}$, BrO^{+}, and $CBr_2O^{\bullet +}$ are −2610.130 515, −5182.756 00, −2685.403 58, −2760.293 96, −2647.221 56, and −5257.829 04 hartrees, respectively. These energies were used to evaluate reaction enthalpies; the reaction $CBr_2^{\bullet +} + O_2$ to yield $Br_2^{\bullet +}$ and CO_2 is exothermic by −133.7 kcal mol^{-1}. Note that loss of CO_2 from the nascent ion−molecule complex yields $Br_2^{\bullet +}$ in a low energy rearrangement reaction.

Figure 1 shows that a second ion−molecule reaction, oxygenolysis, accompanies decarbonation in the course of ionized carbene/dioxygen collisions. The resulting oxygenated ion $BrCO^{+}$ [22] (and the lower abundance product[23] BrO^{+}, which is not explicitly considered) could arise by (i) reaction of the fragmentation products of $CBr_2^{\bullet +}$ or (ii) fragmentation of an ion−molecule reaction product, $Br_2CO_2^{\bullet +}$, possibly even that proposed as an intermediate in decarbonation (eq 1). Possibilities (i) and (ii) are distinguished by the sequence in which fragmentation and the ion−molecule reaction occur. They are illustrated for the more abundant of the two products, $BrCO^{+}$, in eqs 2 and 3, where the heats of reaction shown are values derived from the G2 calculations. The ion−molecule reaction

$$CBr_2^{\bullet +} \rightarrow CBr^{+} + Br^{\bullet} \qquad \Delta H_{rxn} = 55.9 \text{ kcal/mol} \quad (2a)$$

$$CBr^{+} + O_2 \rightarrow BrCO^{+} + O \qquad \Delta H_{rxn} = -67.1 \text{ kcal/mol} \quad (2b)$$

$$CBr_2^{\bullet +} + O_2 \rightarrow [CBr_2O_2^{\bullet +}] \rightarrow BrCO^{+} + BrO^{\bullet} \qquad \Delta H_{rxn} = -64.7 \text{ kcal/mol} \quad (3)$$

(eq 3) is calculated to be a much lower energy process. This, plus the lack of dissociation products with an inert target, favors eq 3 over eq 2 as the route to oxygenolysis. The oxygenated products might arise from an intermediate with the same connectivity $X_2CO^{\bullet +}$ (eq 1) as is involved in decarbonation (eq 1): $CX_2^{\bullet +}$ would react with O_2 by C−O bond formation to give $X_2CO_2^{+}$, which could either eliminate CO_2 to give $X_2^{\bullet +}$ or rearrange to yield $XC^{+}{=}O$ and, in the competitive process, XO^{+}. The overall energetics of decarbonation are summarized in Scheme 1.

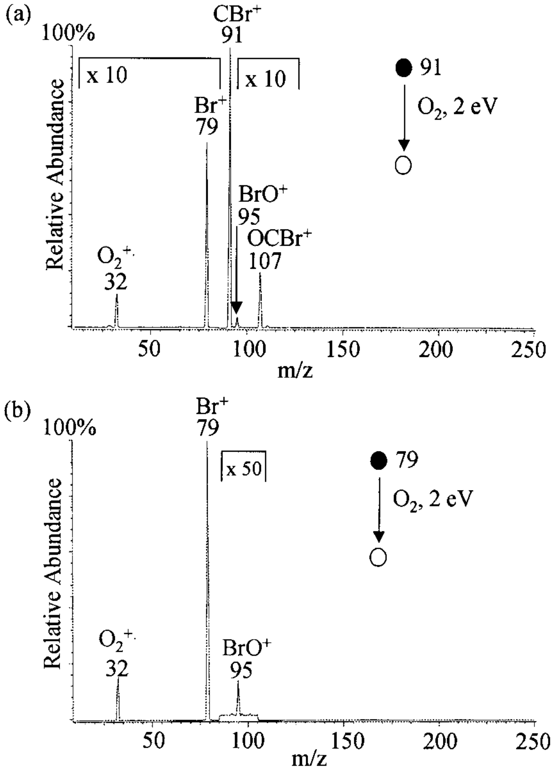


Figure 4. Mass spectrum showing product ions arising from collisions of (a) CBr^+ (*m*/*z* 91) and (b) Br^+ (*m*/*z* 79) with dioxygen. Conditions as for Figure 1.

The fact that oxygenolysis to generate $Br_2^{\bullet+}$ increases as the collision energy in the triple-quadrupole instrument is lowered (Figure 2a) suggests that a thermal or near-thermal process is involved. To investigate the reaction at thermal collision energies and also to study the effect of collisional deactivation of the product ions on the possible excited states of the reactant ion, experiments were performed in a quadrupole ion trap. After collisional cooling for 5 ms with a He/O_2 mixture (total pressure, 1×10^{-4} Torr, partial pressure of O_2, 1×10^{-5} Torr), $CBr_2^{\bullet+}$ was mass-selected and reacted with O_2 for 60 ms. The CO_2 elimination product $Br_2^{\bullet+}$ was formed in high abundance together with a lower abundance of $BrCO^+$. The product ion spectrum after the reaction is shown in Figure 5. The cooling process is expected to thermalize the reactant ion population. It is important to note that no CBr^+ and BrO^+ are generated, a fact that provides further evidence that oxygenolysis proceeds via eq 3, not eq 2. From these data, it is clear that (i) the oxygenolysis reaction is a thermal or near-thermal energy process and (ii) CBr^+ is a secondary product of the fragmentation of $CBr_2^{\bullet+}$. Most of the Br^+ observed appears to be formed by fragmentation of $Br_2^{\bullet+}$. The spectrum shows no BrO^+, which suggests that Br^+ is less reactive than $CBr_2^{\bullet+}$, which is also evident by comparison of Figures 1 and 5. The most important aspect of the result is that $Br_2^{\bullet+}$ can be formed very efficiently by thermal collisions with O_2. This is of considerable interest with respect to the atmospheric chemistry of these systems.

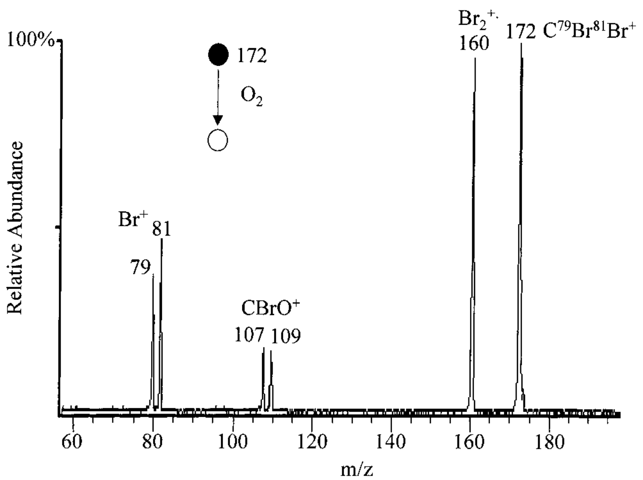
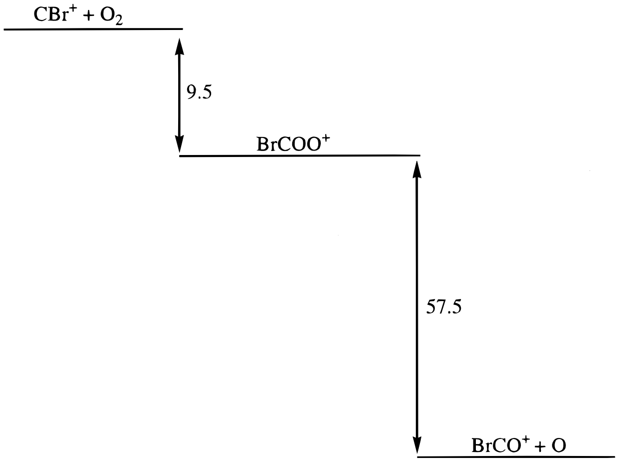


Figure 5. Product ion mass spectrum showing reactions of $CBr_2^{\bullet+}$ with O_2 in an ion trap mass spectrometer. The ions were selected after a cooling time of 5 ms and allowed to react for a period of 60 ms. The O_2 pressure was 1×10^{-5} Torr (uncorrected), and the helium buffer gas pressure was 1×10^{-4} Torr (uncorrected).

SCHEME 2. Energy Diagram for the $CBr^+ + O_2$ System Showing the Ion−Molecule Adduct (2) and the Reaction Product $BrCO^+$[a]



[a] The indicated values are obtained from G2 calculations.

The formation of oxygenated product ions by CID, followed by an ion−molecule reaction via the sequence shown in eq 2, has been ruled out on energetic grounds. Nevertheless, its consideration led to the experimental observation that the $CBr_2^{\bullet+}$ fragmentation products, CBr^+ and Br^+ (Figure 4), both yield mono-oxygenated product ions in low energy collisions with dioxygen, that is, they are also capable of oxygenolysis, although not by the same mechanism as that for $CBr_2^{\bullet+}$. For example, using single 2 eV collisions, the reactant CBr^+ yields the oxygen adduct, $CBrO^+$, in 2% relative abundance, while Br^+ displays BrO^+ in 0.3% relative abundance as its only product besides simple charge exchange (to form O_2^+ in 20% relative abundance). Ab initio calculations were employed to elucidate the process of oxidation of CBr^+ (eq 4). Examination of the potential

$$BrC^+ + O_2 \rightarrow [BrCOO^+] \rightarrow BrCO^+ + O^\bullet \qquad \Delta H_{rxn} = -67.0\ \text{kcal/mol} \quad (4)$$

energy surface revealed that this reaction can proceed through a bound adduct with connectivity $BrCOO^+$ (eq 2) which is 9.5 kcal mol^{-1} more stable than the reactants but 57.5 kcal mol^{-1} less stable than the products $BrCO^+$ and $O^\bullet$ atom. The overall energetics are summarized in Scheme 2.

Similar oxidation processes occur with $C1^+$, $CC1^+$, $CC1_2^+$, F^+, CF^+, and $CF_2^{\bullet+}$ (see Supporting Information). $CC1_2^{\bullet+}$ and $CC1^+$ react with O_2 at a 2 eV collision energy to give $ClCO^+$, in addition to the expected fragmentation products. These reactions are efficient at low energies, and the product intensity decreases rapidly with increased collision energy. Both the projectiles efficiently undergo charge exchange with O_2. Reactions of $CF_2^{\bullet+}$ and CF^+ are similar, except that $CF_2^{\bullet+}$ gives an oxygenated product, $F_2CO^{\bullet+}$, whereas $CF_2^{\bullet+}$ undergoes charge exchange with O_2, CF^+ does not. The reactions of $C1^+$ and F^+ at low collision energies give ClO^+ and FO^+, but with lower efficiency. A recent study[24] on SF_6 ion chemistry shows that SF^+ also abstracts oxygen from O_2. The reactivity of highly electron-deficient positively-charged ions with dioxygen is not surprising, but it is noteworthy that the positive ion chemistry of O_2 is so sparsely explored a topic.

Note that none of the dihalomethylene ions react analogously to $CBr_2^{\bullet+}$ in forming the dihalogen ion and eliminating CO_2 except for $CClBr^{\bullet+}$, which yields $ClBr^{\bullet+}$. The trihalide ions, including CBr_3^+, are uniformly unreactive, and neither $CBr_4^{\bullet+}$, $CHBr^{\bullet+}$, nor $CHBr_2^+$ leads to $Br_2^{\bullet+}$ or $HBr^{\bullet+}$ in low energy gas-phase collisions; nor do the corresponding processes occur with $CCl_2^{\bullet+}$ or $CF_2^{\bullet+}$, either. The narrow scope of this reaction is consistent with the mechanistic requirements already outlined.

Conclusions

Low energy collisions of $CBr_2^{\bullet+}$ with dioxygen in a triple quadrupole result in facile $Br_2^{\bullet+}$ formation by an ion−molecule reaction which involves O═O bond activation and BrO^+ and $BrCO^+$ formation by oxygenolysis. Related oxygen activation and oxygen atom transfer reactions occur for some other halogen and halocarbon ions. Ion trap experiments with collisionally-cooled ions suggest that the ion−molecule oxygenation reaction is a ground-state process that occurs for thermal ions. The ionic product $Br_2^{\bullet+}$ is also formed, but by a different mechanism, in high energy collisions with a solid- or gas-phase target with accompanying (formal) loss of atomic carbon. Activation of molecular oxygen by halocarbon positive ions could be important in the atmosphere, especially if, like $CBr_2^{\bullet+}$, other ions have high reaction efficiencies at low collision energies and their neutral precursors have long lives.[25] The large mixing ratios of dioxygen compared to those of other oxygenated species in the upper atmosphere, the possible transport of halocarbon molecules to the upper stratosphere,[26] the presence of halogen ions in the D-region,[27] and the fact that multiphoton processes are important in halocarbon systems[3b,3c,28] all suggest that consideration be given to the effects of possible production (and destruction[29]) of ozone in the upper atmosphere in the course of activation of O_2 by CX^+ and X^+ ($X = F$, Cl, and Br).

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Supporting Information Available: Mass spectra of surface collisions. This material is available free of charge via the Internet at http://pubs.acs.org.

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