Standard Glbbs Energy of Formation of the Hydroxyl Radical in Aqueous Solution. Rate Constants for the Reaction $ClO_2^- + O_3 \rightleftharpoons O_3^- + ClO_2$

U. K. Kläning,*

Chemistry Department, University of Aarhus, Langelandsgade 140, DK 8000 Aarhus, Denmark

K. Sehested, and J. Holcman

Accelerator Department, Risø National Laboratory, DK 4000 Roskilde, Denmark (Received: July 25, 1984)

The rate constants of the following reactions were determined by pulse radiolysis and stopped-flow experiments: $\text{ClO}_2^- + \text{O}_3 \Rightarrow \text{ClO}_2 + \text{O}_3^-$ ($k_f = (4 \pm 1) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_r = (1.8 \pm 0.2) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$); $\text{ClO}_2 + \text{OH} \rightarrow \text{ClO}_3^- + \text{H}^+$ ($k = (4.0 \pm 0.4) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$); $\text{ClO}_2 + \text{O}^- \rightarrow \text{ClO}_3^-$ ($k = (2.7 \pm 0.4) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$); and $\text{O}_3 + \text{ClO}_2 \rightarrow \text{ClO}_3^-$ + O_2 ($k = (1.05 \pm 0.10) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), where k_f is the forward rate of reaction and k_r is the reverse rate of reaction. The standard Gibbs energy of formation of OH in aqueous solution $\Delta_f G^{\circ}_{so}(OH)$ and the corresponding standard oxidation potential $E^{\circ}_{ao}(OH/OH^{-})$ were determined by means of k_{f} and k_{r} , the equilibrium constant of $O_{3}^{-} \rightleftharpoons O_{2} + O^{-}$, the pK of the hydroxyl radical, $\Delta_f G^{\circ}{}_{ao}$ of O₃, O₂, and OH⁻ in aqueous solution, and $E^{\circ}{}_{ao}(ClO_2/ClO_2^-) = 0.934$ V determined in the present work. $\Delta_f G^{\circ}{}_{ao}(OH) = 26.8 \pm 1$ kJ mol⁻¹ and $E^{\circ}{}_{ao}(OH/OH^-) = 1.91 \pm 0.01$ V are obtained.

Introduction

An experimental determination of the standard Gibbs energy of formation of the hydroxyl radical in aqueous solution, $\Delta_f G^{\circ}_{ao}(OH) = 25.1 \text{ kJ mol}^{-1}$, based on measurements of the equilibrium between hydroxyl radicals and thallium(II)¹ has recently been reported. Until then estimated values in the range $-22 < \Delta_{f} G^{\circ}_{ao}(OH) < 36 \text{ kJ mol}^{-1}$ had been suggested, and in a recent paper Koppenol and Liebman² concluded that 13.4 kJ mol⁻¹ was a reasonable value. The various estimates are based on kinetic measurements³ or obtained from the standard Gibbs energy of formation of the hydroxyl radical in the gas phase $\Delta_f G^{\circ}_{g}(OH)^4$ and estimates for the Gibbs energy of hydration of the hydroxyl radical $\Delta_h G^{\circ}(OH)^{2,5-7}$ (eq 1)

$$\Delta_{\rm f} G^{\circ}_{\rm ao}({\rm OH}) = \Delta_{\rm f} G^{\circ}_{\rm g}({\rm OH}) + \Delta_{\rm h} G^{\circ}({\rm OH}) \tag{1}$$

Here we present an experimental determination of $\Delta_f G^{\circ}_{ao}(OH)$ based on the determination of the rate constant for the oxidation of chlorite by ozone and the rate constant for the reverse reaction, oxidation of the ozonide radical ion by chlorine dioxide

$$\mathrm{ClO}_2^- + \mathrm{O}_3 \rightleftharpoons \mathrm{ClO}_2 + \mathrm{O}_3^- \tag{2}$$

 k_2 was determined by stopped-flow kinetic measurements and k_{-2} by pulse radiolysis of aqueous alkaline O2-containing ClO2 solutions. The measurements of k_2 and k_{-2} enables us to determine $\Delta_{f}G^{\circ}_{a0}(OH)$ in the following way.⁸ The standard Gibbs energy change of reaction 2, ΔG° , may be expressed by the equation

$$-\Delta G^{\circ} = RT \ln k_2 / k_{-2} = \Delta_{\mathrm{f}} G^{\circ}_{\mathrm{ao}}(\mathrm{ClO}_2^{-}) + \Delta_{\mathrm{f}} G^{\circ}_{\mathrm{ao}}(\mathrm{O}_3) - \Delta_{\mathrm{f}} G^{\circ}_{\mathrm{ao}}(\mathrm{ClO}_2) - \Delta_{\mathrm{f}} G^{\circ}_{\mathrm{ao}}(\mathrm{O}_3^{-})$$
(3)

Since O_3^- is in equilibrium with O_2 and O^- :

$$O_3^- \rightleftharpoons O_2 + O^-$$
 (4)
 $k_4 = 3.3 \times 10^3 \text{ s}^{-1} (\text{ref } 9)$
 $k_{-4} = 3.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} (\text{ref } 10)$

- Schwarz, H. A.; Dodson, R. W. J. Phys. Chem. 1984, 88, 3643.
 Koppenol, W. H.; Liebman, J. F. J. Phys. Chem. 1984, 88, 99.
 Heckner, K.-H.; Landsberg, R. Z. Phys. Chem. 1965, 230, 63.
 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, Suppl. 1982, 11, No. 2.
- (5) Stein, G. J. Chem. Phys. 1965, 42, 2586.
 (6) Baxendale, J. H.; Ward, M. D.; Wardman, P. Trans. Faraday Soc. 1971, 67, 2532.
 - (7) Hickling, A.; Hill, S. Trans. Faraday Soc. 1950, 46, 557.
 (8) Koppenol, W. H. FEBS Lett. 1982, 140, 169.

 $\Delta G^{\circ}_{ao}(O_3)$ may be expressed by the equation

$$\Delta G^{\circ}_{a0}(O_{3}^{-}) = \Delta_{f} G^{\circ}_{a0}(O_{2}) + \Delta_{f} G^{\circ}_{a0}(O^{-}) + RT \ln k_{4}/k_{-4} \quad (5)$$

The conjugate acid to O^- is the hydroxyl radical:

$$OH \rightleftharpoons H^+ + O^- pK_{OH} = 11.9 \text{ (ref 11)}$$
 (6)

thus

$$\Delta_{\rm f} G^{\circ}_{\rm ao}({\rm O}^{-}) = \Delta_{\rm f} G^{\circ}_{\rm ao}({\rm OH}) + RT p K_{\rm OH} \ln 10 \tag{7}$$

Elimination of $\Delta_1 G^{\circ}_{a0}(O_3^{-})$ in eq 3 by means of eq 5 and 7 leads to the equation

$$\Delta_{f} G^{\circ}{}_{ao}(OH) = RT(\ln (k_{-2}k_{-4}/(k_{2}k_{4})) - pK_{OH} \ln 10) + \Delta_{f} G^{\circ}{}_{ao}(ClO_{2}^{-}) + \Delta_{f} G^{\circ}{}_{ao}(O_{3}) - \Delta_{f} G^{\circ}{}_{ao}(O_{2}) - \Delta_{f} G^{\circ}{}_{ao}(ClO_{2})$$
(8)

from which $\Delta_f G^{\circ}_{ao}(OH)$ may be obtained.

Experimental Section

The apparatus and procedure for pulse radiolysis experiments are described elsewhere.¹² The dose of the electron pulse irradiation was 1.5-45 krd/pulse. Stopped-flow experiments were carried out on an Aminco-Morrow apparatus.¹³ Changes in absorbance were measured with a modified Beckman spectrophotometer. The output which was proportional to the absorbance change was recorded on a Tectronix 5103 N storage oscilloscope fitted with a C-59 oscilloscope camera. The dead time of the stopped-flow apparatus was $\sim 3 \times 10^{-3}$ s.

Ozone was generated in an electric discharge ozonizer and purified by passing the outlet ozone containing O₂ gas over silica gel at -78 °C.¹² Stock solutions containing oxygen and (2-4) × 10⁻⁴ mol dm⁻³ ozone were prepared by bubbling the purified gas from the ozonizer through 10⁻⁴ mol dm⁻³ aqueous sulfuric acid cooled in ice water. The ozone concentration was measured spectrophotometrically by taking the extinction coefficient at 260 nm, $\epsilon(O_3)_{260} = 3300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1.14}$ Spectrophotometric measurements of O₃ in presence of ClO₂ (stopped-flow and pulse

(14) Hart, E. J.; Sehested, K.; Holcman, J. Anal. Chem. 1983, 55, 46.

⁽⁹⁾ Gall, B. L.; Dorfman, L. M. J. Am. Chem. Soc. 1969, 91, 2199. (10) Farhataziz; Ross, A. B. Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.) 1977, No. 59.

⁽¹¹⁾ Dorfman, L. M.; Adams, G. E. Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.) 1973, No. 46.

⁽¹²⁾ Schested, K.; Holcman, J.; Hart, E. J. J. Phys. Chem. 1983, 87, 1951. (13) Kläning, U. K.; Schested, K. J. Chem. Soc., Faraday Trans. 1 1978, 74, 2818.

radiolysis) were made in the wavelength region $240 < \lambda < 280$ nm in which the extinction coefficient of ClO_2 is small, $\epsilon(ClO_2)_{260}$ $\sim 50 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

Stock solutions of ClO_2 in water containing N_2O were prepared by transferring ClO₂ formed in an acidified sodium chlorite solution¹⁵ to water bubbling N_2O through the acidified sodium chlorite and through water.

Concentrations of ClO2 were measured spectrophotometrically by taking the extinction coefficient at 360 nm equal to 1250 dm³ mol⁻¹ cm⁻¹.¹⁶ Spectrophotometric detection of ClO₂ in presence of O_3 was made at $360 < \lambda < 420$ nm in which region the contribution from O_3 is negligible.

Gases were "Dansk Ilt og Brint" N₂O (99.5%), Ar (99.99%), and O_2 (99.7%). NaOH, HClO₄, and H₂SO₄ were Merck p.a. or Suprapur. NaClO₂ (Matheson Coleman and Bell analytical grade or Hopkins and Williams technical grade) was assayed iodometrically.

Electrometric measurements were made with a Radiometer PHM 64 Research pH Meter using a Radiometer P101 bright platinum electrode and a Radiometer K 401 saturated calomel electrode.

Alkaline ClO₂ solutions for pulse radiolysis were prepared immediately before the electron pulse irradiation by rapid mixing equal volumes of alkaline solutions with neutral ClO₂ solutions and flowing the mixed solution through the pulse radiolysis cell.¹²

Computations were performed by the program CHEMSIMUL¹⁷ on the Burroughs 7800 at Risø National Laboratory. Stoppedflow and pulse radiolysis experiments were made at ambient temperature 22 ± 1 °C.

Results and Discussion

Reaction of Chlorite with Ozone. Chlorine dioxide and chlorate is formed by oxidation of chlorite with ozone.¹⁶ The yield of chlorine dioxide increases and the yield of chlorate decreases with increasing ratio between the chlorite and the ozone concentration.¹⁶ At $[ClO_2^-]/[O_3] > 200$, chlorate ceases to be a product of the reaction and 2 mol of ClO₂ are formed per mol of O₃ reacted.¹⁶ These findings suggest that further reactions of chlorine dioxide with ozone or reactions of intermediates with chlorine dioxide and ozone take place.

A mechanism consisting of reaction 2 and -2, 4 and -4 followed by reactions 6 and 9-16 may explain these observations. The

$$OH + ClO_2^- \rightarrow ClO_2 + OH^-$$
(9)

$$k_9 = 4.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (ref 18)}$$

$$O^- + ClO_2^- \xrightarrow{H_2O} ClO_2 + 2OH^-$$
(10)

$$k_{10} = 7.6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (ref 18)}$$

$$OH + ClO_2 \rightarrow ClO_3^- + H^+$$
(11)

$$O^- + ClO_2 \rightarrow ClO_3^-$$
(12)

$$O_3 + ClO_2 \rightarrow ClO_3 + O_2 \tag{13}$$

$$\text{ClO}_2 + \text{ClO}_3 \xrightarrow{\text{H}_2\text{O}} 2\text{ClO}_3^- + 2\text{H}^+$$
 (14)

$$O_3 + OH \rightarrow O_2 + O_2^- + H^+$$
 (15)

$$k_{15} = 1.1 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (ref 19)}$$

$$O_3 + O^- \to O_2 + O_2^-$$
 (16)

importance of reactions 9-16 for the kinetics of the reaction of

chlorite with ozone can be estimated as follows: Since $k_{15} \ll$ $k_9 \sim k_{11}$ and $[ClO_2^-] > [O_3]$ at pH ≤ 11 in the present experiments, reactions 15 and 16 can be neglected. The relative importance of reactions 11-14 was determined in separate experiments. The rate constants $k_{11} = (4.0 \pm 0.4) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{12} = (2.7 \pm 0.4) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ were found by pulse radiolysis in N₂O-saturated neutral and alkaline dilute solutions of ClO_2 in which the hydrated electron is converted to O^-/OH

$$e_{ac}^{-} + N_2 O \rightarrow N_2 + O^{-}$$
 (17)

The rate of decrease in [ClO₂] was monitored by absorbance measurements at 360 nm.

The rate of the reaction of chlorine dioxide with ozone, reaction 13, was measured in stopped-flow experiments with solutions at 3 < pH < 11 containing $4 \times 10^{-4} < [ClO_2] < 4 \times 10^{-3}$ mol dm⁻³ and $2 \times 10^{-5} < [O_3] < 7 \times 10^{-5}$ mol dm⁻³. O₃ and ClO₂ were monitored by absorbance measurement at 260 and 360-420 nm, respectively. Two moles of ClO₂ were consumed per mol of O₃ reacted, corresponding to the stoichiometry of reactions 13 and 14 combined. The decrease in O_3 and ClO_2 concentrations were found to be pseudo-first-order processes with rate constants proportional to [ClO₂]. These observations show that $k_{14} >> k_{13}$. From a plot of the pseudo-first-order rate constants vs. [ClO₂], we find $k_{13} = (1.05 \pm 0.10) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Since $k_{13} \ll 10^{-1} \text{ s}^{-1}$. k_2 (see below), $[ClO_2^-] > [O_3]$ and pH ≤ 11 reactions 13 and 14 can be neglected. Thus we conclude that only reactions 9-12 are important in the present investigations.

In the stopped-flow kinetic measurements of the reaction of chlorite and ozone, solutions at 3 < pH < 11 containing $2.5 \times$ $10^{-5} < [ClO_2^{-1}] < 1 \times 10^{-4} \text{ mol dm}^{-3} \text{ and } 1 \times 10^{-5} \text{ mol dm}^{-3} [O_3]$ were used. The disappearance of O_3 and the formation of ClO_2 were monitored by absorbance measurements at 260 and 360 nm, respectively. Even at very low concentrations used in our experiments, 35-85% of the reaction takes place during the dead time of the apparatus ($\sim 3 \times 10^{-3}$ s). A value of $k_2 = (4 \pm 1)$ \times 10⁶ dm³ mol⁻¹ s⁻¹ was found by trial and error from the numerically integrated rate equations corresponding to reactions 2 and 9-12 using the CHEMSIMUL program.¹⁷

The number of moles ClO₂ formed per mole of O₃ reacted after the dead-time period as calculated from the measurements of absorbance change at 360 and 260 nm was 0.9-1.1 in solutions containing 10^{-5} mol dm⁻³ O₃ and 2.5×10^{-5} mol dm⁻³ ClO₂ in agreement with the calculated value 1.06.

The Reaction of Chlorine Dioxide with the Ozonide Radical Ion. Previously an oxidation of the ozonide radical ion to ozone by the halogen oxides ClO, BrO, and BrO₂ was observed in laser flash photolysis of alkaline oxygen-containing solutions of hypochlorite, hypobromite, and bromate.²⁰ The fact that the corresponding reaction with ClO_2 (reaction -2) was not observed suggested that $k_{-2} < 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.^{20}$

In the present study we have determined k_{-2} by pulse radiolysis experiments in alkaline O₂-containing ClO₂ solutions which were half-saturated with N_2O to avoid formation of O_2^- from the hydrated electron. The disappearance of O_3^- formed in oxygencontaining alkaline solutions by reaction -4 was monitored by absorbance measurements at 470 nm (ϵ (470)(O₃⁻) = 1000 dm³ $mol^{-1} cm^{-1})^{21}$ where the absorbance of ClO₂ can be neglected. An increase of absorbance at 240 < λ < 280 nm taking place simultaneously with the disappearance of absorbance due to $O_3^$ was observed. The relative difference between the spectra in O_2 -containing and O_2 -free solutions measured at 240 < λ < 280 nm after O_3^- has disappeared is shown in Figure 1. The resulting spectrum is assigned to O_3 on basis of the agreement with the ozone spectrum.14

The decay of O_3^- was measured as a first-order process. Figure 2 shows the measured rate constant, k_{app} , vs. [ClO₂] in solutions at pH 12 and 13. At constant pH, k_{app} increases with increasing ClO₂ concentration asymptotically approaching a straight line

⁽¹⁵⁾ Masschelein, W. J. "Chlorine Dioxide"; Ann Arbor Science Publishers: Ann Arbor, MI, 1979

⁽¹⁶⁾ Emerich, D. E. Ph.D. Thesis, University Microfilms International, Ann Arbor, MI, 1984.

⁽¹⁷⁾ Bjergbakke, E.; Lang Rasmussen, O. CHEMSIMUL-A Program Package for Numerical Simulation of Chemical Reaction Systems, Risø-R-395, Risø National Laboratory, DK 4000 Roskilde, Denmark, 1984. (18) Kläning, U. K.; Wolff, T., to be published.

¹⁹⁾ Sehested, K.; Holcman, J.; Bjergbakke, E.; Hart, E. J. J. Phys. Chem. 1984. 88. 4144.

⁽²⁰⁾ Kläning, U. K.; Sehested, K.; Wolff, T. J. Chem. Soc., Faraday Trans. 1 1984, 80, 2969.

⁽²¹⁾ Sehested, K.; Holcman, J.; Bjergbakke, E.; Hart, E. J. J. Phys. Chem. 1982. 86. 2066.



Figure 1. Difference between the absorbance in O_2 -containing and O_2 -free ClO₂ solutions relative to the difference at 260 nm after electron pulse irradiation. (O and +) [ClO₂] = 2.9×10^{-3} mol dm⁻³; dose, (O) 17 krd, (+) 35 krd. (Δ) [ClO₂] = 5.4×10^{-3} mol dm⁻³; dose, 35 krd.



Figure 2. The rate constant for the disappearance of O_3^- , k_{app} , vs. [ClO₂]; (O) pH 12; (Δ) pH 13. Curves calculated from eq 18.

which intercepts the ordinate axis at 3.3×10^3 s⁻¹ and has a slope $k_s = (3.6 \pm 0.2) \times 10^5$ dm³ mol⁻¹ s⁻¹. At constant ClO₂ concentration k_{app} increases with decreasing pH. From the rate equations for reactions -2, 4, -4, 11, and 12 and the assumption that O⁻ and OH are in steady-state concentrations and in equilibrium (eq 6) the following expression for k_{app} may be derived:

$$k_{\rm app} = k_{\rm s}[{\rm ClO}_2] + k_4 k' [{\rm ClO}_2] / (k_{-4} X_{\rm O} [{\rm O}_2] + k' [{\rm ClO}_2])$$
(18)

where $k' = k_{11}(1 - X_{O^-}) + k_{12}X_{O^-}$ and $X_{O^-} = [O^-]/([O^-] + [OH]) = 10^{\text{pH}-pK_{OH}}/(1 + 10^{\text{pH}-pK_{OH}}).$

Measured and calculated values of k_{app} are shown in Figure 2.

 k_{-2} was determined from measurements of the ozone and ozonide radical ion yields (Figure 3):

$$[O_3]/[O_3^-] = k_{-2}[ClO_2]/k_{app}$$
(19)

From the slope of the straight line in Figure 3 we find $k_{-2} = (1.8 \pm 0.2) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The fact that $k_{-2} < k_s$ can be accounted for by introducing reaction 20 parallel to reaction -2:

$$O_3^- + ClO_2 \rightarrow O_2 + ClO_3^-$$
(20)

$$k_{20} = k_{\rm s} - k_{-2} = (1.8 \pm 0.3) \times 10^5 \,\rm dm^3 \, mol^{-1} \, s^{-1}$$



 $[ClO_2]/k_{app} \times 10^7 \text{ dm}^{-3} \text{ mol s}$ Figure 3. Ratio of ozone and ozonide radical ion yields vs. $[ClO_2]/k_{app}$. Dose 40-45 krd.



Figure 4. $E^{\circ}_{ao}(ClO_2/ClO_2^{-})$ plotted against the temperature t: (O) data from ref 23; (+) this work.

Parallel reactions of O_3^- have been observed previously between O_3^- and OH radicals.²²

$$OH + O_3^- \rightarrow O_3 + OH^- \tag{21}$$

 $k_{21} = 2.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

$$OH + O_3^- + OH^- \rightarrow 2O_2^- + H_2O$$
 (22)

 $k_{22} = 6.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

 $\Delta_f G^{\circ}_{ao}(OH)$ and the Standard Electrode Potential E°_{ao} (OH/OH^{-}) of the Hydroxyl Radical/Hydroxyl Ion Couple. By inserting in eq 8 the values of k_2 and k_{-2} and values of $\Delta_f G^{\circ}_{ao}$ from the NBS tables⁴ we obtain for $\Delta_f G^{\circ}_{ao}(OH)$ the value 13.2 kJ mol⁻¹ and for the half-cell reaction

$$OH_{ao} + e^- \rightarrow OH^-_{ao}$$

a value of $E^{\circ}_{ao}(OH/OH^{-}) = 1.77$ V at 25 °C in agreement with the value calculated by Koppenol and Liebman.² However, the values of $\Delta_f G^{\circ}_{ao}(ClO_2)$ and $\Delta_f G^{\circ}_{ao}(ClO_2^{-})$ listed in the NBS tables⁴ are inconsistent with published values of $E^{\circ}_{ao}(ClO_2/ClO_2^{-})$. The NBS values of $\Delta G^{\circ}_{ao}(ClO_2)$ and $\Delta G^{\circ}_{ao}(ClO_2^{-})$ give $E^{\circ}_{ao}(ClO_2/ClO_2^{-}) = 1.066$ V at 25 °C; the direct determination, however, gives $E^{\circ}_{ao}(ClO_2/ClO_2^{-}) = 0.936$ V²³ and 0.919 V.²⁴

⁽²²⁾ Sehested, K.; Holcman, J.; Bjergbakke, E.; Hart, E. J. J. Phys. Chem. 1984, 88, 269.

⁽²³⁾ Troitskaya, N. V.; Mishenko, K. P.; Flis, I. E. Russ. J. Phys. Chem. (Engl. Transl.) 1959, 33, 77.

We have made a redetermination of $E^{\circ}_{ao}(ClO_2/ClO_2^{-})$ at 25 °C. We measured the potential of a platinum electrode against the SCE electrode at the temperatures 11.0, 22.0, 23.0, and 29.0 °C in unbuffered ClO_2/ClO_2^- solutions containing 2×10^{-3} mol $dm^{-3} ClO_2$ and $4 \times 10^{-4} < [ClO_2^-] < 10^{-2} mol dm^{-3}$. E°_{ao} (ClO_2/ClO_2) was then calculated from the Nernst equation in which the activity coefficient of ClO_2 was set equal unity and that of ClO_2^- was calculated from the Debye-Hückel law. Figure 4 shows a plot of $E^{\circ}_{ao}(ClO_2/ClO_2^{-})$ calculated from the present measurements against the temperature together with those determined previously.²³ By interpolation we find at 25 °C E° as $(ClO_2/ClO_2) = 0.934 \pm 0.002$ V. Using this value and a value for $\Delta_{f} G^{\circ}_{ao}(O_{3}) = 174.9 \text{ kJ mol}^{-1}$ calculated from the NBS value of $\Delta_f G^{\circ}_{g}(O_3)^4$ and a recently determined value of Henry's law constant for ozone,²⁵ we find $\Delta_f G^{\circ}_{ao}(OH) = 26.8 \pm 1.0 \text{ kJ mol}^{-1}$ and $E^{\circ}_{a0}(OH/OH^{-})$ at 25 °C = 1.91 V in agreement with the

values determined by Schwarz and Dodson¹ ($\Delta_f G^{\circ}_{ao}(OH) = 25.1$ kJ mol⁻¹ and $E^{\circ}_{ao}(OH/OH^{-}) = 1.89$ V). The standard Gibbs energies of formation, $\Delta_f G^{\circ}_{ao}$, for OH, O⁻, and O₃⁻ are 26.8, 94.7, and 77.1 kJ mol⁻¹, and the standard oxidation potentials, E°_{ao} (OH), of the couples OH/OH⁻, OH/H₂O, O⁻/OH⁻, and O₃/O₃⁻ are 1.91, 2.74, 1.78, and 1.01 V.

Acknowledgment. The authors are indebted to H. Schwarz, BNL, for, after the submission of this paper, bringing to their attention a discrepancy between the NBS's values of standard Gibbs energy of formation and standard oxidation potential of ClO_2/ClO_2^- . We are grateful to E. Bjergbakke for performing the computations. We thank R. Brodersen and N. Jørgensen, Institute of Biochemistry, Aarhus University for making the stopped-flow apparatus available to us. We thank H. Corfitzen for technical assistance and T. Johansen for skillful operation of the Risø Linac. U.K.K. thanks the Danish Natural Science Research Council for financial support.

Registry No. ClO₂, 10049-04-4; O₃, 10028-15-6; O₂, 7782-44-7; OH, 14280-30-9; O₃⁻, 12596-80-4; ClO₂⁻, 14998-27-7.

Surface-Enhanced Raman Spectroscopy as a Monitor of Iron(III) Protoporphyrin **Reduction at a Silver Electrode in Aqueous and Acetonitrile Solutions: Vibronic Resonance Enhancement Amplified by Surface Enhancement**

Luis A. Sanchez and Thomas G. Spiro*

Department of Chemistry, Princeton University, Princeton, New Jersey 08544 (Received: July 9, 1984)

Raman spectra are reported for anodized silver electrodes held at various potentials in contact with hemin (iron(III) protoporphyrin IX) chloride dissolved in aqueous base (pH 10.5) or with the dimethyl ester dissolved in acetonitrile. Good quality spectra were obtained with 406.7-nm excitation, showing features characteristic of Raman spectra which are resonant with the porphyrin B band. At -0.3 V vs. SCE, the frequencies of the Raman bands correspond to those of a 5-coordinate high-spin Fe^{III} heme; there are slight frequency shifts attributable to the surface interaction, which is suggested to involve the peripheral vinyl groups for the dimethyl ester, and the propriorate groups for aqueous hemin. As the electrode potential is made more negative, the Fe^{III} spectrum is replaced by another, which is characteristic of a high-spin Fe^{II} heme. The midpoint of this transition for aqueous hemin, \sim -0.65 V (vs. SCE) corresponds to the average of the anodic and cathodic peak potentials (-0.72 and -0.58 V) of the Ag electrode cyclic voltammogram; the cathodic peak is 0.40 V more negative than at a Pt electrode, suggesting strong adsorption of the hemin at the silver surface. The Raman spectral transition is quite gradual; the fraction of reduced hemin varies approximately linearly with the potential instead of in a Nernstian fashion. This behavior may reflect differential rates of adsorption and desorption of the oxidized and reduced species. Raman spectra at increasing wavelengths (488.0, 514.5, 647.1, 676.4 nm) show a gradual transition to a set of bands which arise from vibronically active nontotally symmetric vibrations. The enhancement pattern is quite similar to that observed in resonance Raman spectra of metalloporphyrins in solution, implying that the molecular electronic states are not significantly altered by the interaction with the surface. The data are therefore consistent with straightforward electromagnetic enhancement of the molecular resonances by the Ag surface.

Introduction

The discovery that the Raman scattering from molecular vibrations can be enhanced by several orders of magnitude when the molecules are adsorbed on roughened silver electrodes¹ or silver colloids² has led to intense interest in the applicability of surface-enhanced Raman (SER) spectroscopy to the characterization of molecules at surfaces.³ When the laser wavelength lies near electronic absorption bands of the molecule, then the metal surface can further amplify the resonance-enhanced Raman spectrum;^{1a,4,5} an additional advantage is that fluorescence can be effectively quenched by the metal surface.⁴ It was recently shown, for example, that fluorescence-free resonance Raman spectra can be obtained at exceedingly low (submicromolar) concentrations for flavoproteins adsorbed on silver colloids;6 ordinarily, flavin RR spectra are quite difficult to obtain because of the intense natural fluorescence of the chromophore. In the case of glucose oxidase, it was shown that the activity of the enzyme remained nearly intact, while it was adsorbed on the colloid, and was fully recovered upon desorption from the colloid following laser irradiation.⁶ This result is reassuring with respect to the possibility of applying SER

⁽²⁴⁾ Zolutukhin, V. M.; Flis, I. E.; Mishenko, K. P. Zh. Prikl. Khim. (Leningrad) 1965, 38, 359; Chem. Abstr. 1965, 62, 12494a.

⁽²⁵⁾ Roth, J. A.; Sullivan, D. E. Ind. Eng. Chem. Fundam. 1981, 20, 137.

^{(1) (}a) Jeanmaire, D. L.; van Duyne, R. P. J. Electroanal. Chem. 1977, 84, 1-20. (b) Albrecht, M. G.; Creighton, J. A. J. Am. Chem. Soc. 1977, 99, 5215-8.

⁽²⁾ Creighton, J. A.; Blatchford, C. G.; Albrecht, M. G. J. Chem. Soc., Faraday Trans. 2 1979, 75, 790-8.
(3) (a) Van Duyne, R. P. In "Chemical and Biochemical Application of Lasers"; Moore, C. B., Ed.; Academic Press: New York, 1979; Vol. 4, Chapter
5. (b) Chang, R. K.; Furtak, T. E., Eds. "Surface Enhanced Raman Scattering"; Plenum Press: New York, 1982. (c) Birke, R. L.; Lombardi, J. R.; Sanchez, L. A. In "Electrochemical Studies of Biological Redox Components"; Kadish, K. M., Ed.; American Chemical Society, Washington, DC 1982; Adv. Chem. Ser. No. 4 DC, 1982; Adv. Chem. Ser. No. 4.

⁽⁴⁾ Lippitsch, M. E. Chem. Phys. Lett. 1981, 79, 2.

⁽⁵⁾ Weitz, D. A.; Garoff, S.; Gertsten, J. I.; Nitzan, A. J. Chem. Phys. 1983, 78, 5324-38

⁽⁶⁾ Copeland, R. A.; Fodor, S. P. A.; Spiro, T. G. J. Am. Chem. Soc., in press.