Evidence for a Lower Enthalpy of Formation of Hydroxyl Radical and a Lower Gas-Phase Bond Dissociation Energy of Water

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There are two experimental approaches to determining $\Delta H^\circ_{f,0}(OH)$, which produce values of this key thermodynamic quantity that differ by $>0.5$ kcal/mol. The apparent uncertainty of the positive ion cycle approach resides in the measurement of the appearance energy of $OH^+$ from $H_2O$, while the uncertainty of the spectroscopic approach resides in the determination of the dissociation energy of $OH(A^2\Sigma^+)$. In this note we present an independent experimental determination of the appearance energy that confirms the accuracy and enhances the precision of the existing positive ion cycle value for $\Delta H^\circ_{f,0}(OH)$. We also present electronic structure calculations of the $OH(A^2\Sigma^+)$ potential energy curve, which suggest that the extrapolation method used to obtain the spectroscopic dissociation energy is in error. Finally, we present the largest ab initio electronic structure calculations ever performed for $\Delta H^\circ_{f,0}(OH)$ that have an apparent uncertainty much less than 0.5 kcal/mol and support only the positive ion cycle value. Although all major thermochemical tables recommend a value of $\Delta H^\circ_{f,0}(OH)$ based on the spectroscopic approach, the correct value is that of the positive ion cycle, $\Delta H^\circ_{f,0}(OH) = 8.83 \pm 0.09$ kcal/mol, $D_0(\text{H}^-\text{OH}) = 117.57 \pm 0.09$ kcal/mol, and $D_0(\text{OH}) = 101.79 \pm 0.09$ kcal/mol.

Introduction

The O–H bond dissociation energy of water, $D_0(\text{H}^-\text{OH})$, is of fundamental importance because of the ubiquity of the OH radical in environmental, industrial, and combustion processes. Its correct value, together with the corresponding enthalpy of formation of hydroxyl radical, $\Delta H^\circ_{f,0}(OH)$, are crucial constituents of any serious thermochemical table because the properties of many other species are measured with reference to this bond energy. Realistic models to describe the chemical behavior of complex systems, such as those common in atmospheric or combustion processes, contain hundreds of reactions, many of which are sensitive to minute inaccuracies in the enthalpies of formation of a key highly reactive species such as OH.

The comprehensive thermochemical table by Gurvich et al. gives the formation enthalpy of OH as $\Delta H^\circ_{f,0}(OH) = 9.35 \pm 0.05$ kcal/mol, from which the best available $D_0(\text{H}^-\text{OH})$ becomes $118.08 \pm 0.05$ kcal/mol [assuming the accepted values for $\Delta H^\circ_{f,0}(\text{H}_2\text{O})$ and $\Delta H^\circ_{f,0}(\text{H})$]. Gurvich et al. use $D_0(\text{OH}, \text{X}^2\Pi_{\text{gg}}) = 35420 \pm 15$ cm$^{-1}$ (101.27 $\pm 0.04$ kcal/mol) of Carlone and Dalby (see Table 1), which is based on a short extrapolation (~1.5 vibrational levels) of $\Delta G^\circ_{\text{v}+1/2}$ of the $A^2\Sigma^+$ state, yielding $D_0(\text{OH}, A^2\Sigma^+) = 18847 \pm 15$ cm$^{-1}$ to $\text{O}^1\text{D}_2$. 
To further substantiate their value, Carlone and Dalby measured $D_0$(OD, $A^2S^+$), producing a congruent $D_0$(OD), and forwarded as additional corroborative evidence the patterns of broadening of rotational lines in OH and OD, attributed to predissociation. Other more widely used thermochemical tables, such as JANAF\(^4\) or the NIST-JANAF Tables\(^7\) list $\Delta H^0_f$(OH) = 9.18 ± 0.29 kcal/mol\(^8\) (see Table 1) because they reference an earlier measurement of $D_0$(OH, $A^2S^+$) by Barrow\(^9\) that involves a longer and therefore more uncertain extrapolation than the subsequent and more accurate measurements of Carlone and Dalby.\(^6\) Inexplicably, JANAF\(^7\) and NIST-JANAF\(^7\) lower without reference\(^6\) the $\Delta H^0_f$(OH) = 9.26 ± 0.29 kcal/mol value implied by Barrow by 0.08 kcal/mol to arrive at the value quoted above.

In contrast to the recommended\(^2\) $D_0$(H−OH) implied by Gurvich et al.,\(^1\) the positive ion thermochemical cycle appears to suggest a significantly lower value, as noted by Berkowitz et al.\(^2\),\(^10\). This is surprising, since the positive ion cycle has a track record of yielding accurate and reliable experimental bond energies from photoionization and photoelectron measurements. In this case the cycle involves the 0 K appearance of the OH$^+$ fragment from water, $AE_0$(OH$^+$/H$_2$O), and the adiabatic ionization energy of OH, IE(OH), from which $D_0$(H−OH) = $AE_0$(OH$^+$/H$_2$O) − IE(OH). $AE_0$(OH$^+$/H$_2$O) was initially reported\(^11\) (without any correction for the internal energy) as a “sharp onset” at 18.05 eV. McCulloh\(^12\) subsequently performed a very detailed photoionization study, providing a value $AE_0$(OH$^+$/H$_2$O) = 18.115 ± 0.008 eV, which has not been challenged since. IE(OH) = 104989 ± 2 eV is known from a ZEKE study,\(^13\) which was preceded\(^14\)−\(^16\) and followed\(^17\) by other photoelectron studies giving 13.01 eV. Earlier photoionization values,\(^11\),\(^12\),\(^18\) which are lower, are really indirect, hinging, inter alia, on auxiliary thermochemical values, including $\Delta H^0_f$(OH). Recent photoionization studies of the OH radical\(^19\)−\(^21\) also suggest lower onsets, but that effect is attributed to rotational hot bands.\(^20\),\(^21\)

Taking the best available values,\(^12\),\(^13\) $AE_0$(OH$^+$/H$_2$O) = 18.115 ± 0.008 eV and IE(OH) = 13.0170 ± 0.0003 eV, results in $D_0$(H−OH) = 117.57 ± 0.18 kcal/mol, implying $\Delta H^0_f$(OH) = 8.83 ± 0.18 kcal/mol and $D_0$(OH) = 15600 ± 65 cm$^{-1}$ (101.79 ± 0.18 kcal/mol). This value of $\Delta H^0_f$(OH) is more than 0.5 kcal/mol lower than that of Gurvich et al.,\(^1\) and the difference is more than twice the sum of the error bars assigned to the two values.

Such a large difference between the two values implies that at least one of the following has to be true: (a) the spectroscopic $D_0$(OH, $A^2S^+$) is too low; (b) IE(OH) is too high; (c) $AE_0$(OH$^+$/H$_2$O) is too low.

### Studies of Hypothesis c

The basic photoionization apparatus used to remeasure $AE_0$(OH$^+$/H$_2$O) has been recently described elsewhere.\(^23\) Small Ne I emission lines superimposed on the He Hopfield continuum provided an accurate internal energy calibration. The light intensity was monitored by an external photomultiplier, coupled to a sodium salicylate transducer. $AE_0$(OH$^+$/H$_2$O) was extracted from fragment photoion yield curves by fitting with a model function employing a procedure described in detail elsewhere.\(^24\) The fit produces $AE_0$(OH$^+$/H$_2$O) = 18.115 ± 0.004 eV, in perfect agreement with the value of McCulloh.\(^12\) While the level of agreement is admittedly fortuitous, given the error bars, for hypothesis c to hold, the threshold in question would need to have other, more mysterious problems. However, presently it is not clear what those problems might be.

### Studies of Hypothesis a

The Birge−Sponer extrapolation used by Carlone and Dalby\(^6\) to obtain $D_0$(OH, $A^2S^+$) is notorious for inaccuracies, particularly when excited electronic states are used.\(^25\),\(^26\) However, the Carlone and Dalby extrapolation is extremely short and reproduces the expected isotope effect. To test this extrapolation, multifrequency single and double excitation (CAS+$1+1$ with Davidson correction) calculations\(^27\) were carried out on the OH($A^2S^+$) potential curve with an aug-cc-pV5Z basis set.\(^28\)
The computed dissociation energy is not expected to be accurate to more than ~0.5 kcal/mol, but the number of bound levels in both OH and OD is exactly the same (10 and 14, respectively) as that deduced by Carlone and Dalby. Applying the same Birge–Sponer extrapolation to the theoretical levels that are analogous to those directly measured by Carlone and Dalby produced an estimate of $D_0(\text{OH}, A^2\Sigma^+)$ for the theoretical curve that was 115 cm$^{-1}$ below that of the corresponding computed dissociation limit. This suggests that this hypothesis might well be correct.

**Direct Ab Initio Calculation of $\Delta H^0_{f0}(\text{OH})$**

To provide a completely independent determination of $\Delta H^0(\text{OH})$, CCSD(T)/aug-cc-pVnZ, ab initio electronic structure calculations were carried out for OH, $\text{OH}^+$, and $\text{H}_2\text{O}$. These calculations are by far the highest-level ab initio electronic structure calculations ever done for this system. The calculations were performed using MOLPRO, Gaussian 98, and ACESII. The geometries were optimized at the frozen core CCSD(T) level of theory. Frozen core energies were extrapolated to the complete basis set limit energies by using a mixed exponential/Gaussian expression from aug-cc-pVnZ. All major thermochemical tables recommend values for $\Delta H^0(\text{OH})$, $\Delta H^0(\text{H}_2\text{O})$, and $\Delta H^0(\text{OH}^+)$.

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Slight overlap with the upper limit of the computed value. In most comprehensive application leads to $D_0(\text{OH}) = 35420 \pm 15$ cm$^{-1}$ and hence $\Delta H^0_0(\text{OH}) = 9.35 \pm 0.05$ kcal/mol. Contrary to this, the positive ion cycle approach, which is based on photoionization and photoelectron measurements, leads to $\Delta H^0_0(\text{OH})$ that is lower by ~0.5 kcal/mol. In this study we have remeasured the key value entering the positive ion cycle, namely the appearance energy of OH$^+$ from $\text{H}_2\text{O}$, and obtained 18.115 ± 0.004 eV, in complete accord with the slightly less precise literature value. Together with the existing value for the ionization energy of OH, the new measurement produces $\Delta H^0_0(\text{OH}) = 8.83 \pm 0.09$ kcal/mol. We have used high quality electronic structure calculations to critique the method used experimentally to extract from the measured data the key property in the spectroscopic approach, namely the dissociation energy of $\text{OH}(A^2\Sigma^+)$. This critique indicates that the extrapolation is in error in a direction that supports the positive ion cycle value for $\Delta H^0_0(\text{OH})$. Finally, we present the highest level ab initio electronic calculations ever performed on this system to directly calculate $\Delta H^0_0(\text{OH})$ to an error much less than the difference between the two contending values. Only the positive ion cycle value falls within the error bar of the computed value, $\Delta H^0_0(\text{OH}) = 8.87 \pm 0.16$ kcal/mol. Thus, we believe that the best available experimental value is $\Delta H^0_0(\text{OH}) = 8.83 \pm 0.09$ kcal/mol, based on $D_0(\text{H}^-\text{OH}) = 41120 \pm 30$ cm$^{-1}$ (117.57 ± 0.09 kcal/mol) and implying $D_0(\text{OH}) = 35600 \pm 30$ cm$^{-1}$ (117.59 ± 0.09 kcal/mol). The corresponding 298 K values are $H_f^0(\text{OH}) = 8.89 \pm 0.09$ kcal/mol, $D_{298}(\text{H}^-\text{OH}) = 118.79 \pm 0.09$ kcal/mol, and $D_{298}(\text{OH}) = 102.77 \pm 0.09$ kcal/mol. A forthcoming paper will provide a more detailed account of the experimental and computational results mentioned here and their implications.

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**References and Notes**

8. A different value. $\Delta H^0_0(\text{OH}) = 9.26 \pm 0.29$ kcal/mol, which correctly results from the selected $D_0(\text{OH}) = 35450 \pm 100$ cm$^{-1}$ (following Barrow) is quoted explicitly in the discussion of
JANAF,\(^{3,7}\) together with the remark that it is "in good agreement with the last JANAF selection", namely \(\Delta H_\text{f}^0(\text{OH}) = 9.29 \pm 0.3\) kcal/mol from: Stull, D. R.; Prophet, H. JANAF Thermochemical Tables, 2nd ed.; NSRDS-NBS 37; U.S. Government Printing Office: Washington, DC, 1971. The latter value is also based on Barrow,\(^{9}\) but for some reason the adopted \(D_\text{OH}(\text{H})\) is 35440 \pm 100 cm\(^{-1}\). However, the actual table of thermochemical properties\(^{8}\) inexplicably lists and uses \(\Delta H_\text{f}^0(\text{OH}) = 9.17 \pm 0.29\) kcal/mol [which corresponds to \(D_\text{OH}(\text{H})\) = 35480 \pm 100 cm\(^{-1}\)].

(9) Barrow, R. F. Ark. Fys. 1956, 11, 281; extrapolated \(D_\text{OH}(\text{H})\) is actually 35427 cm\(^{-1}\), which was increased to 35450 \pm 100 cm\(^{-1}\) by the author to compensate for suspected underestimate.

(10) Berkowitz et al.\(^2\) list the discrepancy as a curiosity, commenting that "the precise reason [for this] is not known".


(33) Rittby, M.; Bartlett, R. J. J. Chem. Phys. 1988, 92, 3033. R(UCCSD(T)) is requested in MOLPRO by the keyword "UCCSD(T)" when combined with an ROHF wave function.

(34) The differences in the atomization energies between the CCSD(T)/aug-cc-pV6Z and the CCSD(T)/CBS(nmix) values for the atomization energies are 0.09 kcal/mol for OH and 0.16 kcal/mol for H₂O.
