EXPERIMENTAL DETERMINATION OF THE HO-Br BOND ENERGY AND ITS
RELEVANCE TO THE STRATOSPHERIC AND TROPOSPHERIC OZONE CYCLES

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The HO-Br bond energy (and consequently the heat of formation of HOBr) has been determined experimentally for the first time. HOBr can be photolyzed in the stratosphere to form Br and OH, both of which can react with ozone, and destroy it. Previous calculations modeling stratospheric reactions have assumed a lower stability than that found in the current research. Drs. B. Ruscic and J. Berkowitz at Argonne National Laboratory determined the stability of HOBr by measuring the threshold for formation of Br⁺ from this molecule, using the technique of photoionization mass spectrometry. Their work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences.

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Introduction

One of the cycles that is believed to contribute to ozone destruction in the stratosphere is^{1,2}

As first introduced by Yung et al.,¹ this cycle was believed to be relatively unimportant unless reaction 2 had a rate constant $> 4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, an unlikely possibility". Recent measurements^{2,3} have found $k_2 = (3.4 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with a resulting increase in ozone depletion from this cycle, according to the model used.² The rate of photolysis (reaction 3) is, to the best of our knowledge, still not known.

An additional role has recently been suggested⁴ for tropospheric HOBr. In this model, HOBr is dissolved in sulfuric acid aerosols, forming aqueous Br_2 , which volatilizes and is photolyzed by reaction 3, thereby contributing to ozone depletion at ground level.

Although it is the rates of the various reactions that enter the modeling (rather than the thermochemistry), Bridier et al.³ have drawn attention to the correlation of rate constants with the exothermicity of the reaction for the series

In this sequence, they found that the rate constant increased from 0.5 to 3.4 to about $7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $X = \text{Cl}, \text{Br}, \text{I}$, whereas the exothermicity varied from -46 to -52 to -65 kcal/mol (at 298 K). Although Bridier et al.³ did not state the sources of their thermochemical values, it is possible to reconstruct $\Delta H_{f298}^\circ(\text{ClO}) = 24.4$, $\Delta H_{f298}^\circ(\text{HOCl}) = -19$, $\Delta H_{f298}^\circ(\text{BrO}) = 30.1$, $\Delta H_{f298}^\circ(\text{HOBr}) = -19$, $\Delta H_{f298}^\circ(\text{IO}) = 41$, and $\Delta H_{f298}^\circ(\text{HOI}) = -21$, all in kcal/mol. The values for ClO and HOCl appear to be firmly established. Those for IO and HOI are poorly known. Of particular interest for the present investigation is the value chosen for HOBr. It is essentially an estimate of Benson's,⁵ which has been maintained in two recent compilations^{6,7} used for stratospheric modeling. It differs from two recently reported values, -9^{+1}_{-4} kcal/mol⁸ and -14.2 ± 1.6 kcal/mol.⁹ Had Bridier et al. used either of these later values, their correlation of rate constants with exothermicity would be much less convincing.

Both of the recently reported values are based on ab initio calculations. McGrath and Rowland⁹ used G2 theory, and some semiempirical corrections, supplemented by spin-orbit corrections, to arrive at their $\Delta H_{f298}^\circ(\text{HOBr})$, whereas Monks et al.⁸ calculated the proton affinity (PA) of BrO and combined this information with an experimental ionization potential of HOBr to infer $\Delta H_{f298}^\circ(\text{HOBr})$. Their calculation of PA (BrO) appeared to proceed by successive approximation. After learning that $\Delta H_{f298}^\circ(\text{HOBr}) \leq -9$ kcal/mol, based on the rapid reaction

(vide infra), they found that the first order configuration interaction (FOCI) calculation of PA (BrO) was insufficient ($\Delta H_{f298}^\circ = -2$), and finally extended the calculation to the second order multiconfiguration interaction level (SOCi) to arrive at a $\Delta H_{f298}^\circ(\text{HOBr}) = -9$ kcal/mol, which matched the allowed upper limit. The intermediate value of -2 kcal/mol was used in a contemporary publication by Monks et al.¹⁰

Still lacking is a purely experimental determination of $\Delta H_f^\circ(\text{HOBr})$, which is the subject of the present research.

Experimental Approach

The approach we utilized here to infer ΔH_f° (HOBr) was to measure the appearance potential of known fragments that, together with the corresponding IP of the ionic fragment, establishes an upper limit to that particular bond energy, and a lower limit to the stability of HOBr. It can readily be established that the lowest energy dissociative ionization process forms $\text{Br}^+ + \text{OH}$. Because this process involves a simple bond cleavage, one can anticipate little or no activation energy. The major problem is to avoid other sources of Br^+ , which could confuse the threshold measurements. Of major concern is Br_2 , which can give rise to Br^+ with a threshold close to that expected for Br^+ from HOBr. Consequently, it is important to prepare a sample of HOBr with minimal presence of Br_2 . The sample purity could be monitored from the relative abundance of the parent peaks, HOBr^+ and Br_2^+ .

Previous authors¹¹ had generated HOBr by reacting an excess of liquid bromine with a slurry of HgO in water. We examined this method, and variations of it. However, our best preparation, both in terms of the HOBr: Br_2 ratio and in the absolute abundance of HOBr, was achieved by stirring an excess of water with bromine in an ice bath, and then adding Ag_2O powder. The vessel was loosely sealed and stirred for about 2 hrs, during which time the solution became orange, then pale yellow. The pale yellow liquid was decanted, and placed in a vessel maintained at -20°C . Under these conditions, the HOBr^+ intensity was ca. five times that of Br_2^+ at 800 Å. Because the fragmentation ratio ($\text{Br}^+:\text{Br}_2^+$) is about 1:10, whereas that of $\text{Br}^+:\text{HOBr}^+$ was found to be $\sim 1:4.5$, the contribution of Br_2 to the Br^+ signal was $\lesssim 10\%$ throughout most of the region of interest. This contribution was subtracted from the measured Br^+ signal by establishing the photoion yield curve of Br^+ from Br_2 in a separate experiment, and then utilizing this function with a measured Br_2^+ abundance to determine the quantity to be subtracted.

The photoionization mass spectrometric apparatus, previously described,¹² consists of a 3 m vacuum ultraviolet monochromator and a quadrupole mass spectrometer. The hydrogen many-line emission spectrum was utilized as a light source in re-examining the parent ionization of HOBr in the lower energy region, whereas the helium Hopfield continuum was employed to measure Br^+ and HOBr^+ at higher energies. The wavelength resolution was 0.83 Å FWHM. Calibration wavelengths in the hydrogen region included atomic Lyman α , β , and well-known molecular emission bands. In the helium region, various impurity emission lines served as calibrants.

Experimental Results

Figure 1a presents an expanded section of our photoion yield curve of the parent ion, encompassing the region of autoionizing structure and extending below the threshold. Figure 1b, taken from a recent publication,⁸ displays the same region. Although the synchrotron source used in that study is presumably much more intense than our laboratory source, the data in Fig. 1a are obtained with almost four times better resolution. Besides poorer resolution, the peaks in Fig. 1b are shifted to shorter wavelength by $\sim 2.2\text{--}4.4$ Å, averaging about 3.5 Å. Also, the curve declines rapidly below ~ 1100 Å, missing the last sequence of peaks. Finally, the step structure near threshold, clearly visible in our data, and quite important in the accurate determination of the ionization potential, seems to be completely washed out in Fig. 1b.

The photoion yield curve of the Br^+ fragment from HOBr is presented in Fig. 2. The experimental data prior to subtraction (representing Br^+ from a mixture of Br_2 and HOBr) and after subtraction of $\text{Br}^+(\text{Br}_2)$ are shown. A linear kernel function, convoluted with a thermal broadening function, is fitted to the latter data. From a least squares fit, the 0 K threshold is found to be 13.915 ± 0.018 eV. Upon subtracting the value of the ionization potential of Br (11.8138 eV) from the above appearance potential, one obtains $D_0(\text{HO-Br}) \leq 2.101 \pm 0.018$ eV, or 48.45 ± 0.42 kcal/mol, which is a rigorous upper limit to this quantity. Because the dissociative ionization process measured is the lowest energy one, and involves a simple bond scission, it is plausible to assume that this upper limit is very close to the true value.

This upper limit refers to the reaction

By utilizing the well-established values $\Delta H_{f_0}^\circ(\text{OH}) = 9.34 \pm 0.05$ kcal/mol and $\Delta H_{f_0}^\circ(\text{Br}) = 28.18 \pm 0.03$ kcal/mol, we compute $\Delta H_{f_0}^\circ(\text{HOBr}) \geq -10.93 \pm 0.42$ kcal/mol, and $\Delta H_{f_{298}}^\circ(\text{HOBr}) \geq -13.43 \pm 0.42$ kcal/mol. This experimental result is in surprisingly good agreement with the recently reported⁹ calculated value, $\Delta H_{f_{298}}^\circ(\text{HOBr}) = -14.2 \pm 1.6$ kcal/mol, considering that this molecule contains a third-row atom.

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Figure Captions

- Figure 1 a. The photoion yield curve of HOBr^+ from HOBr between 1080-1190 Å, present data.
b. The same as in a, taken from ref. 8. The jogged dotted lines indicate the mismatch of the peaks in the two data sets. The threshold region is shown enlarged in the inset.
- Figure 2. Photoion yield curve of Br^+ from HOBr . The upper curve consists of Br^+ from a mixture of HOBr and ~10% Br_2 . In the lower curve, the contribution of Br^+ from Br_2 has been subtracted. The smooth curve drawn through the points is the best fit of a linear kernel function, convoluted with a thermal broadening function. The sloping line to higher energy is the hypothetical 0 K kernel function.

FIGURE 1

FIGURE 2