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# Chemistry of the Superoxide Radical ($O_2^-$) in Seawater: Reactions with Inorganic Copper Complexes

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Copper-catalyzed dismutation has been proposed as an important sink of photoproduced superoxide radical ($O_2^-$) in seawater. We have determined the effective rate constants of the reactions of superoxide with Cu(I) and Cu(II) in seawater, using pulse radiolysis and kinetic spectrophotometry. Due to the effects of ionic strength and complexation, the observed rate constants, $1.98(\pm0.05) \times 10^9$ $M^{-1}$ $s^{-1}$ and $0.663(\pm0.071) \times 10^9$ $M^{-1}$ $s^{-1}$, for Cu(I) and Cu(II), respectively, are 1 order of magnitude lower than those reported for $Cu^+$ and $Cu^{2+}$ in low ionic strength media. Measurements of the rate of $O_2^-$ decay in the presence of catalytic concentrations of dissolved Cu agreed well with predictions based on the independently measured rate constants. Observed steady-state concentrations of Cu(I) in solutions exposed to a constant flux of $O_2^-$ were also consistent with the measured rate constants. From these results and available data regarding Cu speciation in coastal and open oceans, we calculate that $O_2^-$ reactions with Cu will be a more important sink of $O_2^-$ than bimolecular dismutation, even if all organically complexed Cu species are unreactive.

## Introduction

Superoxide radical ($O_2^-$) is one of the main products of the photooxidation of colored dissolved organic matter (CDOM) in sunlit surface waters:[1,2]

$$\mathrm{CDOM} + O_2 \xrightarrow{h\nu} \mathrm{CDOM_{ox}}^+ + O_2^- \qquad (1)$$

Formation rates of $O_2^-$ in seawater are roughly proportional to CDOM absorbance and range from $2 \times 10^{-12}$ M $s^{-1}$ in the open ocean to $2 \times 10^{-10}$ M $s^{-1}$ in coastal and estuarine waters.[2] Despite these relatively high formation rates, the radical's main sinks in natural waters are not well understood.

Surprisingly long lifetimes (~hours) and high steady-state concentrations ($10^{-8} - 10^{-7}$ M) of $O_2^-$ in open ocean waters are predicted if one assumes that bimolecular dismutation is the only significant sink of $O_2^-$:[3−5]

$$HO_2 + O_2^- \ (+H^+) \rightarrow H_2O_2 + O_2 \qquad (2)$$

The reaction is slow in seawater (overall $k_2 = 3 \times 10^4$ $M^{-1}$ $s^{-1}$, where $d[O_2^-]/dt = 2k_2[O_2^-]^2$) because most of the radical is present as $O_2^-$ at a pH of 8:[3]

$$HO_2 = O_2^- + H^+ \quad pK_a(\text{in seawater}) = 4.6 \qquad (3)$$

However, other sinks of $O_2^-$ may be much more important than bimolecular dismutation: Reactions with dissolved metal ions, organic matter, and the enzyme superoxide dismutase have all been suggested as possibilities,[3] but their importance in natural waters has not been fully assessed.

**TABLE 1: Calculated α Values of Cu(I) Species in Experimental Solutions[a]**

| pH | $Cu^+$ | $CuCl^0$ | $CuCl_2^-$ | $CuCl_3^{2-}$ |
|---|---|---|---|---|
| Seawater | | | | |
| 8.0 | <0.01 | <0.01 | 0.74 | 0.26 |
| Carbonate-Free Seawater | | | | |
| 7.4 | <0.01 | <0.01 | 0.74 | 0.26 |
| 0.7 M NaCl/2.5 mM $NaHCO_3$ | | | | |
| all pH values | <0.01 | <0.01 | 0.69 | 0.31 |

[a] All equilibrium constants and ionic strength corrections used are from Turner et al.[30]

Reactions with dissolved metal ions ("M") are especially interesting because of their potential for maintaining steady-state concentrations of metals in unstable oxidation states:

$$M^{n+} + O_2^- \ (+2H^+) \rightarrow M^{n+1} + H_2O_2 \qquad (4a)$$

$$M^{n+1} + O_2^- \rightarrow M^{n+} + O_2 \qquad (4b)$$

If oxidation and reduction of the metal by $O_2^-$ are faster than all other metal redox reactions, a steady-state fraction of reduced versus oxidized metal is reached, so that

$$[M^{n+}]_{ss}/[M^{n+1}]_{ss} = k_{4b}/k_{4a} \qquad (5)$$

where $k_{4a}$ and $k_{4b}$ are the effective (speciation-dependent; see below) second-order rate constants of reactions 4a,b. Reactions with $O_2^-$ have been identified as a possible source of the surprisingly high Cu(I) and Fe(II) concentrations measured in sunlit surface seawater.[6−8]

Among the transition metals, Cu is the most likely catalytic sink of $O_2^-$. At low ionic strength, Cu ions react with $O_2^-$ at nearly diffusion-controlled rates,[9,10] and Cu is present at

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**TABLE 2: Calculated α Values of Cu(II) Species in Experimental Solutions**[a]

| pH | $Cu^{2+}$ | $CuOH^+$ | $Cu(OH)_2{}^0$ | $CuCl^+$ | $CuSO_4{}^0$ | $CuCO_3{}^0$ | $Cu(CO_3)_2{}^{2-}$ | $CuHCO_3{}^+$ | $CuCO_3OH^-$ |
|---|---|---|---|---|---|---|---|---|---|
| Seawater | | | | | | | | | |
| 8.0 | 0.06 | 0.05 | 0.01 | 0.02 | <0.01 | 0.75 | 0.06 | <0.01 | 0.05 |
| Carbonate-Free Seawater | | | | | | | | | |
| 7.4 | 0.59 | 0.14 | <0.01 | 0.20 | 0.06 | | | | |
| 0.7 M NaCl/2.5 mM $NaHCO_3$ | | | | | | | | | |
| 5.0 | 0.70 | <0.01 | <0.01 | 0.30 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| 5.5 | 0.69 | <0.01 | <0.01 | 0.29 | <0.01 | 0.01 | <0.01 | <0.01 | <0.01 |
| 6.0 | 0.66 | 0.01 | <0.01 | 0.28 | <0.01 | 0.05 | <0.01 | 0.01 | <0.01 |
| 6.5 | 0.53 | 0.02 | <0.01 | 0.22 | <0.01 | 0.22 | <0.01 | 0.01 | <0.01 |
| 7.0 | 0.33 | 0.03 | <0.01 | 0.14 | <0.01 | 0.50 | <0.01 | 0.01 | <0.01 |
| 7.5 | 0.14 | 0.04 | <0.01 | 0.06 | <0.01 | 0.72 | 0.02 | <0.01 | 0.02 |
| 8.0 | 0.05 | 0.04 | 0.01 | 0.02 | <0.01 | 0.76 | 0.08 | <0.01 | 0.05 |

[a] All equilibrium constants and ionic strength corrections are from Byrne and Miller,[31] except for the ionic strength corrected formation constant of $CuCl^+$, which is from Turner et al.[30]

nanomolar concentrations in most parts of the ocean.[11−13] However, the effective rate constants $k_{4a}$ and $k_{4b}$ cannot be assumed to equal previously measured constants for the reactions of aqueous $Cu^+$ and $Cu^{2+}$ with $O_2{}^-$ in low ionic strength media, because in seawater dissolved Cu is almost entirely complexed by inorganic and organic ligands. The main Cu(I) species are $CuCl_2{}^-$ and $CuCl_3{}^{2-}$ (Table 1). Most Cu(II) is complexed by organic ligands whose structure has not yet been determined. The Cu(II) not complexed by organic ligands (<0.1%−10% of total Cu(II)[11−14]) mostly consists of $CuCO_3{}^0$ and $Cu(CO_3)_2{}^{2-}$ (Table 2).

The effective rate constants $k_{4a}$ and $k_{4b}$ can be expressed as sums of the contribution of each Cu species present:

$$k_{4a} = \sum \alpha_i k_i = \alpha_{Cu^+} k_{Cu^+} + \alpha_{CuCl_2{}^-} k_{CuCl_2{}^-} + \alpha_{CuCl_3{}^{2-}} k_{CuCl_3{}^{2-}} + ... \quad (6a)$$

$$k_{4b} = \sum \alpha_i k_i = \alpha_{Cu^{2+}} k_{Cu^{2+}} + \alpha_{CuCO_3} k_{CuCO_3} + \alpha_{CuHCO_3{}^+} k_{CuHCO_3{}^+} + \alpha_{CuOH^+} k_{CuOH^+} + ... \quad (6b)$$

where $k_i$ is the second-order rate constant of the reaction of $O_2{}^-$ with species $i$ at the ambient ionic strength and $\alpha_i$ is the fraction of the total Cu(I) or Cu(II) present as this species. None of the rate constants in eqs 6a,b have previously been measured except $k_{Cu^+}$ and $k_{Cu^{2+}}$, and even these may differ in seawater due to ionic strength effects and complexation of $O_2{}^-$ by $Ca^{2+}$ and $Mg^{2+}$ ions.[5,15] Given the small values of $\alpha_{Cu^+}$ and $\alpha_{Cu^{2+}}$ in seawater, Cu's ability to act as a catalytic sink of superoxide would be diminished if reactions with the complexes were slower than the reactions with the free ions.

Preliminary observations of the effect of Cu on superoxide decay rates in seawater (Zafiriou, unpublished data) and measurements of % $[Cu(I)]_{ss}$ in the presence of a constant flux of $O_2{}^-$ in NaCl/$NaHCO_3$ solutions[6] have suggested that reactions of superoxide with the inorganic Cu(I) and Cu(II) complexes in seawater are rapid. The latter study also indicated that $k_{4a} \sim k_{4b}$ in the absence of organic ligands, but because the actual magnitudes of the rate constants could not be determined, an accurate assessment of the effect of these species on superoxide concentrations could not be made.

The goal of this study was to assess the importance of inorganically complexed Cu species as sinks for $O_2{}^-$, and the effect of these reactions on Cu redox speciation in seawater, by examining the effects of inorganic complexation and ionic strength on the effective rate constants of the reactions of Cu(I) and Cu(II) species with $O_2{}^-$. The reactions of $O_2{}^-$ with organically complexed Cu are examined in a companion work (Voelker et al., in preparation).

## Methods

**Materials.** All glassware used in the pulse radiolysis experiments was baked for 4 h at 250 °C, soaked overnight in l N HCl, and rinsed extensively with purified (Millipure) water before use. Cu(II) stock solutions were prepared from $CuCl_2$ in 1−10 mM $H_2SO_4$. Cu(II) concentrations in stock solutions were measured daily using the colorimetric reagent bathocuproine disulfonic acid (0.2 mM) and a reductant ($HONH_3HCl$, ∼1 mM).[6] Cu(I) stock solutions were prepared by dissolving CuBr in deaerated solutions of 1 M NaCl and l mM HCl and kept isolated from the atmosphere in a gastight syringe immersed in $N_2$-sparged water. Cu(I) concentrations were verified colorimetrically using bathocuproine disulfonic acid; Cu(II) was always less than 1% of total Cu. pH was measured colorimetrically using Cresol Red (∼5 μM),[16,17] where the formula given in Millero et al.[16] (eq 25) was corrected by replacing the multiplication sign with a division sign. pH is reported using the free proton scale.

Seawater samples were collected in PVC Niskin bottles with Teflon springs well offshore to avoid high particulate concentrations or high levels of terrestrially-derived dissolved organic compounds. Samples were stored in subdued light in acid-washed Teflon bottles. Their total copper concentrations are expected to be in the range of 1−10 nM.

**Pulse Radiolysis Experiments.** Experiments were performed at the Center for Fast Kinetics Research (CFKR) at the University of Texas in Austin.[3] In this technique,[18] radiolysis of water was used to generate a pulse of primary radicals ($e^-_{aq}$, $H^\bullet$, $HO^\bullet$) in a 2.5-cm flow-through quartz cell. The $e^-_{aq}$ and $H^\bullet$ were converted to $O_2{}^-$, within ∼10 μs by reaction with $O_2$; an organic reagent (methanol or formate) was added to convert $HO^\bullet$ to $O_2{}^-$. A more detailed discussion of reactions of primary radicals in seawater is included in the Supporting Information.

Reaction progress was followed using kinetic spectrophotometry. Signal-to-noise ratio was improved by averaging data sets, normalized to pulse size, from 10−20 pulses (4−10 for multiwavelength data). The flow cell was flushed with fresh experimental solution after each pulse. Data averaging and analysis were performed on a PC using CFKR's in-house software. Dosimetry was performed in $N_2$-saturated Milli-Q water containing 2% (v/v) *tert*-butanol by extrapolating the absorption of the hydrated electron at 715 nm to the beginning of the pulse.

Cu(II) experimental solutions were prepared by adding Cu(II) from a stock solution and MeOH (HPLC grade, 0.3 M) or formate (recrystallized 3×, 0.01−0.1 M) to seawater samples. In a few experiments, pH was adjusted with $H_2SO_4$ and $Na_2B_4O_7$ (total additions of each <l mM). Solutions were then sparged with oxygen prior to pulsing. Cu(II) concentrations (if high enough to be detectable) and pH were remeasured after the experiment. We observed no evidence of Cu(II) precipitation and/or sorption to the glassware.

Cu(I) solutions could not be prepared the same way because oxygenated Cu(I) solutions are unstable ($t_{1/2}$ of Cu(I) oxidation in seawater is on the order of minutes).[19,20] Instead, solutions of oxygen-saturated seawater and Cu(I) in de-aerated seawater (both containing MeOH or formate) were prepared in separate gastight syringes. A syringe drive and a T-mixer were then used to mix the two solutions in equal ratios and deliver the mixture to the pulse radiolysis flow cell within 1−2 s.

Carbonate was removed from some seawater samples by acidifying to pH 3.3 with HCl (∼0.5 mM) and sparging with $O_2$ for 30 min. The pH was adjusted to 7.2−7.4 with $Na_2B_4O_7$ (∼l mM) and HCl (∼0.5 mM).

**Kinetic Data Acquisition and Interpretation.** After conversion of primary radicals to $O_2^-$, the observed absorbance signal as a function of time $t$ is given by

$$A_{\lambda,t}/l = \epsilon_{O_2^-}(\lambda)[O_2^-]_t + \epsilon_{Cu(I)}(\lambda)[Cu(I)]_t + \epsilon_{Cu(II)}(\lambda)[Cu(II)]_t + \text{background} \quad (7)$$

where $\epsilon_{O_2^-}(\lambda)$ is the extinction coefficient of $O_2^-$, $\epsilon_{Cu(I)}(\lambda)$ and $\epsilon_{Cu(II)}(\lambda)$ are the apparent (speciation-dependent) extinction coefficients of inorganic Cu(I) and Cu(II) as a function of the wavelength $\lambda$, and $l$ is the path length of the cell (2.5 cm). The background signal arising from the other light-absorbing species in our seawater samples (such as natural dissolved organic matter) did not change over the course of an observation. Absorbances of other known species (such as hydrogen peroxide formed by reaction 4a) were generally insignificant, although, as discussed below and in the Supporting Information, interference by transient species was observed under some conditions.

After the initial grow-in of $O_2^-$ is completed, $d[O_2^-]_t/dt$ is given by

$$d[O_2^-]_t/dt = -(k_{4a}[Cu(I)]_t + k_{4b}[Cu(II)]_t + k_{other})[O_2^-]_t - 2k_2[O_2^-]_t^2 \quad (8)$$

where $k_{other}$ is the pseudo-first-order rate coefficient of reactions of $O_2^-$ with other reactants present in the water.

Pulse radiolysis experiments were performed under three different sets of conditions: (1) with only Cu(I) and $O_2^-$ initially present and $[Cu(I)]_0 \gg [O_2^-]_0$; (2) with only Cu(II) and $O_2^-$ initially present and $[Cu(II)]_0 \gg [O_2^-]_0$; (3) with only Cu(II) and $O_2^-$ initially present and $[Cu(lI)]_0 \ll [O_2^-]_0$. These conditions were chosen to produce data that follow pseudo-first-order kinetics:

$$d[O_2^-]_t/dt = -k_{obs}[O_2^-]_t \qquad [O_2^-]_t = [O_2^-]_0 \exp(-k_{obs}t) \quad (9)$$

In the first case, with $[Cu(I)]_0 \gg [O_2^-]_0$, [Cu(I)] remains approximately constant over time and the reaction of $O_2^-$ with Cu(II) is insignificant. If the second-order term in eq 8 is also insignificant, the equation reduces to eq 9, with

$$k_{obs} = k_{4a}[Cu(I)]_0 + k_{other} \quad (10)$$

The observed absorbance signal at any time reflects the stoichiometric consumption of $O_2^-$ and Cu(I) and formation of Cu(II).

$$[Cu(I)]_t = [Cu(I)]_0 - [O_2^-]_0 + [O_2^-]_t \quad (11)$$

$$[Cu(II)]_t = [O_2^-]_0 - [O_2^-]_t \quad (12)$$

Substituting into eqs 7 and 9, we obtain

$$A_{\lambda,t}/l = [O_2^-]_0\{\epsilon_{O_2^-}(\lambda) + \epsilon_{Cu(I)}(\lambda) - \epsilon_{Cu(II)}(\lambda)\} \times \exp(-k_{obs}t) + \epsilon_{Cu(I)}(\lambda)\{[Cu(I)]_0 - [O_2^-]_0\} + \epsilon_{Cu(II)}(\lambda)[O_2^-]_0 + \text{backgrd} \quad (13)$$

For the second type of experiments, with $[Cu(II)]_0 \gg [O_2^-]_0$, analogous assumptions can be made:

$$k_{obs} = k_{4b}[Cu(II)]_0 + k_{other} \quad (14)$$

$$A_{\lambda,t}/l = [O_2^-]_0\{\epsilon_{O_2^-}(\lambda) - \epsilon_{Cu(I)}(\lambda) + \epsilon_{Cu(II)}(\lambda)\} \times \exp(-k_{obs}t) + \epsilon_{Cu(II)}(\lambda)\{[Cu(II)]_0 - [O_2^-]_0\} + \epsilon_{Cu(I)}(\lambda)[O_2^-]_0 + \text{backgrd} \quad (15)$$

In the third case ($[Cu(II)]_0 \ll [O_2^-]_0$), Cu catalyzes the dismutation of superoxide, reaching a steady-state Cu(I)/Cu(II) ratio (eq 5), so that

$$k_{obs} = k_{cat}[Cu]_T + k_{other} \quad (16)$$

where

$$k_{cat} = 2k_{4a}k_{4b}/(k_{4a} + k_{4b}) \qquad [Cu]_T = [Cu(I)] + [Cu(II)] = [Cu(II)]_0 \quad (17)$$

Because [Cu(I)] and [Cu(lI)] are small, the Cu species are not a significant term in $A_{\lambda,t}$, and

$$A_{\lambda,t}/l = \epsilon_{O_2^-}(\lambda)[O_2^-]_0 \exp(-k_{obs}t) + \text{background} \quad (18)$$

After obtaining measurements of $k_{4a}$ and $k_{4b}$, we verified the assumptions on which the simplified equations derived above are based with kinetic model calculations (Table S1 of the Supporting Information; the software used was Acuchem[21]). In a few cases, pathways assumed to be insignificant sinks of $O_2^-$ in the simplified treatment above were actually somewhat significant (>5% of total), most notably reaction with Cu(I) when only Cu(II) was present initially. Also, because of Cu redox reactions with transient species taking place in the first few μs after the pulse (see discussions in the Supporting Information), the expected magnitudes of $\Delta A_{\lambda,t}/l$ immediately after the pulse and at the end of the reaction differed slightly from the simplified equations shown above. Finally, in the presence of high Cu(I), $O_2^-$ decayed on a time scale comparable to its formation, so that its total yield appeared lower than expected. However, for all of these cases, our calculations showed that an exponential increase or decrease in $A_{\lambda,t}/l$ should still be observed with a first-order rate coefficient that does not differ appreciably from the value predicted by eqs 10, 14, or 16.

**Generation of Experimental and Predicted Spectra.** Absorbance spectra of Cu(I) and Cu(II) in seawater were measured in our laboratory. Observed Cu(I) extinction coefficients were not sensitive to Cu(I) concentrations or to small differences in pH. Cu(II) extinction coefficients varied with Cu(II) concentrations above 20 $\mu$M (at pH 7.9), probably indicating formation of dinuclear (or polynuclear) species. At higher pH (8.3), the change in extinction coefficient occurred at lower Cu(II) concentration (10 $\mu$M).

Time-dependent spectra were generated from kinetic spectrophotometry data collected for the same system at a number of wavelengths. As a consequence of the steep decrease in lamp intensity, the raw data had to be corrected at short wavelengths ($\lambda < 280$) because a filter to block higher-order diffracted light was accidentally omitted in the experimental set-up (Donald O'Connor, personal communication). Corrections were based on measurements of incident light measured at monochromator settings of 230−270 nm when the flow cell was filled with 1 g/L of potassium hydrogen phthalate to block transmission of all light with wavelengths shorter than 300 nm. In all of our experiments, observed changes in absorbance ($\Delta A_\lambda/l$) were small enough that $\Delta A_\lambda/l$ varied approximately linearly with changes in the amount of absorbed light. As a result, the determination of a first-order rate coefficient from the relative changes in signal with time was not affected by this issue.

To generate the predicted spectra, we used kinetic model calculations including all reactions listed in Table S1 of the Supporting Information. We assumed that $O_2^-$, Cu(I), and Cu(II) are the only light-absorbing species produced or consumed during the reaction.

**Continuous Radiolysis.** Continuous radiolysis by a $^{60}$Co $\gamma$-radiation source was used to examine steady-state Cu redox speciation in the presence of a constant flux of superoxide. The use of this method to study metal redox reactions under environmental conditions has been described previously.[6,22] Solutions containing 0.7 M NaCl, 2.5 mM $NaHCO_3$, and 300 nM Cu(II) were adjusted to the desired pH with $HClO_4$ and irradiated ($O_2^-$ flux 18 nM/s) until a constant concentration of Cu(I) was observed (10−20 min). Cu(I) was measured using bathocuproine disulfonic acid; total Cu was measured using bathocuproine disulfonic acid and a reductant.[6] No color was observed upon adding bathocuproine disulfonic acid to solutions containing only Cu(II) and no reductant.

## Results

**Pulse Radiolysis.** The spectra of $O_2^-$,[18] Cu(I), and Cu(II) (the latter two measured in seawater medium) and the corresponding difference spectra, $\epsilon_{O_2^-}(\lambda) + \epsilon_{Cu(I)}(\lambda) - \epsilon_{Cu(II)}(\lambda)$ and $\epsilon_{O_2^-}(\lambda) - \epsilon_{Cu(I)}(\lambda) + \epsilon_{Cu(II)}(\lambda)$ (see eqs 13 and 15), are shown in Figure 1. Overall, expected changes in absorbance are small for the range of $[O_2^-]_0$, 2−8 $\mu$M, used in our experiments. Furthermore, because the spectra overlap extensively and are similar in magnitude, there is no wavelength for which monitoring of a signal due entirely to product grow-in or reactant decay is feasible. (Above 320 nm, the absorbance is only due to Cu(II) but is quite weak and overwhelmed by other signals discussed in the Supporting Information.)

The first type of experiment, in which only Cu(I) was present initially and $[Cu(I)]_0 \gg [O_2^-]_0$, allowed a direct measurement of the rate constant of reaction 4a (eq 10). To determine the best wavelength for observation and to verify that reactions other than those of $O_2^-$ with Cu(I) were not interfering significantly, we examined $A_{\lambda,t}$ at a range of wavelengths (Figure 2a). The general shape of the time-dependent spectrum, including an isosbestic point near 265 nm, is consistent with kinetic calculations (Figure 2b). The initial spectrum closely matches our expectations, indicating that $O_2^-$ is formed at high yield and that no transients are formed within microseconds which absorb light in this wavelength range. For the final spectrum, the observed absorbance was higher than predicted at wavelengths shorter than 240 nm and smaller than predicted at wavelengths longer than 270 nm. Data at 230, 260, and 290 nm generated using formate agree with the spectra shown in Figure 2a (acquired in methanol), indicating that unknown transients

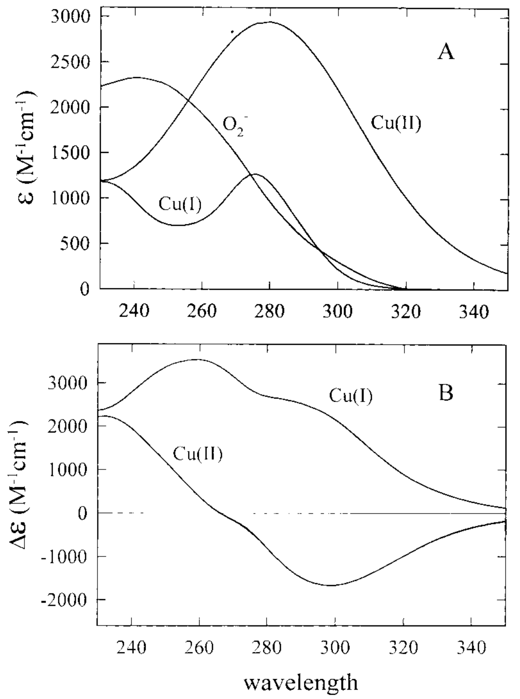

**Figure 1.** (a) Absorbance spectra of Cu(I) and Cu(II) species present in seawater. The $O_2^-$ spectrum is from Bielski et al.[18] (b) Difference spectra for systems initially containing only Cu(I) ($\epsilon_{O_2^-}(\lambda) + \epsilon_{Cu(I)}(\lambda) - \epsilon_{Cu(II)}(\lambda)$) or Cu(II) ($\epsilon_{O_2^-}(\lambda) - \epsilon_{Cu(I)}(\lambda) + \epsilon_{Cu(II)}(\lambda)$) (see eqs 13 and 15).

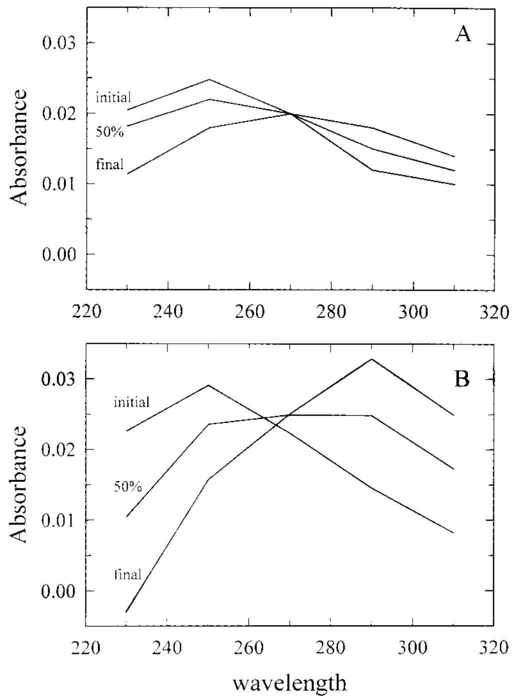

**Figure 2.** (a) Observed time-dependent spectra with $[Cu(I)]_0 = 40$ $\mu$M and $[O_2^-]_0 = 1.8-3.2$ $\mu$M, normalized to unit dose (where a dose of 1.00 corresponds to 8.1 $\mu$M $[O_2^-]_0$). (b) Calculated time-dependent spectra for this system, including the same normalization factor. See the Supporting Information for a table of reactions included in kinetic calculations.

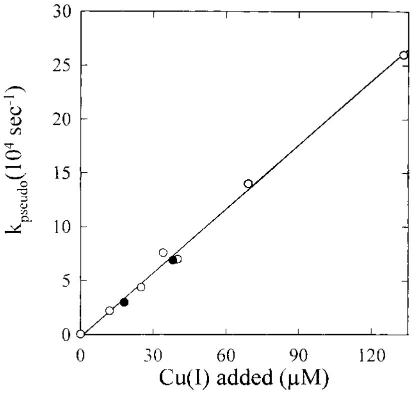

**Figure 3.** First-order rate coefficient $k_{obs}$ of signal observed at 290 nm as a function of added [Cu(I)] in seawater at pH 8.1. $[O_2^-]_0$ = 4.0−6.5 $\mu$M. Either 0.3 M MeOH (○) or 0.1 M formate (●) were used to convert HO to $O_2^-$. The solid line is a linear regression of all points, giving a second-order rate constant of the reaction of $O_2^-$ with Cu(I) of 1.98(±0.05) × $10^9$ $M^{-1}$ $s^{-1}$.

specific to the use of methanol are not responsible for this discrepancy.

A possible explanation for the interfering signal at short wavelengths is light scattering by colloidal Cu(0). Some formation of Cu(0) is expected from reduction of Cu(I) by $e^-_{aq}$, and rapid aggregation to colloidal Cu has previously been observed[23] (Supporting Information).

The discrepancy at longer wavelengths is more puzzling, since it is not possible to explain smaller-than-predicted signals in terms of formation of minor, but strongly colored products. Data acquired using a previous set-up at CFKR, in preliminary experiments with a formate−seawater−Cu(I) system, gave signal changes that were closer to our calculations, suggesting that our a posteriori corrections to the observed absorbance signals (see Methods section) for the current cell/optical set-up are only approximate.

A linear relationship between the observed exponential decay rate coefficient ($k_{obs}$) and $[Cu(I)]_0$ was found, as expected from eq 10 (Figure 3). Most observations were made at 290 nm, where the observed (precorrection) change in absorbance was highest. The choice of HO scavenger (methanol vs formate) did not affect $k_{obs}$ (solid circles in Figure 3). The rate constant of reaction 4a for Cu(I) species in seawater, $k_{4a}$, was obtained from the slope of the regression line for all data points in Figure 3 and was found to have a value of 1.98(±0.05) × $10^9$ $M^{-1}$ $s^{-1}$.

The second type of experiment, with $[Cu(II)]_0 \gg [O_2^-]_0$, was used to determine $k_{4b}$ (eq 14). Under these conditions, the agreement between predicted and observed spectra (Figure 4) was satisfactory at the shorter wavelengths and again diverged somewhat at the longer wavelengths (probably for the same reasons as discussed above). We conducted our subsequent observations at 230 nm.

A linear relationship between $k_{obs}$ and $[Cu(II)]_0$ was observed (Figure 5). The value of $k_{4b}$, derived from the slope of the regression line, is (6.63 ± 0.71) × $10^8$ $M^{-1}$ $s^{-1}$ (eq 14). This value was not strongly pH-dependent (triangles).

In the third type of experiment, with $[O_2^-] \gg [Cu(II)]_0$, the expected linear relationship between $[Cu]_T$ and $k_{obs}$ was again observed (○ symbols in Figure 6), giving a $k_{cat}$ of (1.00 ± 0.01) × $10^9$ $M^{-1}$ $s^{-1}$ (eq 16). Comparable values of $k_{cat}$ were measured in seawater samples containing much lower levels (10−50 nM) of $[Cu]_T$, whenever the samples were first UV-oxidized to destroy organic complexing agents (data not shown).

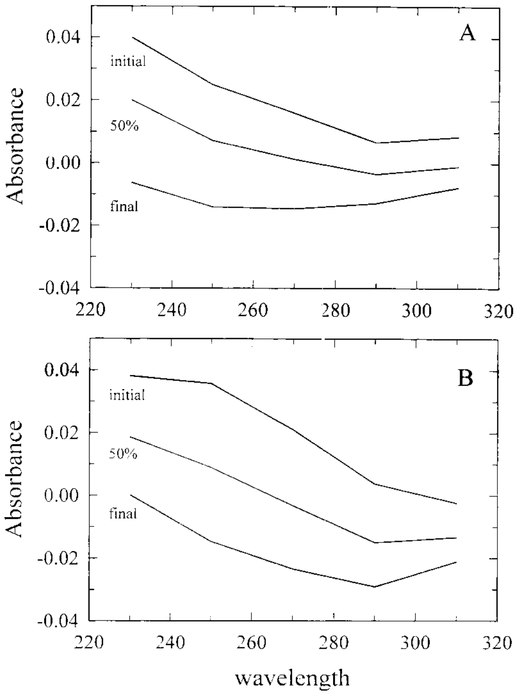

**Figure 4.** Same as Figure 2 but with $[Cu(II)]_0$ = 20 $\mu$M and $[O_2^-]_0$ = 1.6−3.2 $\mu$M.

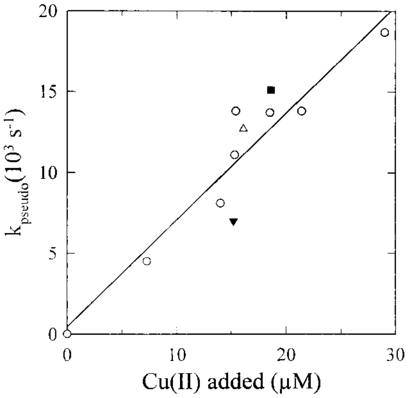

**Figure 5.** Observed first-order rate coefficient $k_{obs}$ as a function of added [Cu(II)] in seawater at pH 8.0 (○), 6.9 (△), or 8.3 (▼) and 0.1 M (■) or 0.3 M (all others) MeOH. $[O_2^-]_0$ = 1.6−3.2 $\mu$M. Only the pH 8.0 points (○) were used for the linear regression (solid line), giving a second-order rate constant of the reaction of $O_2^-$ with Cu(II) of (6.63 ± 0.71) × $10^8$ $M^{-1}$ $s^{-1}$.

In carbonate-free seawater (☐ symbols in Figure 6), the value of $k_{cat}$ was (1.38 ± 0.01) × $10^9$ $M^{-1}$ $s^{-1}$.

**Continuous Radiolysis.** The effect of low fluxes of $O_2^-$ on Cu redox speciation was demonstrated in continuous radiolysis experiments using 0.7 M NaCl solutions. The measured concentration of Cu(I) at steady state increased with increasing pH from pH 3 to 5.5, peaked at 35% of $Cu_T$ at pH values near 6, and then decreased again at higher pH (Figure 7).

## Discussion

**Effective Rate Constants in Seawater.** Our measurements of the effective rate constants of inorganically complexed Cu(I) and Cu(II) species with $O_2^-$ are summarized in Table 3. The measured value of $k_{cat}$ was consistent with the value calculated from our measurements of $k_{4a}$ and $k_{4b}$ (eq 17).

Equation 17 will be strictly valid only if the rates of inorganic complex formation and dissociation are fast compared to the reactions with $O_2^-$, so that Cu(I) and Cu(II) species are always

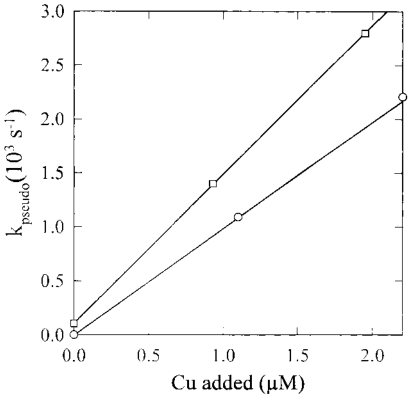

**Figure 6.** Observed first-order rate coefficient as a function of $Cu_T$ (added in catalytic concentrations) in seawater at pH 8.0 (○) and $CO_2$-free seawater at pH 7.4 (□). $[O_2^-]_0 = 6.3-8.9\ \mu M$ and $[MeOH] = 0.3$ M. $k_{cat}$ values (slopes of shown regression lines) are $(1.00 \pm 0.01) \times 10^9$ and $(1.38 \pm 0.01) \times 10^9\ M^{-1}\ s^{-1}$, respectively.

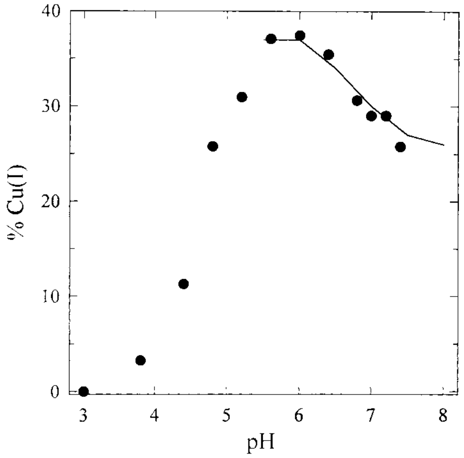

**Figure 7.** Steady-state % Cu(I) in the presence of an $O_2^-$ flux of 18 nM/s in buffered salt solutions (0.7 M NaCl, 2.5 mM $NaHCO_3$, formaldehyde, $Cu_T = 300$ nM). The solid line shows predicted % Cu(I) based on the rate constants of Cu species with $O_2^-$ (Table 3) and calculated decreases in concentration of Cu(II)−carbonate complexes with decreasing pH (Table 2). For pH values smaller than 5.5, reactions of Cu with $HO_2$ would also have to be considered.

**TABLE 3: Summary of Second-Order Rate Constants of Inorganic Cu(I) and Cu(II) Species ($10^9\ M^{-1}\ s^{-1}$) in Seawater**

| | |
|---|---|
| $k_{4a}$ (overall) | 1.98(±0.05) |
| $k_{4b}$ (overall) | 0.663(±0.071) |
| $k_{cat}$ (obsd, pH 8.0) | 1.00(±0.01) |
| $k_{cat}$ (calcd, pH 8.0) | 0.99(±0.11) |
| $k_{cat}$ ($CO_2$-free water, pH 7.4) | 1.38(±0.01) |
| $k_{4b}$ (“carbonate” species)[a] | 0.619(±0.079) |
| $k_{4b}$ (“non-carbonate” species)[a] | 1.06(±0.05) |
| ionic strength 2−3 mM[9,10] | |
| $k_1$ ($Cu^+$) | 9.4(±0.8) |
| $k_2$ ($Cu^{2+}$) | 8.0(±0.5) |

[a] Calculated from $k_{cat}$ in $CO_2$-free seawater and the overall $k_{4b}$ in seawater, using Cu speciation data in Table 2. We assumed that $CuCl^+$ and $CuOH^+$ have approximately the same rate constant as $Cu^{2+}$ and that other Cu−carbonate complexes have the same constant as $CuCO_3$ (see text).

present in their equilibrium distribution. Because of Cu(II)’s high water-loss rate, rate constants of complexation reactions with monodentate ligands tend to approach the diffusion-controlled limit ($10^9-10^{10}\ M^{-1}\ s^{-1}$);[24,25] the dissociation reactions of fairly weak complexes, such as those with chloride or carbonate, are of course correspondingly fast. Less information is available regarding Cu(I) ligand exchange kinetics. Complexation of $Cu^+_{aq}$ by maleate and fumarate proceed at nearly diffusion-controlled rates, indicating a fast water-loss rate,[26] as expected for a large, monovalent cation with a $d^{10}$ configuration.

The internal consistency of our results supports our assumptions that re-equilibration of Cu(I) or Cu(II) species is fast compared to reaction with $O_2^-$ and that the discrepancies between the predicted and observed spectra shown in Figures 2 and 4 are not due to factors which interfered with our measurements of rate constants.

**Effects of Cu Speciation on Rate Constants.** The difference between $k_{cat}$ in seawater versus carbonate-free seawater (Figure 6) is due to an effect of Cu(II) speciation on $k_{4b}$. The removal of carbonate and the slight decrease in pH has little effect on Cu(I) speciation, which is dominated by chloride complexes (Table 1). The value of $k_{4a}$ should therefore be the same in both systems. Using the previously measured value of $k_{4a}$ and eq 17, we can calculate the effective $k_{4b}$ for carbonate-free seawater from the measured $k_{cat}$. Direct measurement of $k_{4b}$ in carbonate-free seawater with $[Cu(II)]_0 \gg [O_2^-]_0$ was not possible because Cu(II) was lost from these solutions when Cu(II) concentrations exceeded a few micromolar.[9] The calculated $k_{4b}$ in carbonate-free seawater, $1.06(\pm 0.05) \times 10^9\ M^{-1}\ s^{-1}$, is 35% higher than $k_{4b}$ in carbonate-containing seawater, indicating that non-carbonate complexes react more quickly with $O_2^-$ than carbonate complexes.

The data shown in Figure 7 are consistent with a pH-dependent change in the extent of Cu(II) complexation by carbonate. We estimated the effect of the change in speciation on % Cu(I) by calculating apparent $k_{4b}$ values for reaction of $O_2^-$ with “non-carbonate complexes” and with “carbonate complexes”. The former is simply the $k_{4b}$ measured in carbonate-free seawater, while the latter is derived from subtracting the contribution of the non-carbonate complexes from the $k_{4b}$ measured in seawater. An overall $k_{4b}$ for each pH in Figure 7 can then be derived by adding the contribution of the non-carbonate and carbonate species using calculations of Cu speciation as a function of pH (Table 2). These calculations are only approximate, because the relative amounts of the individual species are not constant in all the systems being compared. Nevertheless, this approach successfully explains the variation in steady-state % Cu(I) with pH in 0.7 M NaCl/2.5 mM $NaHCO_3$ solutions (solid line in Figure 7). (Below pH 5.5, reactions with $HO_2$ would also have to be considered.)

**Electrostatic Effects on Rate Constants.** The observed overall rate constant for Cu(I), $k_{4a}$, is a factor of 5 lower than the constant for $Cu^+$ measured in low ionic strength media. This is consistent with the expected effects of complexation and ionic strength on a diffusion-controlled rate constant. At low ionic strength, the diffusion-controlled rate constants for the reactions of $O_2^-$ with a −1 ion ($CuCl_2^-$) and a −2 ion ($CuCl_3^{2-}$) are expected to be a factor of 4 and 11 lower, respectively, than the corresponding constant for $Cu^+$ (Debye−Huckel potentials and a constant critical reaction radius of 0.5 nm were assumed for these calculations[27]). Because of shielding effects, the $CuCl_2^-$ and $CuCl_3^{2-}$ rate constants should increase with increasing ionic strength. We therefore expect the $CuCl_2^-$ and $CuCl_3^{2-}$ rate constants in seawater to be somewhat less than 4 and 11 times smaller than the $Cu^+$ constant in dilute solutions, if only electrostatic effects played a role (precise calculations cannot be made using this approach because Debye−Huckel potentials are not valid at seawater ionic strength). The only

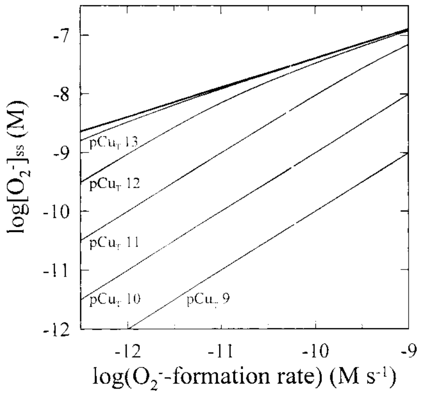

**Figure 8.** Calculated effect of inorganically complexed Cu species on steady-state $[O_2^-]$ as a function of $O_2^-$ formation rate and total Cu, where $pCu_T = -\log$ [total inorganically complexed Cu]. Organically complexed Cu was assumed to be unreactive.

significant contributors to $k_{4a}$ in eq 6a are $CuCl_2^-$ and $CuCl_3^{2-}$, with $CuCl_2^-$ predominating. The minor species ($\alpha < 0.01$) would have to have much larger rate constants than those of the major species to affect $k_{4a}$, which is impossible since the latter already approach the diffusion-controlled limit. The observed $k_{4a}$ is therefore consistent with a purely electrostatic effect of complexation and ionic strength on the rates of diffusion-controlled reactions.

Similarly, the diffusion-controlled rate constant for the reaction of $O_2^-$ with $CuCO_3^0$ is expected to be a factor of 3 lower than the constant for $Cu^{2+}$ in low ionic strength media. Increasing ionic strength should not have a large effect on the rate of the reaction with the neutral complex. In this case, a larger than expected effect was observed: the rate constant for Cu−carbonato complexes in seawater was a factor of 12 lower than that for $Cu^{2+}$ in low ionic strength media. However, the difference between the rate constants of $Cu^{2+}$ and $CuCO_3$ complexes in seawater (approximated as the rate constants of the "non-carbonate" and "carbonate" species, respectively) is small (less than a factor of 2); most of the effect arises from the difference in $Cu^{2+}$ reactivity with $O_2^-$ in low ionic strength medium and seawater.

It is possible that complexation by $Ca^{2+}$ and $Mg^{2+}$ ions lowers the activity of $O_2^-$ in seawater.[5,15] However, it is not clear whether the $Ca^{2+}$ or $Mg^{2+}$ complexes would actually be unreactive toward Cu species. The observation that rate constants determined in seawater were consistent with the steady-state experiment performed in the absence of $Ca^{2+}$ and $Mg^{2+}$ (Figure 7) implies that if there is a $Ca^{2+}/Mg^{2+}$ complexation effect, both the reduction and the oxidation rate constants are affected equally.

**Effect of $O_2^-$ on Cu Speciation in Seawater.** Applying eq 5 with the measured rate constants, we find that up to 25% of inorganically complexed Cu will be present as Cu(I) in sunlit seawater, as long as $k_{4a}[O_2^-]_{ss}$ and $k_{4b}[O_2^-]_{ss}$ are much greater than $k_{O_2}[O_2]$, where $k_{O_2}$ is the effective second-order rate constant of reaction of Cu(I) with $O_2$. (Other possible Cu redox reactions, such as reduction of Cu(II) by $H_2O_2$, are less significant[28,29].) Using a previously measured value of $\sim 8 \times 10^{-4}$ s$^{-1}$ for $k_{O_2}[O_2]$ in surface seawater,[19] this condition will be met whenever $[O_2^-]_{ss}$ exceeds $10^{-12}$ M. However, since inorganically complexed Cu represents only a small fraction (< 1%) of total dissolved Cu in most surface seawaters,[11−13] reactions of $O_2^-$ with inorganic Cu species will not lead to significant buildup of Cu(I).

**Effect of Inorganically Complexed Cu Species on $[O_2^-]_{ss}$ in Seawater.** If the only significant sinks of $O_2^-$ are reactions with inorganically complexed Cu species and bimolecular dismutation, the steady-state concentration $[O_2^-]_{ss}$ is given by

$$[O_2^-]_{ss} = \text{formation rate}/(k_{4a}[\text{Cu(I)}] + k_{4b}[\text{Cu(II)}] + 2k_2[O_2^-]) \quad (19)$$

If the % [Cu(I)] reaches the steady-state value expected from reaction with superoxide (see above), $k_{cat}[Cu]_T$ can be substituted for $k_{4a}[\text{Cu(I)}] + k_{4b}[\text{Cu(II)}]$. The calculated effect of Cu on $[O_2^-]_{ss}$ as a function of the $O_2^-$ and total inorganically complexed Cu, assuming a steady state of Cu(I), is shown in Figure 8. If there are additional significant sources of Cu(I), such as photo-induced ligand-to-metal charge transfer reactions of organic Cu(II) complexes,[7] these calculations will underestimate the effect of Cu.

Typical values of total inorganically complexed Cu in surface seawater range from $10^{-14}$ to $10^{-12}$ M in the open ocean[11−13] and from $10^{-12}$ to $10^{-9}$ M in coastal waters.[14] Typical values of $O_2^-$ formation rates range from $2 \times 10^{-12}$ M s$^{-1}$ in the open ocean to $2 \times 10^{-10}$ M s$^{-1}$ in coastal waters.[2] Our results demonstrate that even at the low concentrations of inorganically complexed Cu generally found in surface seawaters, reactions with these species will be a more significant sink of $O_2^-$ than bimolecular dismutation under most conditions. This work therefore places an upper limit on $[O_2^-]_{ss}$ in seawater that is up to 2 orders of magnitude smaller than estimates neglecting the effect of inorganic Cu species.

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**Supporting Information Available:** Text providing pulse radiolysis details and Table S1, listing reactions and rate constants (4 pages). Ordering information is given on any current masthead page.

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