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Matrix-isolation infrared spectra of HOOBr and HOBrO produced upon VUV light irradiation of $HBr/O_2/Ne$ system

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ABSTRACT

Vacuum ultraviolet (VUV) light photolysis of an HBr/O₂ mixture in a Ne matrix has produced HO₂Br isomers (HOOBr and HOBrO), which are important reaction intermediates in atmospheric chemistry. The observed bands have been assigned with an aid of a quantum chemical calculation at CCSD/aug-cc-pVDZ. These assignments have been confirmed by the experimental results using isotopic species of ¹⁸O₂ or DBr. Their characteristic bands are discussed in comparison with those of HOOCI and HOCIO from an HCl/O₂ mixture [7]. Both HOOBr and HOBrO are found to be photolyzed with the UV light below 385 nm.

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1. Introduction

Accurate knowledge of halogen-atom cycles in the atmosphere is imperative for understanding ozone depletion in the stratosphere. Since Molina and Rowland reported that the chlorine atom produced from chlorofluorocarbons (CFCs) upon UV irradiation catalytically consumed numerous ozone molecules [1], the chlorine cycle has been investigated by numerous experimental and theoretical researchers [2,3]. In order to understand the accurate reaction mechanisms, it is required to know molecular properties of the related species as well as individual elementary reactions in great detail. However, it is hard to characterize short-lived species produced in the collisions or reactions using experimental data based on spectroscopy and thermodynamics. A powerful tool to study such unstable species is the technique of low-temperature matrix isolation, which has provided infrared (IR) spectra of many related species such as ClO [4], ClOO radical [5], HOClO [6], HClO₂ [6], HOOCI [7], HOOCIO₂ [8], ClOOCI [9] and ClOx [10].

In contrast, atmospheric bromine chemistry has not been explored in such detail, though Br atom is suggested to decompose ozone more effectively than Cl atom [11–13]. Nonetheless, the spectra of Br-containing free radicals related to atmospheric chemistry have been measured by matrix-isolation IR spectra for BrO, HOBr, BrBrO, BrOO and OBrO [14–17]. Since the BrO radical is supposed to effectively contribute to ozone depletion, the reactions related to the production and depletion of this radical deserve careful studies. The reaction between the BrO and OH radicals is considered to be especially important as an elementary reaction of the

bromine cycle to decompose ozone, on which the following reactions have been proposed [18]:

$$BrO + OH \rightarrow (HOOBr) \rightarrow Br + HO_2 \tag{1}$$

 $BrO + OH \rightarrow (HOOBr) \rightarrow HBr + O_2$ (2)

The expected short-lived intermediate, HOOBr (bromous acid), has never been identified [19–23], and accurate spectroscopic information is required for systematic detection of the various intermediates in the atmosphere. Three isomeric structures for HOOBr have been proposed theoretically [24], as shown in Figure 1.

In the present study, we have measured the IR spectrum of HOOBr produced upon the VUV irradiation of HBr/O_2 in a low-temperature Ne matrix. Unlike all reported studies based on gaseous discharge flows [2,3,15], where unstable species like intermediates of atmospheric reactions are frequently produced, the present method of VUV photolysis under isolated matrix conditions at low-temperature provides precise information on such chemically-unstable species. We have recently reported the IR spectrum of HOOCI for the first time using the same photolysis/analysis method [7]. The present letter follows this line to report the IR spectroscopic detection and characterization of HOOBr and HOBrO isomers, being supported by quantum chemical calculations.

2. Experimental and calculation methods

Hydrogen bromide (HBr) and deuterium bromide (DBr) were prepared from hydrobromic acid (Wako) and deuterium hydrobromic acid (Tokyo Kasei), respectively, by passing through a silica-gel trap to remove water vapor. Oxygen gas (Taiyo Nissan, 99.999%) and $^{18}O_2$ (Shoko, 99%) were used without further purification. The mixed samples of HBr/O₂/excess Ne (Spectra Gases, 99.9999%) were



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Figure 1. Three isomers of bromous acid. Optimized geometrical parameters and relative energies (in kJ mol^{-1}) calculated at the CCSD/aug-cc-pVDZ level are shown in parentheses.

introduced into a vacuum chamber through a stainless steel pipe and deposited on a CsI plate cooled at \sim 6 K by a closed-cycle helium refrigerator (Iwatani, Cryomini).

Infrared spectra of the matrix isolated samples were measured with a Fourier transform (FT) IR spectrophotometer (Jeol, SPX200ST). The spectral resolution was 0.5 cm⁻¹, and the accumulation number was 100. Two xenon lamps (Ushio, UER-20 and Asahi spectra, Max-302UV) were employed as VUV and UV irradiation sources, respectively. Some short-wavelength cut filters (Asahi spectra) were used to select an irradiating UV region. Other experimental details were reported in Refs. [25,26].

Quantum chemical calculations were performed using GAUSSIAN 03 program [27] on TSUBAME, a supercomputer at Tokyo Institute of Technology. The CCSD/aug-cc-pVDZ level calculation was performed, when high-level quantum chemical calculations were required to optimize the geometries of HOOH-type molecules and estimate their vibrational frequencies.

3. Results and discussion

3.1. VUV photolysis products from HBr/¹⁶O₂

Figure 2a shows a difference IR spectrum associated with the 240-min VUV irradiation ($\lambda = 155-195$ nm, $\lambda_{max} = 172$ nm) of HBr/O₂/Ne, with a mixing ratio of 1/1/1000, where bands increasing with the VUV irradiation time were assigned to photoproducts. According to Refs. [7,14–17,25,28], most of the increasing bands in Figure 2a were assignable to known species; O₃ (1038.6 and 1039.8 cm⁻¹), HOO (1098.0, 1391.6 and 1394.7 cm⁻¹), BrOO (splitting bands at 1476.0, 1478.9, 1481.1, 1484.2 and 1487.1 cm⁻¹), HOBr (1163.1 and 1164.0 cm⁻¹) and OBrO (846.3 and 848.5 cm⁻¹), though we could not detect a band around 730 cm⁻¹ due to BrO. Then we focused our attention on the other unidentified increasing bands: three pairs of doublet bands at (819.8–821.5), (823.4–825.1) and (1102.3–1103.3) cm⁻¹, and a multiplet of bands at (1354.4, 1356.4, 1356.9, 1357.6, 1358.6) cm⁻¹.

On the analogy of the VUV photolysis system of $HCl/O_2/Ne$ [7], we expected the formation of HOOBr and HOBrO isomers in the present HBr/O₂/Ne system. Their optimized structures and relative energies are illustrated in Figure 1, and their simulated IR bands are shown in Figure 2b. The calculated IR bands seem to be located around the unassigned bands observed in Figure 2a. The simulated IR spectra of other candidate photoproducts (HOOOBr, HOOOOBr,



Figure 2. IR spectra of VUV photoproducts from HBr/O₂. (a) A difference IR spectrum associated with the 240-min VUV irradiation of an HBr/O₂/Ne system (the mixing ratio of 1/1/1000), and (b) a 1:1 composite spectrum of HOOBr and HOBrO simulated at the CCSD/aug-cc-pVDZ level.

BrOBr, BrOOBr, and HOOBrO etc.), which are possibly yielded from $(HBr)_2-O_2$ and $HBr-(O_2)_2$ in a Ne matrix cage, do not correspond to the observed spectral bands. In addition, the IR spectrum of the matrix-isolated sample prepared under the experimental mixing ratio of $HBr/O_2/Ne = 1/1/1000$ suggests that monomers and small-sized complexes like $HBr-O_2$ and $(HBr)_2$ are dominant chemical species in the matrix cage.

A group of two bands (here denoted as **a**) at 819.8 and 1356.9 cm⁻¹ exhibit a common time behavior upon UV irradiation, and another group of bands at 823.4, 825.1 and 1102.3 cm⁻¹ (denoted as **b**) also exhibit a common but different behavior. This suggests that the bands **a** and **b** should be assigned to different product species. In the 700–1600 cm⁻¹ region, the CCSD/aug-cc-pVDZ level calculation predicts that HOOBr has intense bands at 867.9 and 1414.7 cm⁻¹, which are close to the bands **a** observed at 819.8 and 1356.9 cm⁻¹, respectively. The bands calculated at 805.5 and 1164.7 cm⁻¹ for HOBrO seem to correspond to the bands **b** observed at 825.1 and 1102.3 cm⁻¹, respectively. The 825.1 cm⁻¹ band in **b** accompanied by a side band at 823.4 cm⁻¹ with a similar intensity is assigned to the Br–O stretching mode of HOBrO. Table 1 summarizes the observed and calculated wavenumbers for the VUV photoproducts from HBr/¹⁶O₂. Isotope-labeled experiments have confirmed these assignments, as discussed below.

3.2. VUV photolysis products from DBr/¹⁶O₂ and HBr/¹⁸O₂

Figure 3 shows the difference spectra associated with the VUV photolysis of (a) $DBr/^{16}O_2$, (b) $HBr/^{16}O_2$, and (c) $HBr/^{18}O_2$. In Figure 3a, some VUV photoproducts from $DBr/^{16}O_2$ are identified as O_3 , DOBr, DOO, BrOO, and OBrO by comparison with previous reports [14–17], while several new bands have been observed at 819.8, 820.8, 826.8, 828.2 and 1012.2 cm⁻¹. The VUV photoproducts of $HBr/^{18}O_2$ shown in Figure 3c are identified as $^{18}O_3$, $H^{18}OBr$, $Br^{18}O^{18}O$, $^{18}OBr^{18}O$, and $H^{18}O^{18}O$, while new bands at 775.7, 784.9, 786.8, 1099.0 and 1350.6 cm⁻¹ are assigned to either HOOBr or HOBrO species, as discussed below.

Table 2 lists the experimental and theoretical wavenumbers for HOOBr and HOBrO, together with their isotope-labeled species.

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Table 1

Observed vibrational wavenumbers (in cm⁻¹) of VUV photoproducts from HBr/O₂ in a Ne matrix and their assignments.

Observed		Calculated ^b		Assignment
This study ^a	Reported	HOOBr	HOBrO ^c	
		316.4 385.4	245.8 (245.3) 359.0 (359.0)	OOBr/OBrO bend. wag.
819.8/821.5		616.4 867.9	589.4 (588.1)	O–Br str. O–O str.
823.4 825.1 846.3 848.5 1038.6/1039.8 1098.0 <u>1102.3</u> /1103.3	843.0 ^d 845.3 ^d 1038.6/1039.8 ^e 1101.3 ^f		(803.8) 805.5 1164.7 (1164.7)	⁸¹ Br–O str. 79 Br–O str. O^{81} BrO O^{79} BrO O_3 HOO HOBr bend.
<u>1163.1</u> /1164.0 1354.4/1356.4/ <u>1356.9</u> /1357.6/1358.6 1374.7 <u>1391.6</u> /1394.7 1476.0/1478.9/ <u>1481.1</u> /1484.2/1487.1	1164 ^g 1391.5 ^e 1485.1 ^d	1414.7 3740.9	3767.8 (3767.8)	HOBr HOO bend. Unidentified HOO BrOO O–H str.

¹ Underlined wavenumbers are the strongest bands among the blended ones.

^b Calculated at the CCSD/aug-cc-pVDZ level.

^c Calculated wavenumbers for HO⁷⁹BrO and (HO⁸¹BrO).

^d In Ar matrix, Ref. [15].

^e In Ne matrix, Ref. [7].

^f In Ar matrix, Ref. [28].

^g In Ar matrix, Ref. [16].



Figure 3. Comparisons of IR spectra recorded with the VUV photolysis of three isotopomer systems: (a) $DBr/^{16}O_2/Ne$, (b) $HBr/^{16}O_2/Ne$ and (c) $HBr/^{18}O_2/Ne$.

The 819.8 cm⁻¹ band shown in Figures 2 and 3b is assigned to the O–O stretching mode of HOOBr. According to the CCSD calculation,

the isotope shifts \varDelta are estimated to be 1.0 cm^{-1} for DOOBr and 49.6 cm^{-1} for H¹⁸O¹⁸OBr, which seem to be consistent with the 820.8 cm⁻¹ band (\varDelta = +1.0 cm⁻¹) in DBr/¹⁶O₂ and the 775.7 cm⁻¹ band (\varDelta = 44.1 cm⁻¹) in Figure 3c. Opposite red- and blue-isotope shifts are recognized in the observation and calculation of the O–O stretching mode for HOOBr and DOOBr, and a similar problem has also been discussed in the wavenumbers of HOOCl and DOOCl calculated at the CCSD(T)/cc-aug-pVDZ level [7]. This discordance is probably originated from theoretical difficulty that the vibrational wavenumbers of HOOH-type molecules drastically depend on the levels of theory from which the optimized structures are derived [29–31].

The 1356.9 cm⁻¹ band shown in Figures 2 and 3b is assigned to the HOO bending mode of HOOBr. The calculated wavenumber shifts from the normal species are 370.4 and 7.1 cm⁻¹ for DOOBr and $H^{18}O^{18}OBr$, respectively, which agree with the experimental values of 344.7 cm⁻¹ for DBr/¹⁶O₂ and 6.3 cm⁻¹ for HBr/¹⁸O₂ as shown in Table 2.

The bands observed at 823.4 and 825.1 cm⁻¹ are assigned to the ${}^{81}\text{Br}-{}^{16}\text{O}$ and ${}^{79}\text{Br}-{}^{16}\text{O}$ stretching modes of HO ${}^{81}\text{BrO}$ and HO ${}^{79}\text{BrO}$, respectively. The isotope shifts for these bands are calculated to be 1.0 cm⁻¹ for DO ${}^{79}\text{BrO}$ (0.9 cm⁻¹ for DO ${}^{81}\text{BrO}$) and 38.1 cm⁻¹ for H ${}^{18}\text{O}{}^{79}\text{Br}{}^{18}\text{O}$. The corresponding experimental values are +3.1 cm⁻¹ for DO ${}^{79}\text{BrO}$ and 38.3 cm⁻¹ for H ${}^{18}\text{O}{}^{79}\text{Br}{}^{18}\text{O}$.

Table 2

Experimental and theoretical wavenumbers (in cm^{-1}) of HOOBr and HOBrO, together with their isotope-labeled species.

Vibrational modes	HBr/ ¹⁶ O ₂		HBr/ ¹⁸ O ₂		$DBr/^{16}O_2$	
	Observed	Calculated	Observed (shift) ^a	Calculated (shift) ^a	Observed (shift) ^a	Calculated (shift) ^a
HOOBr						
O-O stretch	819.8	867.9	775.7 (-44.1)	818.4 (-49.6)	820.8 (1.0)	867.0 (-1.0)
HOO bend	1356.9	1414.7	1350.6 (-6.3)	1407.6 (-7.1)	1012.2 (-344.7)	1044.3 (-370.4)
HOBrO						
⁸¹ Br–O stretch	823.4	803.8	784.9 (-38.5)	765.6 (-38.2)	826.8 (3.4)	802.9 (-0.9)
⁷⁹ Br–O stretch	825.1	805.5	786.8 (-38.3)	767.3 (-38.1)	828.2 (3.1)	804.5 (-1.0)
HOBr bend	1102.3	1164.7	1099.0 (-3.3)	1161.1 (-3.7)	819.8 (-282.5)	852.2 (-312.5)

^a Isotope shift from the corresponding HBr/¹⁶O₂ species.

The 1102.3 cm⁻¹ band is assigned to the HOBr bending mode of HOBrO. The calculated isotope shifts, 312.5 cm⁻¹ for DOBrO and 3.7 cm⁻¹ for H¹⁸OBr¹⁸O, are consistent with the experimental values of 282.5 and 3.3 cm⁻¹, respectively.

In the DBr/O_2 experiment, the following three bands appear in a narrow region between 820 and 830 cm⁻¹: i.e., the O–O stretching (DOOBr), Br-O stretching (DOBrO), and DOBr bending (DOBrO) modes. However, they are distinguishable because of their unique band shapes: doublet splitting due to the ⁷⁹Br and ⁸¹Br isotopes, relative intensities, and widths. The above-mentioned isotope-labeled experiments strongly support that the chemical species of HOOBr and HOBrO are really generated in the VUV photolysis of HBr/O₂ in a Ne matrix and that the vibrational assignments are reasonable.

3.3. Photoreactivity of HOOBr and HOBrO

The details of the production mechanisms of HOOBr and HOBrO from HBr/O₂ upon the VUV irradiation in a Ne matrix will not be discussed here. Briefly, both reactants of HBr and O₂ can photo-dissociate to prepare H, Br and two O atoms in a Ne matrix cage [32,33], and then these atoms are combined possibly leading to formation of HOOBr and HOBrO. The less stable HBrO₂ isomer shown in Figure 1 has not been observed in the present study. As in the case of the HCl/O₂ system, the primary products of the present HBr/O2 system are four-atomic molecules of HOOBr and HOBrO. The produced atoms are not likely to be sufficiently energetic to escape from the matrix cage. Triatomic products such as HOO, BrOO, HOBr and OBrO seem to be secondary products from HOOBr and HOBrO. Judging from the geometrical structures (Figure 1), HOO and BrOO are probably formed from HOOBr, while HOBr and OBrO are produced possibly from HOBrO. In accordance with the report in Ref. [17], the photo-isomerization of OBrO to BrOO has been observed under the irradiation of visible light $(\lambda \ge 400 \text{ nm})$; The OBrO bands at 846.3 and 848.5 cm⁻¹ decreased in intensity, while the BrOO multiple bands around 1480 cm⁻¹ increased.

In the HCl/O₂ system, the photolysis thresholds of HOOCl and HOClO are found to exceed 365 and 405 nm, respectively, which has enabled individual observation of their spectra by wavelength-selected UV irradiation [7]. As for the present HOOBr and HOBrO cases, we have not selectively photolyzed each species, but we have differentiated the decomposition rates of two species by controlling the irradiation UV wavelength. By irradiating the products with 385 nm light, the intensities of the 1102.3, 825.1 and 823.4 cm⁻¹ bands assigned to HOBrO decreased more rapidly than the 1356.9 and 819.8 cm⁻¹ bands assigned to HOOBr, as shown in Figure 4a. The band intensities of HOBrO were mostly diminished after the irradiation at 385 nm. Subsequent irradiation at 350 nm following the 385 nm illumination depleted HOOBr dominantly, as shown in Figure 4b.

Although triatomic species of HOO, BrOO, HOBr and OBrO were expected to be the photoproducts of VUV as well as UV photolyses of HOOBr and HOBrO, their IR bands were not detectable upon the UV irradiation. Nor was isomerization between HOOBr and HOBrO identified. Though the energy of 350 nm radiation is high enough to photolyze both HOOBr and HOBrO, it would not be sufficient to remove fragment atoms out of the matrix cage. When UV light yields two fragments such as HOO and Br from HOOBr or HOBr and O produced from HOBrO, they would immediately be recombined to hold the reactants in the matrix cage. For the same reason,



Figure 4. Depletion spectra of HOOBr and HOBrO upon (a) the 385 nm light irradiation for 180 min and (b) the subsequent 350 nm light irradiation for 180 min. Bands marked with asterisks are unidentified.

BrO and OH radicals cannot be detected in a matrix cage if they are yielded from HOOBr upon UV irradiation.

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