J. Phys. Chem. A **2001,** *105,* 11041−11044

The Dissociation Energy of $OH(X^2\Pi_{3/2})$ and the Enthalpy of Formation of $OH(X^2\Pi_{3/2})$, ClOH, and BrOH from Thermochemical Cycles

Jeffrey A. Joens*

Department of Chemistry, Florida International University, Miami, Florida 33199

Received: May 14, 2001; In Final Form: September 13, 2001

Through the use of available experimental data and thermochemical cycles, improved values for the enthalpy of formation and dissociation energy of the hydroxyl radical have been found. The results of the analysis give $\Delta H^\circ_{0,f}[OH(X^2\Pi_{3/2})] = 37.14 \pm 0.12$ kJ/mol, $D_0[OH(X^2\Pi_{3/2})] = 35\,584 \pm 10$ cm^{-1}, and $D_0[OH(A^2\Sigma^+)] = 19\,011 \pm 10$ cm^{-1}. These results are consistent with those found from H_2O photoionization experiments but have a factor of 3 smaller uncertainty than the best results from the photoionization studies. The results disagree with the presently accepted values for these quantities, obtained from an analysis of spectroscopic data on the hydroxyl radical. Based on the new value for the enthalpy of formation of hydroxyl radical and additional experimental data, values for the enthalpy of formation have been found for ClOH ($\Delta H^\circ_{0,f} = -73.99 \pm 0.12$ kJ/mol) and BrOH ($\Delta H^\circ_{0,f} = -47.7 \pm 1.8$ kJ/mol).

Introduction

The hydroxyl radical plays a key role in both atmospheric chemistry and high-temperature combustion processes. Because of this, there have been numerous studies on the spectroscopic and thermodynamic properties of hydroxyl radical in both its ground and excited electronic states. Thermochemical data for the hydroxyl radical can also be used in conjunction with other experimental information to determine the enthalpy of formation of other molecules, such as ClOH and BrOH, that are important species in stratospheric ozone chemistry.

The currently accepted[1] value for the enthalpy of formation of hydroxyl radical, $\Delta H^\circ_{0,f}[OH(X^2\Pi_{3/2})] = 38.390 \pm 1.21$ kJ/mol, is based on the dissociation energy for hydroxyl radical reported by Barrow,[2] $D_0[OH(X^2\Pi_{3/2})] = 35\,427$ cm^{-1}, adjusted to a slightly higher value as discussed in refs 1 and 2. Carlone and Dalby,[3] who studied the $B^2\Sigma^+ \rightarrow A^2\Sigma^+$ and $C^2\Sigma^+ \rightarrow A^2\Sigma^+$ emission spectra of OH and OD at high resolution, combined their data with previous measurements by Barrow[2] to determine energies for vibrational levels in the $A^2\Sigma^+$ electronic state for $v = 0-9$ for OH and $v = 0-13$ for OD to within a few hundred wavenumbers of the dissociation energy. A short extrapolation of the Birge−Sponer plot of the data gives $D_0[OH(A^2\Sigma^+)] = 18\,847 \pm 15$ cm^{-1} and a dissociation limit of $51\,287.6 \pm 15$ cm^{-1} relative to the $v = 0$, $J = 3/2$ energy level of $OH(X^2\Pi_{3/2})$. Because $OH(A^2\Sigma^+)$ dissociates into $O(^1D) + H(^2S)$ and $OH(X^2\Pi_{3/2})$ dissociates into $O(^3P_2) + H(^2S)$, it follows that $D_0[OH(X^2\Pi_{3/2})]$ is smaller than the dissociation limit for the $A^2\Sigma^+$ state of hydroxyl radical by 15 867.9 cm^{-1}, the difference in energy between the ^1D and $^3P_2$ electronic states of the oxygen atom.[1] From this, one obtains $D_0[OH(X^2\Pi_{3/2})] = 35\,420 \pm 15$ cm^{-1}, in good agreement with the value given by Barrow. The enthalpy of formation for $OH(X^2\Pi_{3/2})$ can then be found from the relationship

$$\Delta H^\circ_{0,f}[OH(X^2\Pi_{3/2})] = \Delta H^\circ_{0,f}(H) + \Delta H^\circ_{0,f}(O) - D_0[OH(X^2\Pi_{3/2})] \quad (1)$$

The Birge−Sponer extrapolation performed by Carlone and Dalby is shorter than that carried out by Barrow and is therefore expected to have a smaller associated uncertainty, as is reflected in the value for the formation enthalpy of hydroxyl radical given by Gurvich and co-workers,[4] $\Delta H^\circ_{0,f}[OH(X^2\Pi_{3/2})] = 39.12 \pm 0.21$ kJ/mol. Further discussion of these various calculations of the formation enthalpy of hydroxyl radical and some anomalies in the results that are reported is given by Ruscic and co-workers.[5]

The enthalpy of formation of $OH(X^2\Pi_{3/2})$ can also be determined from measurements of the appearance energy of OH^+ formed from photoionization of H_2O. In this case, the dissociation energy of water is given by the expression[5]

$$D_0(H-OH) = AE_0(OH^+/H_2O) - IE[OH(X^2\Pi_{3/2})] \quad (2)$$

where $AE_0(OH^+/H_2O)$ is the appearance energy of OH^+ from H_2O and $IE[OH(X^2\Pi_{3/2})]$ is the ionization energy of hydroxyl radical. The enthalpy of formation of $OH(X^2\Pi_{3/2})$ is then found using

$$\Delta H^\circ_{0,f}[OH(X^2\Pi_{3/2})] = \Delta H^\circ_{0,f}(H_2O) + D_0(H-OH) - \Delta H^\circ_{0,f}(H) \quad (3)$$

The enthalpy of formation of $OH(X^2\Pi_{3/2})$ as determined by photoionization experiments is approximately 1.7 kJ/mol smaller than the value found using spectroscopic data.[6]

In a recent experiment, Ruscic and co-workers[5] remeasured $AE_0(OH^+/H_2O)$. The value that they obtained for the appearance energy of OH^+ is consistent with results previously reported by McCullough[7] and by Wiedmann and co-workers[8] but more accurate than the earlier measurements. Based on their photoionization experiments, Ruscic and co-workers found

---

* To whom correspondence should be addressed. Fax: 305/348-3772. E-mail: joensj@fiu.edu.

10.1021/jp011833u CCC: $20.00

TABLE 1: Summary of Thermodynamic Data[a]

substance	$\Delta H^\circ_{0,f}$ (kJ/mol)
Br	117.92 ± 0.06
Cl	119.621 ± 0.006
H	216.035 ± 0.006
O	246.79 ± 0.10
H_2O	-238.921 ± 0.042
H_2O_2	-129.808 ± 0.2[b]

[a] Values from ref 1 except as noted. [b] Error estimate calculated from the reported uncertainties in the enthalpy of vaporization and enthalpy of decomposition of H_2O_2 reported in ref 11.

$\Delta H^\circ_{0,f}[OH(X^2\Pi_{3/2})] = 36.94 \pm 0.38$ kJ/mol for the enthalpy of formation of hydroxyl radical, significantly smaller than the currently accepted value. If their result is correct, then $D_0[OH(X^2\Pi_{3/2})] = 35\,601 \pm 33$ cm^{-1} and $D_0[OH(A^2\Sigma^+)] = 19\,028 \pm 33$ cm^{-1}, approximately 180 cm^{-1} larger than the values reported by Carlone and Dalby. Ruscic and co-workers also carried out a CCSD(T)/aug-cc-pVnZ ab initio calculation on OH using MOLPRO, Gaussian 98, and ACES−II and found $D_0[OH(X^2\Pi_{3/2})] = 35\,532$ cm^{-1}, in good agreement with the result obtained from their photoionization experiments. A similar high-level calculation by Martin[9] gave $D_0[OH(X^2\Pi_{3/2})] = 35\,588$ cm^{-1}, which also supports a lower value for $\Delta H^\circ_{0,f}[OH(X^2\Pi_{3/2})]$ than the presently accepted value.

The purpose of the present paper is to use thermodynamic cycles for which accurate data are available to find the value for the dissociation energy and enthalpy of formation for the $X^2\Pi_{3/2}$ state of the hydroxyl radical. Results from two different cyclic processes agree within their mutual experimental error and support the values for the dissociation energy and enthalpy of formation for $OH(X^2\Pi_{3/2})$ obtained from the photoionization studies and molecular orbital calculations. However, the present results reduce the uncertainty in these values by a factor of 3 in comparison to the best results from the photoionization experiments. The improved value for the enthalpy of formation of hydroxyl radical and additional experimental data are used to obtain values for the enthalpy of formation for ClOH and BrOH with significantly smaller uncertainties than the currently accepted values.

Determination of D_0 for $OH(X^2\Pi_{3/2})$

To find the value for D_0 for $OH(X^2\Pi_{3/2})$ from a thermochemical cycle requires a set of processes for which accurate data are available for all steps except dissociation of hydroxyl radical. There are two cyclic processes for which such data can be found (note that all reactants and products are in the gas phase).

H_2O cycle		
	$H + OH \rightarrow H_2O$	$-D_0(H{-}OH)$
	$H_2O \rightarrow H_2 + {}^1/_2O_2$	$-\ \Delta H^\circ_{0,f}(H_2O)$
	${}^1/_2O_2 \rightarrow O$	$\Delta H^\circ_{0,f}(O)$
	$H_2 \rightarrow 2H$	$2\Delta H^\circ_{0,f}(H)$
net	$OH \rightarrow O + H$	$D_0[OH(X^2\Pi_{3/2})]$

Values for the enthalpy of formation for H, O, and H_2O are listed in Table 1 and taken from the most recent NIST-JANAF thermochemical tables.[1] A summary of H−OH bond dissociation energy measurements is given in Table 2. The H−OH bond dissociation energy can be obtained indirectly from measurements of the appearance energy of OH^+ in photoionization experiments[5,7,8] using eq 2. However, a direct measurement of the H−OH bond dissociation energy has recently been reported by Harich and co-workers[10] using the Rydberg tagging time-of-flight technique. Their result is in accord with but more accurate than the values found from the H_2O photoionization experiments. Therefore, the value for $D_0(H{-}OH)$ reported by Harich and co-workers is used in the calculation of the dissociation energy of the hydroxyl radical. Combining the data on the formation enthalpies of H, O, and H_2O with the value for $D_0(H{-}OH)$ from Harich and co-workers gives $D_0[OH(X^2\Pi_{3/2})] = 35\,579 \pm 11$ cm^{-1}, with the major contribution to the uncertainty due to uncertainty in the enthalpy of formation of the oxygen atom.

TABLE 2: Bond Dissociation Energies

bond	D_0 (cm^{-1})	reference
H−OH	$41\,117 \pm 63$	7[a]
	$41\,141 \pm 5$	10
	$41\,121 \pm 31$	5
HO−OH	$17\,051.8 \pm 3.4$	13
Cl−OH	$19\,288.8 \pm 0.6$	14
	$19\,290.3 \pm 0.6$	15
	$19\,000 \pm 1000$	16
Br−OH	$\leq 16\,946 \pm 150$	18
	$17\,225 \pm 350$	19

[a] As recalculated in ref 5.

H_2O_2 cycle		
	$2OH \rightarrow H_2O_2$	$-D_0(HO{-}OH)$
	$H_2O_2 \rightarrow H_2 + O_2$	$-\ \Delta H^\circ_{0,f}(H_2O_2)$
	$H_2 \rightarrow 2H$	$2\Delta H^\circ_{0,f}(H)$
	$O_2 \rightarrow 2O$	$2\Delta H^\circ_{0,f}(O)$
net	$2OH \rightarrow 2O + 2H$	$2D_0[OH(X^2\Pi_{3/2})]$

Values for the enthalpy of formation for H, O, and H_2O_2 are, as before, taken from the most recent NIST-JANAF thermochemical tables and given in Table 1. For H_2O_2, the uncertainty in the enthalpy of formation is calculated using the experimental uncertainties in the heat of vaporization (±0.13 kJ/mol) and heat of decomposition (±0.08 kJ/mol) reported in the original calorimetric measurements of Giguère and co-workers,[11] from which the formation enthalpy was found.[12] The HO−OH bond dissociation energy, $17\,051.8 \pm 3.4$ cm^{-1}, is taken from the infrared−optical double resonance measurements of Luo and co-workers.[13] Combining the data gives $D_0[OH(X^2\Pi_{3/2})] = 35\,589 \pm 12$ cm^{-1}. The main contributions to the uncertainty in this result are uncertainty in the enthalpy of formation of oxygen atom and of hydrogen peroxide.

The agreement in the value for $D_0[OH(X^2\Pi_{3/2})]$ found from the H_2O cycle and H_2O_2 cycle is excellent. Because the uncertainty in the thermodynamic data common to both cycles (the enthalpy of formation for hydrogen and oxygen atoms) is small, the above results are essentially independent determinations of the bond dissociation energy for the hydroxyl radical. Combining the results from the two cycles give $D_0[OH(X^2\Pi_{3/2})] = 35\,584 \pm 10$ cm^{-1}, $D_0[OH(A^2\Sigma^+)] = 19\,011 \pm 10$ cm^{-1}, and $\Delta H^\circ_{0,f}[OH(X^2\Pi_{3/2})] = 37.14 \pm 0.12$ kJ/mol. This is in agreement with the values found from the photoionization experiments but reduces the uncertainty in the values reported by Ruscic and co-workers by a factor of 3. This result indicates that the Birge−Sponer extrapolation used by Carlone and Dalby to obtain $D_0[OH(A^2\Sigma^+)]$ gives a value that is too low (by about 164 cm^{-1}), as has been previously suggested.[5]

$\Delta H^\circ_{0,f}$ for ClOH and BrOH

The value for the enthalpy of formation of hydroxyl radical found above can be combined with appropriate thermodynamic data to find improved values for the enthalpy of formation for other molecules important in atmospheric chemistry. As examples, we consider the following cyclic processes involving XOH, where X = Cl or Br (as before, all reactants and products are assumed to be in the gas phase except for $Br_2(l)$).

$$\begin{array}{lll}
\text{XOH cycle (X = Cl, Br)} & & \\
 & X + OH \rightarrow XOH & -D_0(X{-}OH) \\
 & {}^1/_2X_2 \rightarrow X & \Delta H^\circ_{0,f}(X) \\
 & {}^1/_2O_2 + {}^1/_2H_2 \rightarrow OH & \Delta H^\circ_{0,f}[OH(X^2\Pi_{3/2})] \\
\text{net} & {}^1/_2X_2 + {}^1/_2O_2 + {}^1/_2H_2 \rightarrow XOH & \Delta H^\circ_{0,f}(XOH)
\end{array}$$

Values for the enthalpy of formation for Br and Cl are taken from the most recent NIST-JANAF thermochemical tables and are listed in Table 1. The value used for $\Delta H^\circ_{0,f}[OH(X^2\Pi_{3/2})]$, 37.14 ± 0.12 kJ/mol, is that obtained as described above. Values for $D_0(X{-}OH)$ and the corresponding values for the enthalpy of formation of XOH are as follows.

ClOH. Barnes and co-workers[14] and Wedlock and co-workers[15] have independently determined $D_0(^{35}Cl{-}OH)$ from double resonance overtone spectroscopy experiments and have obtained values that differ by only 1.5 cm^{-1}. Fujiwara and Ishiwata[16] have also obtained a value for the Cl−OH bond dissociation energy using photofragment Doppler spectroscopy but with a much larger uncertainty than that observed in the double resonance experiments. These results are summarized in Table 2. The present calculations use the average of the results from Barnes and co-workers and Wedlock and co-workers, $D_0(^{35}Cl{-}OH) = 19\,289.6 \pm 1.5\ cm^{-1}$. Combining this result and the enthalpy of formation data gives $\Delta H^\circ_{0,f}(ClOH) = -73.99 \pm 0.12$ kJ/mol.[17]

BrOH. On the basis of the appearance energy for Br^+ in the photoionization of BrOH, Ruscic and Berkowitz[18] found $D_0(Br{-}OH) \leq 16\,946 \pm 150\ cm^{-1}$. On the basis of the process involved in the dissociative ionization, they believe that the actual value for the Br−OH bond dissociation energy is close to the upper limit found in their experiment. In a study of the near threshold photodissociation dynamics of BrOH, Lock and co-workers[19] found $D_0(Br{-}OH) = 17\,225 \pm 350\ cm^{-1}$, slightly larger than the upper limit reported by Ruscic and Berkowitz. The present calculation assumes that the value for $D_0(Br{-}OH)$ is equal to the upper limit reported by Ruscic and Berkowitz, which we believe is the more accurate method for determination of the dissociation energy. Combining this value with the appropriate formation enthalpies gives $\Delta H^\circ_{0,f}(BrOH) = -47.7 \pm 1.8$ kJ/mol.

Discussion

The value for the enthalpy of formation for OH($X^2\Pi_{3/2}$) obtained from the H_2O and H_2O_2 thermochemical cycles is consistent with that found from H_2O photoionization experiments but with a factor of 3 smaller uncertainty than the result recently reported by Ruscic and co-workers.[5] It follows from this that the value for $D_0[OH(A^2\Sigma^+)]$ found by Carlone and Dalby from a Birge−Sponer analysis of vibrational data for this electronic state is approximately 160 cm^{-1} smaller than the actual dissociation energy for this state. It is interesting to note that Carlone and Dalby, in a Birge−Sponer analysis of vibrational data for the $B^2\Sigma^+$ state of the hydroxyl radical, found a dissociation limit that was 110 cm^{-1} larger than that predicted on the basis of the dissociation limit for the $A^2\Sigma^+$ state, a difference that they attributed to a barrier in the potential energy curve for the $B^2\Sigma^+$ state.[3] The present results indicate that this barrier does not in fact exist.

TABLE 3: $\Delta H^\circ_{0,f}$ for ClOH[a]

$\Delta H^\circ_{0,f}$ (kJ/mol)	reference
∼ −72	20[b,c]
−71.5 ± 2.1	21[b,c]
−71.5 ± 2.5	22[b,c]
−71.5 ± 3.8	23[b,c]
−72.8 ± 3.8	23[c,d]
−73.0	24[c,e]
−71.8 ± 1.2	25[e]
−73.99 ± 0.12	present result

[a] Based on experimental measurements, except as noted. [b] Found using $\Delta H^\circ_{298,f}(Cl_2O) = 81.42 \pm 1.7$ kJ/mol, as discussed in ref 1. [c] Adjusted to 0 K using $\Delta H^\circ_{0,f}(ClOH) - \Delta H^\circ_{298,f}(ClOH) = 2.9$ kJ/mol.[1] [d] Based on kinetic data for the Cl + ClOH ↔ Cl_2 + OH reaction and recalculated as discussed in the text. [e] Obtained from molecular orbital calculations.

TABLE 4: $\Delta H^\circ_{0,f}$ for BrOH[a]

$\Delta H^\circ_{0,f}$ (kJ/mol)	reference
∼ −69	26[c]
−49.1 ± 6.7	27[b,c]
−27	28[b,c]
−48.0	24[c,d]
−45.9 ± 4.1	25[d]
−45.7 ± 1.8	18
−49.5 ± 4.	19
−49.9 ± 2.	29[c]
−47.7 ± 1.8	present result

[a] Based on experimental measurements, except as noted. [b] Obtained from a combination of molecular orbital calculations and experimental data. [c] Adjusted to 0 K using $\Delta H^\circ_{0,f}(BrOH) - \Delta H^\circ_{298,f}(BrOH) = 10.5$ kJ/mol.[27] [d] Obtained from molecular orbital calculations.

Molina and Molina,[20] Knauth and co-workers,[21] Niki and co-workers,[22] and Ennis and Birks[23] have reported values for the enthalpy of formation of ClOH based on measurements of the equilibrium constant for the reaction

$$Cl_2O + H_2O \leftrightarrow 2\,ClOH \tag{4}$$

The results (adjusted to 0 K) are summarized in Table 3. The recommended value given in the NIST-JANAF table,[1] $\Delta H^\circ_{0,f}(ClOH) = -71.5 \pm 2.1$ kJ/mol, is based on a reanalysis of the data from Knauth and co-workers. The results obtained from a reanalysis of the other experiments discussed above differ only slightly from the NIST-JANAF value.

Ennis and Birks also report a value for the enthalpy of formation of ClOH based on room-temperature measurements of the forward and reverse rate constant for the reaction Cl + ClOH ↔ Cl_2 + OH. Their calculation of the enthalpy of formation of ClOH from these data uses the NIST-JANAF value for the enthalpy of formation of hydroxyl radical to determine $\Delta H^\circ_{0,f}(ClOH)$. If the value for $\Delta H^\circ_{0,f}[OH(X^2\Pi_{3/2})]$ from the present study is used instead, the enthalpy of formation of ClOH, adjusted to 0 K, is $\Delta H^\circ_{0,f}(ClOH) = -72.8 \pm 3.8$ kJ/mol. The value for $\Delta H^\circ_{0,f}(ClOH)$ has also been calculated by Glukhovtsev and co-workers[24] at the G2 level and by Hassanzadeh and Irikura[25] using the ACES-II program suite and several different reaction schemes.

The value for $\Delta H^\circ_{0,f}(ClOH)$ found in the present work is larger in magnitude than the results obtained from studies of the equilibrium constant for reaction 4 and from the molecular orbital calculations of Hassanzadeh and Irikura. The present result is in better agreement (although still slightly larger in magnitude) with the values found from the rate constant measurements of Ennis and Birks and the molecular orbital calculations of Glukhovsev and co-workers.

Previous determinations of $\Delta H^\circ_{0,f}(BrOH)$ have used a variety of methods and are summarized in Table 4. Benson[26] estimated $\Delta H^\circ_{0,f}(BrOH) \cong -69.$ kJ/mol on the basis of consideration of the thermodynamics of several reactions involving Br_2. McGrath and Rowland[27] found $\Delta H^\circ_{0,f}$(BrOH) $= -49.1 \pm 6.7$ kJ/mol on the basis of a G2 calculation for molecular energies supplemented with empirical data. Monks and co-workers,[28] using measurements of the photoionization yield spectrum of BrOH, MCSCF calculation on the $BrOH^+$ cation, and the calculated proton affinity of BrO, reported $\Delta H^\circ_{0,f}$(BrOH) $= -27$ kJ/mol. Theoretical values for $\Delta H^\circ_{0,f}$(BrOH) have been obtained by Glukhovtsev and co-workers[24] and by Hassanzadeh and Irikura[25] by the same methods used in calculating $\Delta H^\circ_{0,f}$(ClOH), as described above. Ruscic and Berkowitz[18] found $\Delta H^\circ_{0,f}$(BrOH) $= -45.7 \pm 1.8$ kJ/mol from measurement of the appearance potential of Br^+ from BrOH, while Lock and co-workers,[19] on the basis of the near threshold photodissociation dynamics of BrOH, reported $\Delta H^\circ_{0,f}$(BrOH) $= -49.5 \pm 4.0$ kJ/mol. Finally, Kukui and co-workers[29] found $\Delta H^\circ_{0,f}$(BrOH) $= -49.9 \pm 2.0$ kJ/mol based on determinations of the forward and reverse rate constant for the reaction $BrOH + Cl \leftrightarrow OH + BrCl$. These latter three results are the only values for the enthalpy of formation for BrOH based entirely on experimentally derived data. Because the result obtained in the present paper uses the experimental appearance potential measured by Ruscic and Berkowitz to calculate $\Delta H^\circ_{0,f}$(BrOH), the difference between the present result and that reported by Ruscic and Berkowitz is due to the different value used for $\Delta H^\circ_{0,f}[OH(X^2\Pi_{3/2})]$ in the two calculations of the formation enthalpy. It should be noted that the values for $\Delta H^\circ_{0,f}$(BrOH) given by Lock and co-workers and by Kukui and co-workers also use the NIST-JANAF value for the enthalpy of formation for $OH(X^2\Pi_{3/2})$, so if either of these experimental values for D_0(BrOH) should turn out to be correct, the corresponding value for $\Delta H^\circ_{0,f}$(BrOH) should be changed accordingly.

Finally, we note that the values for the enthalpy of formation for OH, ClOH, and BrOH, reported here at 0 K, can be used to find the formation enthalpies for these molecules at temperatures of interest to atmospheric chemists using the information on $H^\circ(T) - H^\circ(T_r)$ reported in the NIST-JANAF tables[1] for OH and ClOH and by McGrath and Rowland[27] for BrOH, which are unaffected by the new values for $\Delta H^\circ_{0,f}$ found for these species.

Conclusions

Analysis of available experimental data for thermodynamic cycles involving H_2O and H_2O_2 makes it possible to find values for the dissociation energy and enthalpy of formation for $OH(X^2\Pi_{3/2})$. The currently accepted values for these quantities, obtained from an analysis of spectroscopic data, are shown to be systematically in error by approximately 2 kJ/mol. The current results indicate that the values obtained from photoionization studies on H_2O are correct but reduce the uncertainty relative to the photoionization results by a factor of 3. The new value for the enthalpy of formation of $OH(X^2\Pi_{3/2})$ is used to find values for the enthalpy of formation of ClOH and BrOH that improve upon presently accepted values.

Acknowledgment. The author thanks one of the referees for bringing to his attention two papers relevant to the present work.

References and Notes

(1) Chase, M. W., Jr. *NIST-JANAF Thermochemical Tables*, 4th ed.; Journal of Physical and Chemical Reference Data Monograph 9; American Chemical Society: Washington, DC, 1998.
(2) Barrow, R. F. *Ark. Fys.* **1956**, *11*, 281.
(3) Carlone, C.; Dalby, F. W. *Can. J. Phys.* **1969**, *47*, 1945.
(4) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B. *Thermodynamic Properties of Individual Substances*; Hemisphere: New York, 1989; Vol. 1.
(5) Ruscic, B.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Harding, L. B.; Asher, R. L.; Wagner, A. F. *J. Phys. Chem. A* **2001**, *105*, 1.
(6) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.
(7) McCulloh, K. E. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *21*, 333.
(8) Wiedmann, R. T.; Tonkyn, R. G.; White, M. G.; Wang, K. McKoy, V. *J. Chem. Phys.* **1992**, *97*, 768.
(9) Martin, J. M. L. *Spectrochim. Acta, Part A* **2001**, *57*, 875.
(10) Harich, S. A.; Hwang, D. W. H.; Yang, X.; Lin, J. J.; Yang, X.; Dixon, R. N. *J. Chem. Phys.* **2000**, *113*, 10073.
(11) Giguère, P. A.; Morissette, B. G.; Olmos, A. W.; Knop, O. *Can. J. Chem.* **1955**, *33*, 804.
(12) Giguère, P. A.; Liu, I. D. *J. Am. Chem. Soc.* **1955**, *77*, 6477.
(13) Luo, X.; Fleming, P. R.; Rizzo, T. R. *J. Chem. Phys.* **1992**, *96*, 5659.
(14) Barnes, R. J.; Dutton, G.; Sinha, A. *J. Phys. Chem. A* **1997**, *101*, 8374.
(15) Wedlock, M. R.; Jost, R.; Rizzo, T. R. *J. Chem. Phys.* **1997**, *107*, 10344.
(16) Fujiwara, H.; Ishiwata, T. *J. Phys. Chem. A* **1998**, *102*, 3856.
(17) The difference between $D_0(^{35}Cl{-}OH)$ and D_0(ClOH), the dissociation energy weighted for the observed natural abundance of ^{35}Cl and ^{37}Cl, is estimated to be about -0.01 kJ/mol. A correction for this difference has therefore not been applied.
(18) Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1994**, *101*, 7795.
(19) Lock, M.; Barnes, R. J.; Sinha, A. *J. Phys. Chem.* **1996**, *100*, 7972.
(20) Molina, L. T.; Molina, M. J. *J. Phys. Chem.* **1978**, *82*, 2410.
(21) Knauth, H.-D.; Alberti, H.; Clausen, H. *J. Phys. Chem.* **1979**, *83*, 1604.
(22) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *Chem. Phys. Lett.* **1979**, *66*, 325.
(23) Ennis, C. A.; Birks, J. W. *J. Phys. Chem.* **1985**, *89*, 186.
(24) Glukhovtsev, M. N.; Pross, A.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 3498.
(25) Hassanzadeh, P.; Irikura, K. K. *J. Phys. Chem. A* **1997**, *101*, 1580.
(26) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.
(27) McGrath, M. P.; Rowland, F. S. *J. Phys. Chem.* **1994**, *98*, 4773.
(28) Monks, P. S.; Stief, L. J.; Krauss, M.; Kuo, S. C.; Klemm, R. B. *J. Chem. Phys.* **1994**, *100*, 1902.
(29) Kukui, A.; Kirchner, U.; Benter, T.; Schindler, R. N. *Ber. Bunsen-Ges.* **1996**, *100*, 455.