Experimental determination of $\Delta H^0_f$(HOBr) and ionization potentials (HOBr): Implications for corresponding properties of HOI

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The photon yield curves of HOBr+ and Br+ from HOBr are presented. The adiabatic I.P. of HOBr is found to be 10.638±0.003 eV. Autoionizing structure in HOBr+ is tentatively assigned and leads to an adiabatic I.P. of the first excited (A L2 A ' ) state of ~11.46 eV. The 0 K threshold of Br+ from HOBr (13.915±0.018 eV) implies $D_0$(HO-Br)≤2.101±0.018 eV=48.45±0.42 kcal/mol. Together with auxiliary thermochemistry, this value yields $\Delta H^3_{298}(\text{HOBr}) ≥ -13.43 ± 0.42$ kcal/mol, in excellent agreement with a recent ab initio value -14.22±1.6 kcal/mol. The resulting proton affinity of BrO is 163.8 kcal/mol. Trends observed in the properties of OX and HOX (X=F, Cl, Br) are utilized to infer new values for $\Delta H^3_{298}(\text{OI})$ and $\Delta H^3_f$(HOI). Predictions are made for I.P.(HOI).

I. INTRODUCTION

One of the cycles which is believed to contribute to ozone destruction in the stratosphere is

\begin{align}
\text{Br}+\text{O}_3 & \rightarrow \text{BrO}+\text{O}_2, \quad (1) \\
\text{BrO} + \text{HO}_2 & \rightarrow \text{HOBr} + \text{O}_2, \quad (2) \\
\text{HOBr} + h\nu & \rightarrow \text{OH} + \text{Br}, \quad (3) \\
\text{OH} + \text{O}_3 & \rightarrow \text{HO}_2 + \text{O}_2. \quad (4)
\end{align}

net: $2\text{O}_3 \rightarrow 3\text{O}_2$.

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

An additional role has recently been suggested 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 which enter the modeling (rather than the thermochemistry), Bridier et al. have drawn attention to the correlation of rate constants with the exothermicity of the reaction for the series

\begin{align}
\text{XO} + \text{HO}_2 & \rightarrow \text{HOX} + \text{O}_2, \\
\text{X} = \text{Cl, Br, I.}
\end{align}

In this sequence, they found that the rate constant increased from 0.5 to 3.4 to about 7 (×10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) for X = Cl, Br, and I, while the exothermicity varied from −46 to −52 to −65 kcal/mol (at 298 K). Although Bridier et al. did not state the sources of their thermochemical values, it is possible to reconstruct $\Delta H^3_{298}(\text{ClO}) = 24.4$, $\Delta H^3_{298}(\text{HOCl}) = -19$, $\Delta H^3_{298}(\text{BrO}) = 30.1$, $\Delta H^3_{298}(\text{HOBr}) = -19$, $\Delta H^3_{298}(\text{IO}) = 41$, and $\Delta H^3_{298}(\text{HOI}) = -21$, 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, which has been maintained in two recent compilations used for stratospheric modeling. It differs from two recently reported values −9$^{±1}_{±4}$ (Ref. 8) and −14.2±1.6 kcal/mol. 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 Rowland used G2 theory, and some semiempirical corrections, supplemented by spin-orbit corrections, to arrive at their $\Delta H^3_{298}(\text{HOBr})$, while Monks et al. calculated the proton affinity (P.A.) of BrO and combined this information with an experimental ionization potential of HOBr to infer $\Delta H^3_{298}(\text{HOBr})$. Their calculation of P.A.(BrO) appeared to proceed by successive approximation. After learning that $\Delta H^3_{298}(\text{HOBr}) ≤ -9$ kcal/mol, based on the rapid reaction

\begin{align}
\text{OH} + \text{Br}_2 & \rightarrow \text{HOBr} + \text{Br}, \quad (5)
\end{align}

(vide infra), they found that the first order configuration interaction (FOCI) calculation of P.A.(BrO) was insufficient ($\Delta H^3_{298}(\text{BrO}) = -2$), and finally extended the calculation to the second order multiconfiguration interaction level (SOCI) to arrive at $\Delta H^3_{298}(\text{HOBr}) = -9$ 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. Still lacking is a purely experimental determination of $\Delta H^3_f$(HOBr), which is the subject of the present research.

II. EXPERIMENTAL APPROACH

The approach we shall utilize here to infer $\Delta H^3_f$(HOBr) is to measure the appearance potential of known fragments which, together with the corresponding I.P. of the ionic fragment, establishes an upper limit to that particular bond energy, and a lower limit to the stability of HOBr. There are three possible pairs of fragments.

\begin{align}
(1) \text{Br}^+ + \text{OH}, & \quad \text{Br}+\text{OH}^+; \\
(2) \text{BrO}^+ + \text{H}, & \quad \text{BrO}+\text{H}^+;
\end{align}
(3) $O^+ + HBr \rightarrow O + HBr^+$.

In each pair, the species with the lower I.P. is favored, a phenomenon sometimes called Stevenson's rule. Hence, the choices are reduced to $Br^+$, $BrO^+$, and $HBr^+$. Of these, the lowest energy process, based on known heats of formation, is that forming $Br^+$. It is also a simple bond cleavage, whereas $HBr^+$ involves a constrained transition state. The process forming $BrO^+$ introduces some ambiguity because somewhat different ionization potentials have been reported for $BrO$. In fact, we examined the onset of $BrO^+$ in this experiment and found that its appearance potential (A.P.) was much lower than anticipated, and very likely attributable to $Br,O$ as progenitor ($Br_2O^+$ having been observed in the mass spectrum).

Hence, the focus of the investigation was the appearance potential of $Br^+$ from HOBr. Our method of preparation concomitantly generates some $Br_2$. The appearance potential of $Br^+$ from $Br_2$ at 0 K (from well-established thermochemical data) is 13.784 eV = 899.46 Å. (There are still lower energy processes due to ion-pair formation, but these are weak and distinguishable.) This appearance potential is in the region expected for $Br^+$ from HOBr. Therefore, it is important to minimize the abundance of $Br_2$ relative to HOBr in the preparation of the sample and to correct adequately for the contribution of $Br_2$ to the observed $Br^+$ signal.

Mouks et al.8 generated HOBr in a flow tube reactor, according to reaction (5). This approach was certain to provide us with a large abundance of $Br_2$ and $Br^+$, both of which would confuse our appearance potential measurements. We opted instead (initially) for a method utilized by Koga et al.13 who obtained the microwave spectrum of HOBr. These authors produced HOBr by reacting an excess of liquid bromine with a slurry of HgO in water. The sample was degassed, excess bromine was removed by pumping, and the gaseous sample (kept at 20 °C) was introduced into the apparatus. We had moderate success with this method, and somewhat better success by stirring water and bromine in an ice bath, and adding HgO slowly. 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$_2$O powder. The vessel was loosely sealed and stirred for about 2 h, 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 approximately five times that of $Br_2$ at 800 Å. Since the fragmentation ratio ($Br^+:Br_2$) is about 1:10, while that of $Br^+:HOBr^+$ was found to be ~1:4.5, the contribution of $Br_2$ to the $Br^+$ signal was ≈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,14 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 reexamining the parent ionization of HOBr in the lower energy region, while the helium Hopfield continuum was employed to measure $Br^+$ and HOBr$^+$ at higher energies. The wavelength resolution was 0.83 Å full width at half-maximum (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.

III. EXPERIMENTAL RESULTS

Figure 1 is an overview of the photoionization of HOBr between 800 Å and the ionization threshold, displaying
peaks. This behavior is likely attributable to the transmission in Fig. 2(a) displays inherent, rather than instrumentally limited width. Monks et al. were unable to assign the autoionizing structure. We defer discussion of this structure to the following section.

In Fig. 2(a), step-like structure can be seen in the threshold region between ~1150–1165 Å. This region is further amplified in the inset to Fig. 2. The idealized threshold behavior for photoionization is just such a step function. The curvature at the ascent is very likely due to rotational effects, while the spacing between steps corresponds to a vibrational quantum in the electronic ground state of HOBr⁺. This spacing is about 0.089±0.004 eV=720±30 cm⁻¹. The O–Br stretching frequency in neutral HOBr (Ref. 15 and 16) is very nearly 620 cm⁻¹. If this step in HOBr⁺ is identified with the O–Br stretching frequency in the cation, it corresponds to a 16% increase from the value in HOBr, implying that this first ionization energy involves removal of an electron from an antibonding orbital. The halogen and interhalogen molecules, although having D₁₆ and C₁₅₄ symmetries, provide useful comparisons. In each instance, these molecules have πₚ-like uppermost occupied orbitals, which are antibonding. The molecule ClBr comes closest to approximating HOBr, since the ionization potential of Cl is close to that of OH. Dunlavey et al.¹⁷ have obtained the partial He I photoelectron spectrum of ClBr. They observed the spin–orbit split ⁷Σ₂⁺ and ⁷Σ₁⁻ states, each with its vibrational progression. The increase in vibrational frequency from ClBr⁺ was found to be 9% for ⁷Σ₂⁺ and 14% for ⁷Σ₁⁻, similar to that found here for HOBr. Four vibrational peaks could be seen for ⁷Σ₂⁺, the second (ν₁ = 1) being the largest. In an idealized photoionization spectrum, the step height is proportional to the Franck–Condon factor. In the present spectrum [Fig. 2(a)], the height of the second step is seen to be larger than the first or third.

In the He I photoelectron spectra of HOF (Ref. 18) and HOCI,¹⁹ four or five members of a vibrational progression are seen near threshold, with the second peak being the largest.

It seems clear that the threshold region of HOBr⁺ (HOBr) manifests vibrational steps with rotational tailing. In principle, it is possible²⁰ to fit the rotational tail, by superposing the various rotational transitions, and selecting what would be the Q branch. Here, we approximate this solution by choosing the half-rise point of the first step 1165.5±0.3 Å=10.638±0.003 eV. Monks et al.⁸ deduced 10.61±0.03 eV, not too different from the present value. However, it seems to be due to a cancellation of errors. We have already noted that their wavelength scale appears to be off by ~3.5 Å, in a direction which would yield a higher ionization threshold. Their method of arriving at an adiabatic ionization potential is to linearly extrapolate a sloping threshold, which we found to be a step. There is no obvious justification for such an extrapolation, which they extended to their zero background base line. This procedure has the effect of lowering the apparent ionization potential. Thus, the two errors approximately compensate one another.

2. The region of autoionization structure

Figure 3 focuses on the autoionizing region. As mentioned earlier, improved instrumental resolution is not likely

A. Detailed examination of HOBr⁺ from HOBr

1. The threshold region

Figure 2(a) is an expanded curve of the parent ion in the region of autoionizing structure, extending to below the threshold. Figure 2(b) taken from the recent publication of Monks et al. displays the same region. In Fig. 2(a), the wavelength resolution is 0.83 Å, and points are taken at 0.20 Å intervals, while in Fig. 2(b), the stated spectral width is 2.3 Å, and the spacing between points is 1.0 Å. Apart from the resolution, another marked difference between the spectra is the location of the peak positions. The data of Monks et al. appear to shorter wavelength than the present data by ~2.2–4.4 Å, averaging about 3.5 Å. Below ~1100 Å, their ion yield curve declines rapidly, missing the last sequence of peaks. This behavior is likely attributable to the transmission cutoff of the LiF window used in their experiment. We have examined the peak region ~1120 Å at much higher resolution (0.14 Å, FWHM), and found little or no evidence for further splitting. Hence, we believe that the spectrum shown in Fig. 2(a) displays inherent, rather than instrumentally limited width. Monks et al. were unable to assign the autoionizing structure. We defer discussion of this structure to the following section.

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2. The region of autoionization structure

Figure 3 focuses on the autoionizing region. As mentioned earlier, improved instrumental resolution is not likely
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to simplify this spectrum. A plausible assignment of this structure, which rationalizes the major features, appears in the upper half of Fig. 3. The fit is not perfect, but perhaps this cannot be expected without inclusion of perturbations in such a congested spectrum. The attractiveness of the assignment is its simplicity. It consists of a single Rydberg series, each member of which has a progression of four (or more) vibrational states. A single quantum defect $\delta = n - E_n \approx 1.1$ is used to characterize this series, taken to be an $nd$ series.

Two consequences of this assignment are that the adiabatic I.P. is $\approx 11.46$ eV and the vibrational frequency is about $0.083$ eV=$670$ cm$^{-1}$. This implies an excitation of $\approx 6600$ cm$^{-1}$ for the limiting ion state above the ground state.

Monks et al.$^8$ have calculated 6631 cm$^{-1}$ for an $A'$ state above the ground $^2A^\oplus$ state, but appeared to discount Rydberg states converging to this limit because such transitions are "essentially two electron in nature, the transition probability is low, and the Rydberg states of the A state should not contribute significantly to the ionization." Support for the present interpretation comes from the He I PES of HOCl,$^19$ where this first excited state is observed, assigned to the $A'$ state, and found to be of comparable intensity to the ground state.

Weaker structure appearing in Fig. 3 is due probably to one or more additional Rydberg series converging to the same limits of the $A'$ state.

**B. Br$^+$ from HOBr**

A magnified view of the photoion yield curve of Br$^+$ is presented in Fig. 4. The experimental data prior to subtraction (representing Br$^+$ from a mixture of Br$_2$ and HOBr) and after subtraction of Br$^+$ (Br$_2$) are shown. A linear kernel function, convoluted with a thermal broadening function fitted to the latter data (see the Appendix) yields a 0 K threshold of 13.915$\pm$0.018 eV. The vibrational frequencies of HOBr used to calculate the vibrational contribution to the offset were 3589, 1162.3, and 619.5 cm$^{-1}$. The two latter frequencies were taken from McRae and Cohen$^{15}$ and the first from Schwager and Arkell.$^{16}$ Almost the same frequencies have been mentioned by Barnes et al.$^{21,22}$ Together, they account for only 0.106 kcal/mol, whereas rotations contribute 0.889 kcal/mol to the internal thermal energy.

Upon subtracting the value$^{23}$ of the ionization potential of Br (11.8138 eV) from the above appearance potential, one obtains $D_0$(HO-Br)$=2.101\pm0.018$ eV, or 48.45$\pm$0.42 kcal/mol, which is a rigorous upper limit to this quantity. Since 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.

**IV. INTERPRETATION OF RESULTS**

**A. The heat of formation of HOBr**

In Sec. III D, we obtained $\Delta H_f=48.45\pm0.42$ kcal/mol for the reaction.

**FIG. 4.** Photoion yield curve of Br$^+$ from HOBr. The upper curve (crosses) consists of Br$^+$ from a mixture of HOBr and $\approx 10\%$ Br$_2$. In the lower curve (circles), 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 (see the Appendix). The sloping line to higher energy is the hypothetical 0 K kernel function.
\[ \text{HOBr} \rightarrow \text{Br} + \text{OH}. \]

With \( \Delta H_f^0 (\text{OH}) = 9.34 \pm 0.05 \text{ kcal/mol} \), (Ref. 24) and \( \Delta H_f^0 (\text{Br}) = 28.18 \pm 0.03 \text{ kcal/mol} \), we compute \( \Delta H_f^0 (\text{HOBr}) \geq 10.93 \pm 0.42 \text{ kcal/mol} \) and \( \Delta H_{f,298}^0 (\text{HOB}) \geq -13.43 \pm 0.42 \text{ kcal/mol} \). This experimental result is in excellent agreement with the recently reported calculated value, \( \Delta H_{f,298}^0 (\text{HOB}) = -14.2 \pm 1.6 \text{ kcal/mol} \), considering that this molecule contains a third row atom.

Boodaghians et al.25 studied the temperature dependence of reaction (5) (see the Introduction) and found zero activation energy (\( E_a \)), at the 95% confidence limit, with a "maximum value of \( E_a \) that can be accommodated" of 1.3 kcal/mol. With \( \Delta H_{f,298}^0 \) values for OH, Br, and Br2 taken from Gurvich et al.24 and the currently deduced \( \Delta H_f^0 (\text{HOB}) \), we find that reaction (5) is exothermic by 3.48 \pm 0.42 kcal/mol.

V. DISCUSSION

A. Implications for \( \Delta H_f^0 (\text{IO}) \) and \( \Delta H_f^0 (\text{HOI}) \)

In the Introduction, we noted that Brüdier et al.3 had found an apparent correlation between the exothermicities of the reactions (2') and the corresponding reaction rates. With our current value for \( \Delta H_f^0 (\text{HOB}) \), the exothermicities of the ClO+HO2 and BrO+HO2 reactions are virtually identical, although the rates differ by a factor of 6-7.

The heats of formation of XO and HOX (X=F, Cl, Br) now seem to be fairly well established, but the corresponding values of IO and HOI are wildly discordant. In a recent study of the reaction of IO with HO2, presumably forming HOI+O2, one of the variants of reaction (2'), Maguin et al.26 attempted to evaluate the exothermicity of that reaction. They noted wide variations in \( \Delta H_{f,298}^0 (\text{IO}) \), but chose \( \Delta H_{f,298}^0 (\text{IO}) = 53 \pm 3 \text{ kcal/mol} \). This value adopted by Maguin et al. is in agreement with the recently reported calculated value, \( \Delta H_{f,298}^0 (\text{HOI}) = 48.4 \pm 0.4 \text{ kcal/mol} \). These combined results yield \( \Delta H_f^0 (\text{IO}) = 2.05 \pm 0.07 \text{ kcal/mol} \), and consequently, \( \Delta H_f^0 (\text{HOI}) = -19.5 \pm 0.5 \text{ kcal/mol} \) and \( \Delta H_f^0 (\text{HOF}) = -114 \pm 0.4 \text{ kcal/mol} \). This comparison also invites some reexamination of the values of \( \Delta H_f^0 (\text{IO}) \) and \( \Delta H_f^0 (\text{HOI}) \).

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\[ \text{HO}-\text{X} \text{ and } \text{O}-\text{X} \text{ bond energies (in kcal/mol at 0 K).} \]

<table>
<thead>
<tr>
<th>X</th>
<th>( D_f (\text{HO}-\text{X}) )</th>
<th>( D_f (\text{X}-\text{O}) )</th>
<th>( \text{Ratio} )</th>
<th>( D_f (\text{HO}-\text{X})/D_f (\text{X}-\text{O}) )</th>
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<td>47.3 \text{a}</td>
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<td>55.1 \text{a}</td>
<td>63.43 \text{a}</td>
<td>0.85</td>
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</tr>
<tr>
<td>Br</td>
<td>48.45 \pm 0.42 \text{d}</td>
<td>55.3 \pm 0.68 \text{d}</td>
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<tr>
<td>I</td>
<td>56.3 \text{e}</td>
<td>41.5 \text{e}</td>
<td>1.36</td>
<td>1.36</td>
</tr>
</tbody>
</table>

*Present results.

**Values adopted by Maguin et al. (Ref. 26).**
rapid. These authors monitored the OH concentration and assumed that the reaction proceeded to form HOI+CF$_3$, although the products were not measured. Their assumption was based on the presumed parallelism of halogen atom and OH reactions. Jenkin et al. also adopted this reaction pathway “since C–F bonds are too strong to be reactive at room temperature.” Thus, taking $\sim$53.3 kcal/mol as the C–I bond strength, they assumed that the O–I bond strength in HOI must be at least as large, and thereby deduced $\Delta H_{798}^{o}$ (HOI) $\leq$ -18.4 kcal/mol. However, another set of products could be CF$_3$O+HI. Even within the current range of uncertainty of $\Delta H_{798}^{o}$ (CF$_3$O), i.e., between -150 (Ref. 33) and -157 kcal/mol, this reaction is at least 16 kcal/mol more exothermic than one just exothermic enough to yield HOI+CF$_3$. Consequently, until the reaction products of OH+CF$_3$I are established, the upper limit to $\Delta H_{798}^{o}$ (HOI) fixed by Jenkin et al. must be regarded as questionable. Hence, any value $\geq -24.4$ kcal/mol [their derived lower limit for $\Delta H_{798}^{o}$ (HOI)] would appear possible.

If we extrapolate the trend in the ratio $D_{0}(O-X)/D_{0}(O-X)$ in Table I, we estimate this ratio to be $0.86-0.88$ for $X=I$. This, in turn, gives $D_{0}(H-O)=43-44$ kcal/mol and $\Delta H_{798}^{o}$ (HOI) $\approx -8$ to $-9$ kcal/mol. With this value, $D_{0}(H-OI)$ in Table II becomes 94.2–95.2 kcal/mol, which is essentially the value for $D_{0}(H-OBBr)$ and $D_{0}(H-OCl)$. These suggested values in Tables I and II are given in parentheses.

What evidence can be offered in support of these suggested values? While internuclear distances and vibrational frequencies are not reliable guides to dissociation energies, they provide some indications. The molecular structures of HOF, HOCI, and HOBr are known, but that of HOI is not. The OH distances in these molecules are 0.964±0.001, 0.975±0.003, and 0.961±0.001 Å, in the order given. Insofar as they can be correlated with bond energies, they imply roughly constant values, as is observed. It seems unlikely to us that the H–O1 bond energy will increase dramatically (by $\sim$20 kcal/mol) from the other H–OX bond energies, as was implied by the previously used heats of formation. The O–X stretching vibrational frequencies are known for all HOX and OX, and are reproduced in Table III. They display a monotonic decline from HOF to HOI, and from OF to OI. After taking into account the disparate masses, the corresponding force constants maintain this trend (although there is almost no change in force constant between OCl and OBBr). This suggests that the HO–X bond energies might also decline monotonically from HOF to HOI, and we can see that this is not the case for HOF to HOCI. However, fluorine often introduces anomalies; cf. $D_{0}(F_{2})$, $D_{0}(Cl_{2})$, $D_{0}(Br_{2})$ and $D_{0}(I_{2})$, where the bond energies decline monotonically, except between $D_{0}(F_{2})$ and $D_{0}(Cl_{2})$. A similar anomalous behavior between $D_{0}(H-OBr)$ and $D_{0}(H-OI)$ does not seem likely. Finally, we note that the vibrational frequencies of OX are uniformly higher than the O–X stretching frequencies in HOX. It is possible to estimate the HO–X frequencies from the O–X frequencies using Badger’s rule if the corresponding internuclear distances are known. In Table IV, these values are listed (except between $D_{0}(F_{2})$ and $D_{0}(Cl_{2})$). Their assumption that the reaction proceeded to form HOI+CF$_{3}$I, and in Table III, the HO–X frequencies estimated from Badger’s rule are compared with experimental values. The agreement is reasonable and enables us to predict $r(H-OI)=1.959$ Å by Badger’s rule, and 1.995 Å by noting that the ratio $r(H-OX):r(O-X)$ is nearly constant.

These trends in frequencies follow our suggested values for $D_{0}(H-OI)$ and $D_{0}(IO)$. With the preexisting choices for $\Delta H_{798}^{o}$ (HOI) and $\Delta H_{798}^{o}$ (IO), this pattern is not maintained. As seen above, $D_{0}(IO)$ continues to be controversial after decades of study. It is not clear how difficult it will be to determine $\Delta H_{798}^{o}$ (IO), but it has been detected mass spectrometrically, and two vibrational frequencies have been reported for the gas phase. However, the lifetime of HOI in the latter study was only 1–2 min. Perhaps further kinetics studies will be able to test the values suggested here. Our examination of existing studies does not indicate any disparity with the currently suggested values.

With the suggested values for $\Delta H_{798}^{o}$ (IO) and $\Delta H_{798}^{o}$ (HOI), reaction (2') ($X=I$) is exothermic by about 45 kcal/mol. It will be recalled that Bridier et al. correlated the increasing rate constants of reaction (2') with increasing exothermicity, in the sequence X=Cl, Br, I. The presently determined $\Delta H_{798}^{o}$ (HOBr), together with our surmises regarding $\Delta H_{798}^{o}$ (IO) and $\Delta H_{798}^{o}$ (HOI), now leads to the conclusion that these three reactions have approximately the same exothermicity.

<table>
<thead>
<tr>
<th>TABLE IV. O–X internuclear distances for OX and HOX.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>F</td>
</tr>
<tr>
<td>Cl</td>
</tr>
<tr>
<td>Br</td>
</tr>
<tr>
<td>I</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TABLE III. The O–X stretching frequencies (in cm$^{-1}$) in OX$^a$ and HOX$^b$.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
</tr>
<tr>
<td>Cl</td>
</tr>
<tr>
<td>Br</td>
</tr>
<tr>
<td>I</td>
</tr>
</tbody>
</table>

$^a$From Huber and Herzberg (Ref. 28).
$^b$Summary of data given by Barnes et al. (Ref. 22).
$^d$Predicted from Badger’s rule and O–X frequencies.

B. The proton affinities of OX molecules

In Table V, we list the proton affinities of OF, OCl, and OBBr at 0 and 298 K, calculated according to the available heats of formation also shown in the table. There is a large increase in proton affinity between OF and OCl, and a smaller increment between OCl and OBBr. Below, we attempt to predict P.A.(OI).
Since we have already estimated $\Delta H^0_{f_0}(O\cdot I)$ and $\Delta H^0_{f_0}(H\cdot O\cdot I)$, we need only to estimate $I.P.(H\cdot O\cdot I)$. If we consider OH to be a pseudohalogen, we can gain some insight by comparing the adiabatic ionization potentials of XY (Ref. 37) with XOH, where Y is a halogen atom closest in ionization potential to OH. That halogen atom is Cl. The ratio of adiabatic I.P.'s, $XCl/XOH$, is 1.0047, 1.0333, and 1.035 for X=F, Cl, and Br. In the case of Br, the spin–orbit splitting is 0.26 eV; the ratio to the average of the spin–orbit pair becomes 1.047. If we extrapolate this trend to X=I, the ratio is estimated to be 1.04 (1.06 to the spin–orbit average). With $I.P.(ICI)=10.10$ and $10.68$ eV for the spin–orbit split state, we infer $I.P.(HOI)=9.71–9.80$ eV. The proton affinity of OI deduced from these estimates is given in Table V. It is about 20 kcal/mol higher than P.A.(OBr), which is only about 12 kcal/mol higher than OCl. From the observed trends, one might anticipate a somewhat lower value for P.A.(OI). However, had we retained the prior selected values for $\Delta H^0_{f_0}(OI)$ and $\Delta H^0_{f_0}(H\cdot O\cdot I)$, combined with the currently estimated $I.P.(HOI)$, the increment in proton affinity between OBr and OI would have been about 40 kcal/mol. Hence, the derived proton affinity of OI in Table V can be considered an additional criterion favoring the currently suggested values for $\Delta H^0_{f_0}(OI)$ and $\Delta H^0_{f_0}(H\cdot O\cdot I)$. It must also be kept in mind that our estimates began with $D_{f_0}(IO)=50\pm5$ kcal/mol; this uncertainty must be carried through the ensuing considerations.

Incidentally, one may also infer a plausible estimate for $I.P.(IO)$, by examining the ratios of I.P.'s for XOH. These ratios are 12.77 (Ref. 38)/12.71 (Ref. 39)=1.0047 and 12.71+0.01 eV. The proton affinity of OI inferred from these is 12.71+0.01 eV.

Table VI. Adiabatic values of the two lowest ionization potentials for HOX (in electron volts).

<table>
<thead>
<tr>
<th>X</th>
<th>$\Delta X^{2\pi^*}$</th>
<th>$A^{2\pi^*}$</th>
<th>$\Delta (X^{2\pi^<em>}-A^{2\pi^</em>})$</th>
<th>r(H→OX)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOCl</td>
<td>12.69+0.03*</td>
<td>14.50+0.03*</td>
<td>1.80</td>
<td>1.774</td>
</tr>
<tr>
<td>HOBr</td>
<td>12.71+0.01*</td>
<td>12.09+0.01*</td>
<td>0.79</td>
<td>1.421</td>
</tr>
<tr>
<td>HOI</td>
<td>10.638+0.003*</td>
<td>11.46*</td>
<td>0.82</td>
<td>1.464</td>
</tr>
</tbody>
</table>

C. The splitting of the first two states of HOX$^+$

The present results for HOBr, together with earlier studies on HOCl and HOF, enable us to construct Table VI. Here, we list the adiabatic I.P. for formation of the ground state (X$^{2\pi^*}$), the adiabatic value for the first excited state (A$^{2\pi^*}$), and their difference. These two states result from the splitting of a $\Pi$ state in $C_{av}$ geometry into $C_s$ symmetry, with $A^{\pi}$ being the out-of-plane component.

One can envisage a proton approaching OX, giving rise to this splitting. A naive view might anticipate some correlation between P.A.(OX) and the magnitude of the splitting. However, as a perusal of Tables V and VI shows, the actual behavior is contrary. The proton affinity increases as the splitting decreases.

An alternative view might attempt to correlate the splitting with the distance of the H atom (it need not and probably is not H$^+$) to the midpoint of the O–X bond in HOX$^+$. We can test such a hypothesis, with an approximation. The molecular geometries of the HOX neutral molecules except HOI are well-characterized. They will change slightly upon ionization, particularly by a diminution in the OX bond length, but for the purposes of this estimate, such a change is slight. By assuming the neutral geometries, we calculate the distance from H to the OX midpoint to be 1.274, 1.421, and 1.464 Å for HOF, HOCl, and HOBr, respectively. The shorter distance can be expected to lead to a larger splitting, as is observed.

We can extend this analysis to HOI, since we have already made estimates of its structure, i.e., r(O–H)=0.96 Å, r(O–X)=1.999–1.995 Å, and <HOI>=102.4°. These parameters lead to r(H→OI)=1.512–1.526 Å. The apparent de-
dependence of the splitting on the \( r(H\rightarrow OX) \) distance is roughly exponential; the predicted splitting for HOI \(^+\) would be \( -0.62 - 0.67 \) eV.

VI. CONCLUSIONS

The adiabatic I.P. of HOBr forming the \( X \, ^2A'' \) state of HOBr \(^+\), is found to be \( 10.638 \pm 0.003 \) eV. Autoionization structure observed is interpreted as Rydberg series converging to the first excited state \( ^2A' \) with an adiabatic I.P. of \( -11.46 \) eV. The A.P. of Br \(^+\) from HOBr is measured to be \( \leq 13.915 \pm 0.018 \) eV at 0 K. This result leads directly to \( D_0(\text{HO}-\text{Br}) = 2.101 \pm 0.018 \) eV=48.45 \pm 0.42 kcal/mol. With well-established auxiliary data, one arrives at \( \Delta H_{\text{f,ox}}^0(\text{HOBr}) = -10.93 \pm 0.42 \) kcal/mol, and \( \Delta H_{\text{f,ox}}^0(\text{HOBr}) = -13.43 \pm 0.42 \) kcal/mol.

With the thermochemistry of three HOX molecules rather well determined, and the fourth (HOI) poorly known, trends were examined to predict a value for \( \Delta H_{\text{f,ox}}^0(\text{HOI}) = -8 \) to \(-9 \) kcal/mol, much less negative than the quantity in current use \((-21.4 \pm 3.0 \) kcal/mol). The \( X \, ^2A''-A \, ^2A' \) splitting in HOX \(^+\) is found to decrease as X varies from F-Cl-Br. The proton affinity of OX is found to increase in the same order. With a plausible estimate of I.P.(HOI), the trend in proton affinity is maintained, and enables one to estimate the \( X \, ^2A''-A \, ^2A' \) splitting in HOI \(^+\).

The correlation of increasing rate constant with increasing exothermicity for the reactions

\[ \text{XO} + \text{HO}_2 \rightarrow \text{HOX} + \text{O}_2 \]

as X goes from Cl-Br-I is vitiated by the current results. The exothermicity remains approximately constant.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

APPENDIX: CONVOLUTION OF KERNEL FUNCTIONS WITH THE INTERNAL DISTRIBUTION FUNCTION OF A THREE-DIMENSIONAL ROTOR

The three-dimensional rotor has the thermal distribution function

\[ P(E-E_0) = \frac{2}{\sqrt{\pi}} \left( \frac{1}{kT} \right)^{3/2} \exp[-(E-E_0)/kT], \]

where \( E_0 \) is a particular value of the photon energy \( h\nu\). If we choose a kernel (i.e., 0 K) photoion yield curve of the form \( \phi(E-E_i) \), then the convolution takes the following form:

1. Linear kernel function

\[ \phi(E-E_i) = c(E-E_i), \]

where \( c \) is an arbitrary constant.

a. Prethreshold

The integral decomposes into three parts. The first has an analytical solution.

\[ \frac{2c}{\sqrt{\pi}} \int_0^{E_i} \left( \frac{E-E_0}{kT} \right)^{3/2} e^{-c(E-E_0)/kT} dE. \]

The second and third terms can be combined to give

\[ \frac{2c}{\sqrt{\pi}} \int_0^{E_i} \left( \frac{3}{2} + a \right) y^{1/2} e^{-y} dy, \]

where \( a = 0.491532, f = 0.7134769 \), and the correlation is 0.99925.

Combining all the terms, we finally obtain

\[ I(E_0) = \frac{7c}{\sqrt{\pi}} \left( \frac{3\sqrt{\pi}}{4} + \frac{3}{2} a e_0 - a e_0^1 + f e_0^{3/2} \right) e^{-E_0}. \]

b. Post-threshold

These two functions merge when \( E_0 = E_i \), at which point they both give \( c(\sqrt{3}kT) \), the average internal energy for a 3 rotor, multiplied by an arbitrary constant.

2. Exponential kernel function

\[ \phi(E-E_i) = c(1 - e^{-b(E-E_i)}). \]

a. Prethreshold

The integral decomposes into a \( b \)-independent part and a \( b \)-dependent part. The \( b \)-independent part has the form

\[ \frac{2c}{\sqrt{\pi}} \int_0^{E_i} y^{1/2} e^{-y} dy, \]

which we have evaluated above.

Therefore, the \( b \)-dependent part becomes

\[ \frac{2c}{\sqrt{\pi}} \left( \frac{\sqrt{\pi}}{2} + a e_0 \right) e^{-E_0}, \]

where \( e_0, a, \) and \( f \) have the same meanings as before. The \( b \)-dependent part has the form
Thus, at $E = E_o$, the two functions join, with the common value to have the value 0.7, with a weak b dependence, approximating the remainder is fitted numerically to a function $p_x'$. In this manner, good correlation. The final result is with $a$, $b$, $f$, $I$, and $m$ having the values given above.

By analogy with the 4 rotor and the requirement that the prethreshold function must match the post-threshold function at $E = E_o$, we assume the b-dependent part to consist of two terms—one dependent on $(E_t - E_o)$ and the other independent (apart from the exponential $e^{-(E_t-E_o)/kT}$).

Thus, the third and fourth terms are assumed to have the form

$$c \left( \frac{1}{bkT+1} \right)^{3/2} \exp[-(E_t-E_o)/kT] - c \left( \frac{E_t-E_o}{kT} \right)^l \frac{1}{(bkT+1)^m} \exp[-(E_t-E_o)/kT].$$

We evaluate the integral $J$ numerically for various values of $b$ significantly higher and lower than the value $b = 0.1 \text{kcal mol}^{-1}$ previously found for CH$_2$OH$^+$. After dividing $J$ by $e^{-(E_t-E_o)/kT}$ and subtracting $(bkT+1)^{-3/2}$, the remainder is fitted numerically to a function $p_x'$. In this manner, the energy dependence in the fourth term, i.e., $l$, is found to have the value 0.7, with a weak $b$ dependence, approximately $l = -0.0325b + 0.7123$. Finally, for each case of $b$, dividing by $[(E_t-E_o)(kT)^l]$ exposes $(bkT+1)^{-m}$. Since $(bkT+1)$ is known, a numerical fit yields $m = 0.74a$, with good correlation. The final result is

$$I(E_o) = c e^{-\epsilon_0} \left[ 1 + \frac{2a}{\sqrt{\pi}} \epsilon_0 \frac{1}{(bkT+1)^{3/2}} \frac{\epsilon_0}{(bkT+1)^m} \right]$$

with $a$, $\epsilon_0$, $f$, $I$, and $m$ having the values given above.

### b. Post-threshold

The convolution integral has the simple form

$$I(E_o) = c \left[ 1 - e^{-\epsilon_0/(bkT+1)^{3/2}} \right].$$

Thus, at $E_o = E_t$, the two functions join, with the common value

$$c \left[ 1 - (bkT+1)^{-3/2} \right].$$

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