

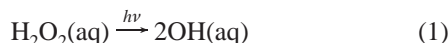
Thermochemistry of Aqueous Hydroxyl Radical from Advances in Photoacoustic Calorimetry and *ab Initio* Continuum Solvation Theory

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Here we report using photoacoustic calorimetry (PAC) to measure the reaction enthalpy and volume for dissociation of hydrogen peroxide, eq 1, ultimately obtaining the enthalpy of formation, $\Delta_f H^\circ$, and partial molal volume, v° , of OH(aq). This, we believe, is the first report of v° OH in solution.



Using v° , we estimate the hydration free energy of OH by novel application of continuum theory to obtain $\Delta_f G^\circ$ OH(aq). The results are in excellent agreement with values derived from other experimental approaches¹ and with recent theoretical predictions.² These results open the way to obtaining thermochemistry for radicals formed by reaction of OH with aqueous substrates. Such data will provide relevant benchmarks for developing theoretical methods.

The photoacoustic calorimetry (PAC) technique is based on the phenomenon that chemical reactions induced by absorption of a light pulse produce a measurable pressure pulse that is related to the enthalpy, reaction volume, and rate of the induced reaction.³ Often used to obtain C–H bond dissociation enthalpies in non-aqueous media,^{3,4} the use of time-resolved PAC for aqueous bond dissociation energies (DH°) is relatively unexplored.^{5a–c} The number of radicals for which there are aqueous thermochemical data is small by comparison to the gas-phase database, and even smaller for radical ions. This situation hinders mechanism elucidation and development of methods for predicting aqueous-phase radical reactions. Advances in PAC techniques, together with improved understanding of how to derive aqueous reaction enthalpy through analysis of the temperature dependence of time-resolved photoacoustic signals, make PAC particularly suitable for measurements of aqueous solutions.^{5–7}

We measured signals for photodissociation of H_2O_2 from 10 to 45 °C using light from a 266-nm pulsed laser. Equation 2 describes the dependence of the normalized signal, ϕ_1 ,

$$\phi_1 = 1 + \frac{\Phi}{E_\lambda} \left(-\Delta_r H_1 + \frac{\Delta_r V_1}{\chi_s} \right) \quad (2)$$

on reaction volume, $\Delta_r V_1$, and reaction enthalpy, $\Delta_r H_1$, for photodissociation of H_2O_2 , where Φ is the primary quantum yield for bond scission, E_λ is the molar energy of the excitation light with wavelength λ , and χ_s is the temperature-dependent solvent quality factor.⁸ Literature values⁹ for the quantum yield of HO–OH bond scission were used to define the dependence of Φ on temperature (see Supporting Information). Typically, we used 30 mM concentrations of H_2O_2 , for which the solution properties of water adequately describe χ_s .¹⁰ Even with this low concentration, the follow-up reaction of OH with H_2O_2 still contributes a small, but observable component, ϕ_2 , to the PAC signal. This second component was resolved from the raw PAC signal by deconvolution of the photoacoustic waveforms.¹¹ Figure 1 shows our data fit to

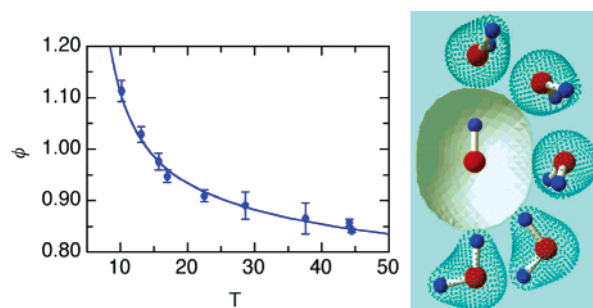


Figure 1. Temperature (°C) dependence of normalized PAC signal from dissociation of H_2O_2 with 266-nm pulsed light and fit to eq 2; OH in a cavity with shape defined by OH–water interactions. Points around waters are the $0.08 \text{ e}^-/\text{au}^3$ isocontour of an isolated water molecule.

eq 2 from which $\Delta_r H_1 = 46.8 \pm 1.4 \text{ kcal/mol}$ and $\Delta_r V_1 = 6.5 \pm 0.4 \text{ mL/mol}$. Given that $\Delta_f H^\circ \text{H}_2\text{O}_2(\text{aq})$ and $\Delta_f H^\circ \text{OH}(\text{g})$ are known,¹² our measurements provide $\Delta_f H^\circ \text{OH}(\text{aq}) = -0.2 \pm 1.4 \text{ kcal/mol}$ and $\Delta_s H^\circ = -9.1 \pm 1.5 \text{ kcal/mol}$ for hydration of OH. The former corresponds to the O–O bond being 2–5 kcal/mol weaker in water than in the gas phase, while the latter is comparable to the hydration enthalpy (-10.5 kcal/mol) of water.¹²

Before discussing further the effects of hydration, we interpret $\Delta_r V_1$. It equates to: $2v^\circ \text{OH} - v^\circ \text{H}_2\text{O}_2$ where v° is the partial molal volume. Given $v^\circ \text{H}_2\text{O}_2 = 22.2 \text{ mL/mol}$,^{10b} then $v^\circ \text{OH} = 14.4 \pm 0.4 \text{ mL/mol}$. The volume is smaller than v° for water (18.0 mL/mol). This is a unique result, as few neutral solutes have v° that even approach that of water,¹³ e.g., $v^\circ \text{H}_2$ is 26.7 mL/mol.^{13a} The v° of a solute may not be a direct measure of the cavity it occupies in solution, because the volume increase on addition of solute may be partially offset by a change in density of water surrounding the solute. However, in this case, Cabral do Couto et al.² compared simulations of OH-in-water and water-in-water and found the density of water surrounding OH is the same as that for water in water.

Knowing the volume that OH occupies in solution, we used theory to predict the hydration free energy of OH: specifically, the scaled particle theory¹⁴ and interaction potentials^{16a} for the cavity/dispersion/repulsion contribution to the free energy of solvation and an approximation^{15a} of the surface volume polarization for electrostatics formulation^{15b} of continuum solvation¹⁶ (see Supporting Information for description of the methods). A key tenet of our modeling is that solute cavities used in these theories should reflect the specific (hydrogen bond) solute–solvent interactions more faithfully than do the various standard empirical protocols for defining molecular-shaped cavities.¹⁷ Thus, we devised a novel *ab initio* cavity definition that captures the strength and specific interactions of the solute with a water solvent molecule. It involves “rolling a water molecule” over the solute molecule to define the trough of minimum energy in the solute–water interaction. A three-

dimensional electron density corresponding to a selected isodensity contour of an isolated water molecule is further attached to the rolling water solvent molecule in all of its positions in the trough. The cavity is then defined as the inside envelop of the "rolling density" (see Figure 1). The isodensity contour of the rolling density was selected to reproduce the experimental volume, $v^* = v^\circ - 1.1 \text{ mL/mol}$.^{14b,18} The cavity for OH, shown in Figure 1, is cylindrical with the continuum approaching most closely in the region above the OH where interaction with water is strongest.² The cavity created for OH in this manner gives $\Delta_s G^* = -3.9 \pm 0.3 \text{ kcal/mol}$.¹⁹ The same methodology applied to water in water gives $\Delta_s G^* = -6.5 \text{ kcal/mol}$. The experimental value is -6.32 .^{18b}

Given that $\Delta_f G^\circ$ of $\text{H}_2\text{O}_2(\text{aq})$ and $\text{OH}(\text{g})$ are known,¹² we obtain $\Delta_f G^\circ = 5.8 \pm 0.4 \text{ kcal/mol}$ for $\text{OH}(\text{aq})$ and $DG^\circ = 43$ for O–O scission of $\text{H}_2\text{O}_2(\text{aq})$, which may be compared to 41 kcal/mol for scission of $\text{H}_2\text{O}_2(\text{g})$. Thus, even though the HO–OH bond is weaker in water by 2–5 kcal/mol, scission is *less* favorable than in the gas phase due to less gain in entropy for the process in water. The effect is similar for scission of water in water. While DH° (HO–H) is the much the same in water as in the gas phase (119 kcal/mol), scission in water is less favorable by >4 kcal/mol. Here, entropy effects make hydration of H atom unfavorable and cause OH to be less favorably solvated than water in water. These observations illustrate that reactivities in solution, especially involving polarizable species, are better understood through free energy relationships, rather than enthalpy changes.

In conclusion, using the PAC technique and modern continuum solvation theory, we determined the effect of hydration on the homolytic bond scission of H_2O_2 . The results validate PAC for measuring the thermochemistry of free radicals in water. Furthermore, we introduce a new advanced approach to defining realistic solute cavities for ab initio continuum models of solvation. Extension of the work in these areas is in progress and will be reported subsequently.

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Supporting Information Available: Explanation of methods, data for Figure 1, and additional discussion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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