J. Phys. Chem. A **2002,** *106,* 11488−11491

Temperature Dependence of the Acid Dissociation Constant of the Hydroxyl Radical

G. A. Poskrebyshev,[†] P. Neta, and R. E. Huie*

Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8381

Received: January 24, 2002; In Final Form: August 20, 2002

The acid dissociation constant of the hydroxyl radical in aqueous solution was determined by pulse radiolysis from the $[OH^-]$ dependence of the rate constant for reaction of the $^\bullet OH/O^{\bullet -}$ radical with benzoate ions. The rate constant and the $pK_a(^\bullet OH)$ values were determined over the temperature range 284−343 K. At 298 K, $pK_{a\,298}(^\bullet OH) = 11.54 \pm 0.04$ and $\Delta_{ion}G°_{298}(^\bullet OH) = (65.9 \pm 0.3)$ kJ mol^{-1}. From the temperature dependence of $K_a(^\bullet OH)$, we calculate $\Delta_{ion}H°_{298}(^\bullet OH) = (24.85 \pm 0.5)$ kJ mol^{-1} and $\Delta_{ion}S°_{298}(^\bullet OH) = (-139 \pm 2)$ J mol^{-1} K^{-1}. The activation energy for the reaction of $^\bullet OH$ with $C_6H_5CO_2^-$ was found to be (8.8 ± 0.6) kJ mol^{-1} and the Arrhenius preexponential factor $(2.4 \pm 0.6) \times 10^{11}$ L mol^{-1} s^{-1}.

Introduction

The hydroxyl radical plays a critical role in chemistry. In the gas phase, it is the key reactive intermediate in both atmospheric and combustion systems. In the aqueous phase, it is central to radiation damage in physiological systems and to the functioning of advanced oxidation technologies. The $^\bullet OH$ radical is the simplest Brønsted-Lowry acid and dissociates rapidly ($k_2 = 1.2 \times 10^{10}$ L mol^{-1} s^{-1}, $k_{-2} = 9.6 \times 10^7$ s^{-1})[1] to generate the oxide radical anion.

$$^\bullet OH \leftrightarrows O^{\bullet -} + H^+;\ K_a \tag{1}$$

$$^\bullet OH + OH^- \leftrightarrows O^{\bullet -} + H_2O;\ K_b = K_a/K_w \tag{2}$$

The $\Delta_{ion}H_{298}(^\bullet OH)$ value for the acid dissociation of $^\bullet OH$ (reaction 1) is a fundamental thermodynamic value for one of the simplest acids and is the basis for many other thermodynamic values.

The $^\bullet OH$ radical is a strong oxidant, $E°(^\bullet OH/OH^-) = 1.90$ V (see Appendix) and $E°(^\bullet OH, H^+/H_2O) = 2.72$ V.[2−4] It reacts rapidly by electron transfer as well as by hydrogen abstraction and by addition to unsaturated bonds. The $O^{\bullet -}$ radical is a weaker oxidant and reacts with most compounds much more slowly than $^\bullet OH$.[5] Because of this difference in reactivity, the pK_a value at room temperature has been determined from the pH effect on the rate of reaction of $^\bullet OH/O^{\bullet -}$ with several ions (ferrocyanide,[6] thiocyanate,[7] and carbonate[8]). The temperature dependence of $pK_a(^\bullet OH)$ was determined from experiments with tetrahydroborate,[9] carbonate,[10] and ferrocyanide ions.[11] The latter two studies resulted in room temperature pK_a values in reasonable agreement with each other and somewhat higher than the earlier study.[9] There does appear to be divergence in the pK_a values at the lower temperatures, however.

Due to the considerable importance of the acid dissociation constant of the hydroxyl radical, this discrepancy should be resolved, preferably with a new reagent. Thus, we have carried out new kinetic measurements aimed at establishing this value, but utilizing the benzoate ion as the reactant. The rate constant for reaction of $^\bullet OH$ with benzoate is close to the diffusion-controlled limit whereas the rate constant for $O^{\bullet -}$ is at least 2 orders of magnitude lower.[5]

$$^\bullet OH + C_6H_5CO_2^- \rightarrow HOC_6H_5CO_2^{-\bullet} \tag{3}$$

$$O^{\bullet -} + C_6H_5CO_2^- \rightarrow {}^-OC_6H_5CO_2^{-\bullet} \quad (+\,H^+ \rightarrow HOC_6H_5CO_2^{-\bullet}) \tag{4}$$

In both cases, the reaction leads to the formation of the OH-adduct. The OH group of this adduct has $pK_a > 14$,[12] so that the $O^{\bullet -}$ adduct undergoes nearly complete protonation up to pH ∼14. The rate constant at each pH was determined from the slope of a linear plot of the rate of formation of the OH-adduct against the benzoate concentration. The present experiments with benzoate provide a simple system for the accurate determination of $pK_a(^\bullet OH)$ as a function of temperature.

Experimental Section[13]

Fresh solutions were prepared with analytical-grade $C_6H_5CO_2H$ (Aldrich), NaOH (50% solution, Fisher), and $Na_2B_4O_7$ (Aldrich) in water that had been purified with a Millipore Super-Q system. The $^\bullet OH$ radicals were generated by pulse irradiation of N_2O-saturated solutions.

$$H_2O \rightsquigarrow {}^\bullet OH,\ e_{aq}^-,\ {}^\bullet H,\ H^+,\ H_2O_2,\ H_2 \tag{5}$$

$$N_2O + e_{aq}^- + H_2O \rightarrow N_2 + {}^\bullet OH + OH^- \tag{6}$$

Electron pulses from a Varian linear accelerator, with a pulse duration of 0.15 μs, provided doses of ≈3 Gy to produce $^\bullet OH$ radicals at concentrations ≈2 μmol L^{-1}. The optical path length of the irradiation zone was 2 cm. The reactions of $^\bullet OH$ and $O^{\bullet -}$ with $C_6H_5CO_2^-$ were monitored by following the formation of the absorption of the OH-adduct at 330 nm.

The rate constants for reactions of $^\bullet OH$ and $O^{\bullet -}$ radicals with $C_6H_5CO_2^-$ were determined at different concentrations of $C_6H_5CO_2^-$ (from 5×10^{-5} mol L^{-1} to 8×10^{-4} mol L^{-1}). Measurements were carried out at pH values from 9 to 14 and

---

* Address correspondence to this author. E-mail: Robert.huie@nist.gov.

[†] On leave from the Institute of Energy Problems of Chemical Physics, Russian Academy of Sciences, Moscow 117829, Russia.

10.1021/jp020239x

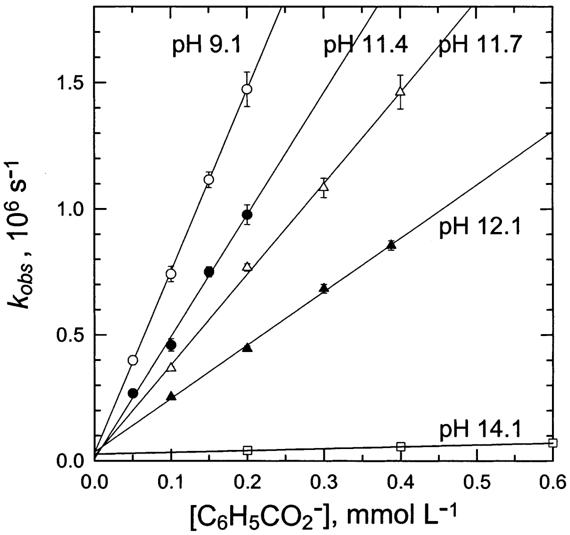

Figure 1. Rate constant (k_{obs}) for reaction of $^•OH/O^{•-}$ radicals with benzoate ions as a function of benzoate concentration at different pH values ($T = 298$ K). Determined by pulse radiolysis of N_2O-saturated aqueous solutions by following the buildup of absorption of the OH-adduct at 330 nm.

at temperatures from 284 to 343 K. The solutions were prepared by dilution of a 50% NaOH solution in order to minimize the effect of dissolved CO_2. For $[OH^-] < 10^{-2}$ mol L^{-1}, the concentration of OH^- was verified by measuring the pH with a glass electrode at room temperature (294 K). The pH meter was calibrated for the range from pH 7 to pH 10 using standard buffer solutions. The reliability of the calibration of the meter for pH values higher than 10 was checked using solutions of sodium hydroxide with concentrations ranging from 10^{-4} to 10^{-2} mol L^{-1}. The concentration of H^+ was assumed to be equal to the activity of the proton in solution up to pH 12. The activity coefficients of H^+ are 0.964, 0.935, and 0.915 at ionic strengths 10^{-4}, 10^{-3}, and 10^{-2} mol L^{-1}, respectively.[14] Good agreement between the measured pH values and values calculated from the concentration of NaOH in solution was found.

In these kinetic measurements, there is a very small effect of $H^•$ atoms. The total yield of $H^•$ is only about 10% of the total yield of $^•OH$ radicals and becomes even lower in highly alkaline solutions (due to reaction with OH^- to form e_{aq}^-). $H^•$ atoms react with benzoate about 7 times more slowly ($k = (8.5$ or $13) \times 10^8$ L mol^{-1} s^{-1})[5] than $^•OH$ radicals and produce adducts which absorb in the same wavelength range. Therefore, the effect of $H^•$ atoms is expressed as a small increase in absorption following the major increase due to $^•OH$ radicals, and the two processes can be easily separated.

Signal averaging was used to improve the signal-to-noise ratio. Each kinetic trace was an average from 16 pulses, each with a new aliquot of the solution, and the averaging was repeated at least 5 times with each solution. First-order kinetic fits were used to derive k_{obs}. The values of k_{obs} were determined with at least four solutions at different benzoate concentrations, and the second-order rate constants (k_{exp}) were derived from the slopes of the linear plots ($k_{obs} = k_{exp}[C_6H_5CO_2^-] + k_0$) such as those shown in Figure 1. The rate constants are reported with their estimated overall standard uncertainties corresponding to one standard deviation. The value of k_{exp} was then determined at several pH values between 9 and 14, and the whole set of experiments was repeated at various temperatures.

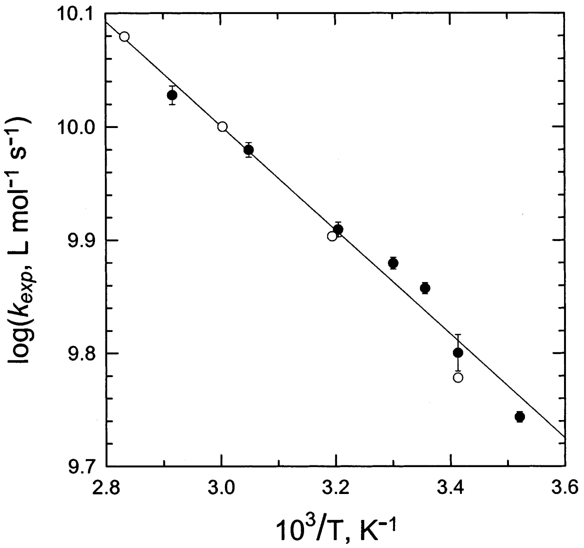

Figure 2. Arrhenius plot for the reaction of $^•OH$ (k_3) with benzoate ions. The values of k_3 were determined at pH 9.1 from linear plots such as those shown in Figure 1. The plot includes the present results (●) and those from ref 15 (○).

TABLE 1: Second-Order Rate Constants for the Reaction of $^•OH$ with Benzoate (pH 9.1)

temperature, K	k_3, L $mol^{-1}s^{-1}$
284	$(5.54 \pm 0.06) \times 10^9$
293	$(6.31 \pm 0.23) \times 10^9$
298	$(7.2 \pm 0.08) \times 10^9$
303	$(7.57 \pm 0.09) \times 10^9$
312	$(8.11 \pm 0.12) \times 10^9$
328	$(9.54 \pm 0.14) \times 10^9$
343	$(1.07 \pm 0.02) \times 10^{10}$

Results and Discussion

The second-order rate constant for reaction of the hydroxyl radical with benzoate ions (k_{exp}) will change with pH due to the varying contributions of reactions 3 and 4. The dependence can be described by

$$k_{exp} = (k_3[H^+] + k_4K_a)/([H^+] + K_a) = (k_3 + k_4K_b[OH^-])/(1 + K_b[OH^-]) \quad (7)$$

where K_a is the ionic dissociation constant of the $^•OH$ radical. Since $k_3 \gg k_4$, only k_3 is important in determining K_a and K_b, although we have determined both rate constants in this work.

The rate constants for the reaction of $^•OH$ with benzoate, k_3, were measured at pH 9.1 where benzoic acid is fully ionized to benzoate ions but where the extent of ionization of the $^•OH$ radical is very low. The pH was maintained by 2 mmol L^{-1} $Na_2B_4O_7$. Second-order rate constants were determined at seven temperatures between 284 and 343 K from the slope of the first-order formation rate constant as a function of the benzoate concentration (Figure 1). These values are listed in Table 1 and shown by the Arrhenius plot in Figure 2. The plot also shows good agreement between the present results (solid circles) and the previous data[15] (open circles) over the range of temperatures from 284 up to 343 K. This plot gives a linear fit (correlation coefficient $r^2 = 0.978$) of log k vs $1/T$, and results in an activation energy of $E_3 = (8.8 \pm 0.6)$ kJ mol^{-1} and a preexponential factor of $A_3 = (2.4 \pm 0.6) \times 10^{11}$ L mol^{-1} s^{-1}, where the uncertainties are the standard errors from the least-squares fit. In the previous study,[15] measured rate constants were essentially constant at 353 K and above, which was interpreted

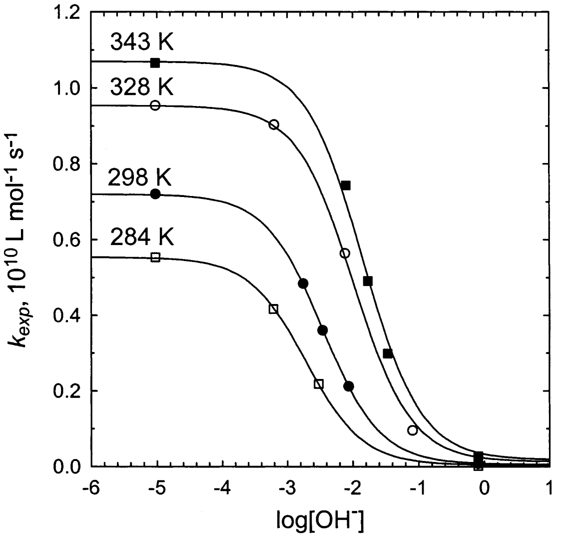

Figure 3. Second-order rate constant (k_{exp}) for the reaction of $^{\bullet}$OH/O$^{\bullet-}$ radicals with benzoate ions as a function of [OH$^-$]. The experimental points were determined from linear plots such as those shown in Figure 1.

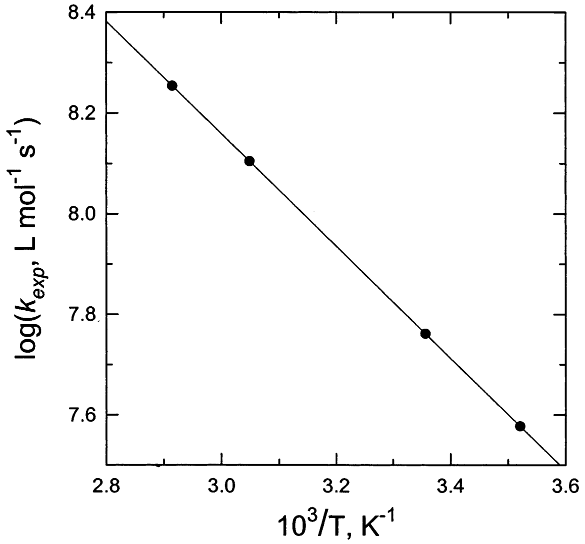

Figure 4. Arrhenius plot for the reaction of O$^{\bullet-}$ (k_4) with benzoate ions. The values of k_4 were derived from the experimental measurements at pH 14.1, which were corrected for the ionic strength dependence of K_a (see text).

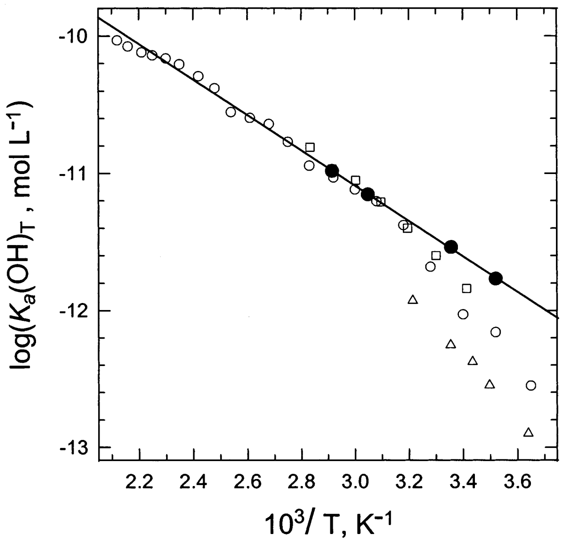

Figure 5. van't Hoff plots of the dissociation constant of the $^{\bullet}$OH radical, showing the values of K_a determined in the present study (●) and those reported in ref 9 (△), ref 10 (○), and ref 11 (□).

as due to the dissociation of the initial adduct in competition with its rearrangement to the observed product.

The values for K_b and approximate values of the rate constant for the reaction of O$^{\bullet-}$ with benzoate, k_4, were determined by measuring the second-order rate constant for the reaction of $^{\bullet}$OH/O$^{\bullet-}$ with benzoate as a function of the hydroxide ion concentration, [OH$^-$]. (The values estimated for k_4 depend strongly on K_b, but not vice versa.) Figure 3 shows plots of the second-order rate constant for the formation of the hydroxyl–benzoate adduct as a function of log [OH$^-$] at T = 284, 298, 328, and 343 K. The statistical uncertainty limits in the values are within the symbols shown. From nonlinear least-squares fits to these data, we obtain the values of K_b and k_4 given in Table 2. The solid curves were calculated by least-squares fits. The values of K_b (Table 2) derived from these plots were multiplied by the values of K_w at the corresponding temperatures[16] to derive K_a (eq 2).

Since $k_3 \gg k_4$, the value measured for k_4 at pH 14.1 contains a significant contribution from k_3. This contribution can be calculated from k_3 and K_a. This correction should take into account the change in the value of K_a at an ionic strength of 1.25 mol L^{-1} compared to the region of 0.01 mol L^{-1}, where it was experimentally measured. We use the activity coefficients of H$^+$ and OH$^-$ (0.734 and 0.604; $\gamma_H\gamma_{OH} = 0.443$, calculated at $\mu = 1$ mol L^{-1} at 298 K) and assume that the activity coefficient of $^{\bullet}$OH does not depend on μ and that the activity coefficient of O$^{\bullet-}$ is close to that of OH$^-$. From the corrected values of K_a, we estimate the corrected values for k_4 listed in Table 2 and presented in Arrhenius form in Figure 4. This plot shows a linear fit of log k_4 vs 1/T, and results in an activation energy of $E_4 = (10.8 \pm 1)$ kJ mol^{-1} and a preexponential factor of $A_4 = (3.3 \pm 2) \times 10^{11}$ L mol^{-1} s^{-1}, where the uncertainties are the standard errors from the least-squares fit.

The logarithm of the acid dissociation constant for the hydroxyl radical is plotted against the reciprocal of the temperature in Figure 5. Our results are presented as the solid circles, and the line is a fit to these data. The slope and intercept correspond to the values $\Delta_{ion}H°_{298}(^{\bullet}\text{OH}) = (24.85 \pm 0.5)$ kJ mol^{-1} and $\Delta_{ion}S°_{298}(^{\bullet}\text{OH}) = (-139 \pm 2)$ J mol^{-1} K^{-1}. The

TABLE 2: Rate Constants and Equilibrium Constants at Different Temperatures

temp, K	K_b, mol L^{-1}	K_w, mol^2 L^{-2}	K_a, mol L^{-1}	k_3, L mol^{-1} s^{-1}	k_4(corr)^a, L mol^{-1} s^{-1}
284	525.7	3.24×10^{-15}	1.7×10^{-12}	5.54×10^{9}	3.8×10^{7}
298	286.3	1.01×10^{-14}	2.9×10^{-12}	7.2×10^{9}	$5.8 \times 10^{7\,b}$
328	96.0	7.30×10^{-14}	7.0×10^{-12}	9.54×10^{9}	1.3×10^{8}
343	68.5	1.52×10^{-13}	10.4×10^{-12}	1.07×10^{10}	1.8×10^{8}

[a] Corrected with K_a adjusted to $\mu = 1.25$ using $\gamma(^{\bullet}\text{O}^-) = \gamma(\text{OH}^-)$. [b] A correction to k_4 at 298 K assuming no ionic strength dependence of K_a gives $k_4 = 4.6 \times 10^7$ L mol^{-1} s^{-1}, and a correction with a simple Debye–Huckel dependence ($\log(\gamma_H\gamma_O) = -\mu^{0.5}$) gives 6.9×10^7 L mol^{-1} s^{-1}.

results from the study involving the use of tetrahydroborate[9] are presented as open triangles; those from the carbonate study[10] are presented as open circles; and the results from the ferrocyanide study[11] are presented as open squares. The results are all in quite good agreement above room temperature, but at this temperature and below they diverge considerably. Although we cannot definitely state the causes of this divergence, we note that the tetrahydroborate study was carried out over a limited range of conditions, with a relatively unstable compound, and partly relied on small intercept values. The carbonate study was carried out over a wide range of conditions, but this system includes additional uncertainties due to the fact that $^{\bullet}$OH reacts with bicarbonate much more slowly than with carbonate and that the pK_a value of HCO_3^-/CO_3^{2-} (=10.3) is close to that expected for $^{\bullet}$OH. The ferrocyanide study was also carried out by measuring the rate constant for reaction of $^{\bullet}OH/O^{\bullet-}$ with ferrocyanide ions as a function of pH and temperature. These results lie between the present results and those of the carbonate study.

The results from the carbonate study[10] were taken over the widest temperature range of any of these investigations. These results showed clear curvature in the plot of log K_a vs $1/T$. A linear relationship was found, however, when the results were plotted for K_b $(=K_a/K_w)$. The present results, however, suggest that there is a linear relationship between log K_a and $1/T$ and that the apparent curvature results from underestimation of K_a at lower temperatures. Additional studies to confirm this conclusion are certainly warranted.

From our result for the dissociation constant at 298 K, $pK_{a\,298}(^{\bullet}OH) = 11.54 \pm 0.04$, we calculate $\Delta_{ion}G°_{298}(^{\bullet}OH) = (65.9 \pm 0.3)$ kJ mol^{-1}. Then, by using the value of $\Delta_f G°_{298}(^{\bullet}OH)_{aq} = (26 \pm 3)$ kJ mol^{-1} (see Appendix), we calculate $\Delta_f G°_{298}(O^{\bullet-})_{aq} = 65.9 + 26 = (92 \pm 3)$ kJ mol^{-1}. With the present value of the enthalpy of ionization of $^{\bullet}$OH and an estimate of the enthalpy of solvation of $O^{\bullet-}$, we can derive estimates of the enthalpies of formation of $O^{\bullet-}$ and $^{\bullet}$OH. First, we calculate $\Delta_{solv}H°_{298}(F^-) = -332.63 - (-255.148) = -77.48$ kJ mol^{-1} and $\Delta_{solv}H°_{298}(OH^-) = -229.994 - (-143.85) = -86.14$ kJ mol^{-1} (where the first value in each case is $\Delta_f H°_{298}$ for the aqueous phase[17] and the second value is $\Delta_f H°_{298}$ for the gas phase[18]). We then take the average value as the enthalpy of solvation of $O^{\bullet-}$, $\Delta_{solv}H°_{298}(O^{\bullet-}) = -80$ kJ mol^{-1}. By taking $\Delta_f H°_{298}(O^{\bullet-})_g = 101.629$ kJ mol^{-1} [18], we calculate $\Delta_f H°_{298}(O^{\bullet-})_{aq} = 22$ kJ mol^{-1}. Since from this work $\Delta_{ion}H°_{298}(^{\bullet}OH) = (24.85 \pm 0.5)$ kJ mol^{-1}, we obtain $\Delta_f H°_{298}(^{\bullet}OH)_{aq} = -3$ kJ mol^{-1}, in good agreement with previous estimates of -4 kJ mol^{-1} [19] and -7 kJ mol^{-1}.[20]

Appendix

To calculate the value of $\Delta_f G°(O^{\bullet-})$ from $\Delta_{ion}G°(^{\bullet}OH)$, we need the value of $\Delta_f G°(^{\bullet}OH)$. Two experimental values of $\Delta_f G°(^{\bullet}OH)$ are available in the literature, 25.1[2] and 26.8[3] kJ mol^{-1}, corresponding to $E(^{\bullet}OH/OH^-) = 1.89$ and 1.91 V, respectively. The former value was measured from equilibrium between $^{\bullet}$OH radicals and thallium ions using the values of $E(Tl^+/Tl^{2+}) = (2.20-2.22)$ V reported earlier.[2] The second value of $E(^{\bullet}OH/OH^-) = 1.91$ V was calculated[3] from $pK_a(^{\bullet}OH)$ and the forward and reverse rate constants of the equilibrium reactions 8 and 9.

$$ClO_2^- + O_3 \leftrightarrows ClO_2^{\bullet} + O_3^{\bullet-} \tag{8}$$

$$O_3^{\bullet-} \leftrightarrows O_2 + O^{\bullet-} \tag{9}$$

The values of k_8 and k_{-8} were measured by the authors,[3] the value of $pK_a(^{\bullet}OH) = 11.9$ was taken from ref 6, and the values of k_9 and k_{-9} were taken from earlier reports.[5,21] If we replace the values of k_9 and k_{-9} used by these authors[3] with more recent measurements[11] that appear to be more reliable, we can recalculate $E(^{\bullet}OH/OH^-) = (1.92 \pm 0.01)$ V. If then we replace the old value of $pK_a^{298}(^{\bullet}OH) = 11.9$ used by the authors[3] with a value of 11.54 from the present study, we calculate $E°(^{\bullet}OH/OH^-) = (1.94 \pm 0.01)$ V. In addition, the molar absorption coefficients of O_3 and $O_3^{\bullet-}$ used by the authors[3] are 40% lower and 15% higher, respectively, than those reported by other authors,[22] and this difference can lead to an increase in the value derived for k_{-8} (from 1.8×10^5 L mol^{-1} s^{-1} to 2.9×10^5 L mol^{-1} s^{-1}). This will decrease the value calculated for $E(^{\bullet}OH/OH^-)$ by ≈0.01 V. Moreover, the measurements of eq 8 were carried out at room temperature, (22 ± 1)°C, and an increase of the temperature to 25 °C probably will lead to a decrease in the values of K_8 and $\Delta_f G°(^{\bullet}OH)$.[23] Thus, the value for $E(^{\bullet}OH/OH^-)$ derived from these complex equilibria has a much larger uncertainty than that derived[2] from direct equilibration with Tl^+/Tl^{2+}. Therefore, despite our recalculations, which show a higher value for $E(^{\bullet}OH/OH^-)$ based on the results of ref 3, we consider the average value of $E(^{\bullet}OH/OH^-) = 1.90$ V recommended by Stanbury[4] as the best available choice, with an uncertainty of ±0.03 V. Thus, $\Delta_f G°_{298}(^{\bullet}OH)_{aq} = (26 \pm 3)$ kJ mol^{-1}.

References and Notes

(1) Buxton, G. V. *Trans. Faraday Soc.* **1970**, *66*, 1656; Zehavi, D.; Rabani, J. *J. Phys. Chem.* **1971**, *75*, 1738.

(2) Schwarz, H. A.; Dodson, R. W. *J. Phys. Chem.* **1984**, *88*, 3643.

(3) Klaning, U. K.; Sehested, K.; Holcman, J. *J. Phys. Chem.* **1985**, *89*, 760.

(4) Stanbury, D. M. *Adv. Inorg. Chem.* **1989**, *33*, 69.

(5) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.

(6) Rabani, J.; Matheson, M. S. *J. Am. Chem. Soc.* **1964**, *86*, 3175; *J. Phys. Chem.* **1966**, *70*, 761.

(7) Adams, G. E.; Boag, J. W.; Currant, J.; Michael, B. D. In *Pulse Radiolysis*; Ebert, M., Keene, J. P., Swallow, A. J., Baxendale, J. H., Eds.; Academic Press: New York, 1965; p 117.

(8) Weeks, J. L.; Rabani, J. *J. Phys. Chem.* **1966**, *70*, 2100.

(9) Baxendale, J. H.; Ward, M. D.; Wardman, P. *Trans. Faraday Soc.* **1971**, *67*, 2532.

(10) Buxton, G. V.; Wood, N. D.; Dyster, S. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 1113.

(11) Elliot, A. J.; McCracken, D. R. *Radiat. Phys. Chem.* **1989**, *33*, 69.

(12) Taniguchi, H.; Schuler, R. H. *J. Phys. Chem.* **1985**, *89*, 335 and 3095.

(13) The mention of commercial equipment or material does not imply endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified are necessarily the best available for the purpose.

(14) *pH Measurements*; Westcott, C. C., Ed.; Academic Press: London, 1978.

(15) Ashton, L.; Buxton, G. V.; Stuart, C. R. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1631.

(16) *Handbook of Chemistry and Physics*, 67th ed.; CRC: Boca Raton, FL, 1986; p D-164. Bignold, G. J.; Brewer, A. D.; Hearn, B. *Trans. Faraday Soc.* **1971**, *67*, 2419.

(17) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11, Suppl. 2*.

(18) *Thermodynamic Properties of Individual Substances*, Fourth ed.; Gurvich, L. V., Veyts, I. V., Alcock, C. B., Eds.; Hemisphere Publishing: Bristol, PA, 1989; Vol. 1.

(19) Schwarz, H. A. *J. Chem. Educ.* **1981**, *58*, 101.

(20) Benson, S. W.; Nangia, P. *J. Am. Chem. Soc.* **1980**, *102*, 2843.

(21) Gall, B. L.; Dorfman, L. M. *J. Am. Chem. Soc.* **1969**, *91*, 2199.

(22) Bühler R. E. *J. Phys. Chem.* **1984**, *88*, 2560.

(23) From the recalculated value of K_9 and $E(ClO_2/ClO_2^-) = 0.934$ V, we estimate $E(O_3/O_3^-) = 1.00$ V.