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Autoxidation of Uranium(V). Catalysis and Inhibition by Copper Ions

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The autoxidation of UO_2^+ in acidic aqueous solutions yields UO_2^{2+} and H_2O_2 as products. The initial step occurs with a rate constant $k_U = 31.4\ M^{-1}\ s^{-1}$. The reaction is catalyzed by aquacopper(II) ions, owing to the reaction between Cu^{2+} and UO_2^+ ($k = 915\ M^{-1}\ s^{-1}$) yielding Cu^+, which is rapidly reoxidized by O_2. Cu^{2+} also reacts with an intermediate produced in the direct reaction of UO_2^+ and O_2, and the combined effects of Cu^{2+} as catalyst and scavenger lead to an unusual dependence of the observed rate constant on $[Cu^{2+}]$. The role of superoxouranium(VI) and $HO_2^\bullet$ as reaction intermediates is discussed.

Introduction

Environmental considerations and the need to conserve energy have made it a high priority to redesign many of the existing industrial processes and create new ones. The use of (sun) light as an energy source would provide a highly desirable alternative to the burning of fossil fuels.

Photochemically-driven oxidations using O_2 and/or H_2O_2 as oxidants are relevant to both the protection of the environment and conservation of fossil fuels. O_2 and H_2O_2 are readily available and yield water as the ultimate oxidant-derived product, thus eliminating the problem of waste disposal. However, the reactivity of O_2 and H_2O_2 toward many relevant substrates is low, and efficient catalysts are required to bring the reaction rates into a useful range.

One possibility for a photocatalytic oxidation of a substrate with molecular oxygen is shown in Scheme 1, where cat stands for catalyst.

Scheme 1

$$\text{cat} + h\nu \rightarrow {}^*\text{cat} \qquad \text{(I-1)}$$

$$^*\text{cat} + \text{substrate} \rightarrow \text{reduced cat} + \text{oxidized substrate} \qquad \text{(I-2)}$$

$$\text{reduced cat} \xrightarrow{O_2} \text{cat} \qquad \text{(I-3)}$$

In order for the scheme to work, the excited state of the catalyst, *cat, has to be strongly oxidizing and sufficiently long-lived to engage in bimolecular reactions with substrates. To ensure high quantum yields for the product formation, the excited state should not be quenched by O_2. Furthermore, the reoxidation of the reduced catalyst by O_2 has to be fast and quantitative.

Visible light photolysis of the aquauranyl(VI) ion, UO_2^{2+}, generates an excited state that is long-lived, strongly oxidizing ($E^\circ = 2.6$ V) and reactive toward a large number of organic materials.[1,2] $^*UO_2^{2+}$ is also strongly luminescent and unreactive toward O_2. It would thus appear that UO_2^{2+} may be a good candidate for a photooxygenation catalyst, according to Scheme 2 and using 2-PrOH as a representative reducing substrate. Reaction II-2 has been shown to yield C-centered radicals as written.[3−5] Reaction II-3 is a complex, multistep process; however the chemistry involved is well understood.[6]

Scheme 2

$$UO_2^{2+} + h\nu\ (\text{visible}) \rightarrow {}^*UO_2^{2+} \qquad \text{(II-1)}$$

$$^*UO_2^{2+} + (CH_3)_2CHOH \rightarrow UO_2^{+} + {}^\bullet C(CH_3)_2OH + H^+ \qquad \text{(II-2)}$$

$$^\bullet C(CH_3)_2OH + O_2 \rightarrow \text{products} \qquad \text{(II-3)}$$

$$UO_2^{+} \xrightarrow{O_2} UO_2^{2+} \qquad \text{(II-4)}$$

The only unknown in Scheme 2 is the final step that converts UO_2^+ back to UO_2^{2+} and closes the catalytic cycle. We thus decided to explore the kinetics and mechanism of autoxidation of UO_2^+, which we recently found to be long-lived in a limited range of concentrations (≤1 mM) and pH (2−3).[7]

Experimental Section

Spectral and kinetic data were collected by use of a Shimadzu 3100 spectrophotometer. Fast reactions were monitored by laser flash photolysis using the flashlamp-pumped dye laser (Phasar) and a Nd-YAG (Applied Photophysics) laser system, which were described in detail earlier.[8,9]

Some of the UO_2^{2+} solutions were available from our previous work,[7] and some were prepared by dissolving UO_3 (Strem) in aqueous $HClO_4$. The two sources of uranium yielded identical results. Solutions of UO_2^+ were prepared photochemically from UO_2^{2+} and 2-propanol.[7]

The molar absorptivity of UO_2^{2+} at the 414-nm maximum in 0.1 M $HClO_4$ was determined to be 7.70 $M^{-1}\ cm^{-1}$, in good agreement with the published spectrum at 3 M ionic strength ($HClO_4$ + $NaClO_4$).[10] The molar absorptivity of UO_2^+ at the 255-nm maximum was

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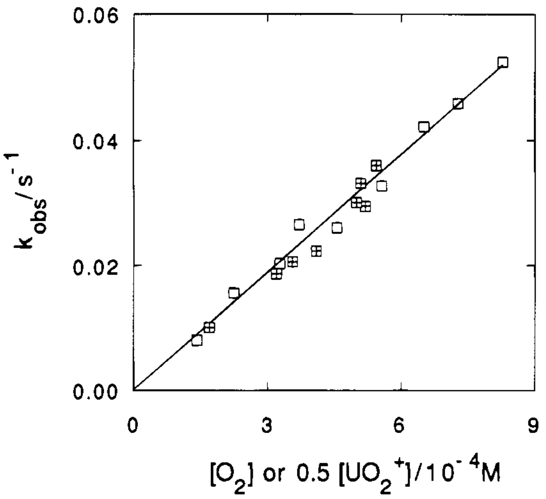

Figure 1. Plot of k_{obs} against the concentration of $[O_2]$ (plain squares) and $0.5[UO_2^+]$ (crossed squares) according to eq 2.

redetermined. Under typical conditions in this work, 5 mM $HClO_4$, 0.2 M 2-PrOH, and 0.02–1 mM UO_2^+, the value is 770 M^{-1} cm^{-1}, somewhat higher than that reported earlier (660 M^{-1} cm^{-1}).[7]

The disproportionation of UO_2^+ was negligibly slow on the time scale of most of the experiments. The acid concentration, 5 mM, was high enough to be considered essentially constant throughout each experiment. In several runs the concentraion of $HClO_4$ was raised to 10 mM without measurable effect on the kinetics of the oxygenation reaction. The ionic strength was determined by the concentrations of $HClO_4$ and the uranium ions, which place it in the range 5–8 mM for most of the work. No additional electrolyte was used to control the ionic strength more precisely, because higher salt concentrations accelerate the second-order disproportionation of UO_2^+ but should have minimal effect on the reaction of interest.[11] The latter point was confirmed in several experiments that had the ionic strength raised to 0.02 M with $LiClO_4$.

Spectrophotometric titrations were carried out at the 255-nm maximum and 232-nm minimum in the UO_2^+ spectrum. Most of the kinetic runs were monitored at 232 nm, where the absorbance increase (caused by the formation of UO_2^{2+}) was greater than the absorbance decrease at 255 nm. In a typical experiment, an air-free (argon saturated) solution of UO_2^+ was prepared in a 1-cm fluorescence quartz cell. The reaction with O_2 was initiated by filling the cell to capacity with a measured amount of O_2-saturated 5 mM $HClO_4$. All the kinetic experiments were carried out at 25 °C.

Results

Stoichiometry. Spectrophotometric titrations yielded the ratio $\Delta[UO_2^+]/\Delta[O_2] = 2.05$ (232 nm) and 2.10 (255 nm), establishing that the reaction takes place as in eq 1. The yield

$$2UO_2^+ + O_2 + 2H^+ \rightarrow 2UO_2^{2+} + H_2O_2 \qquad (1)$$

of H_2O_2 was determined iodometrically. A solution that initially contained equimolar amounts of UO_2^+ and O_2 (1.06×10^{-4} M) produced 4.9×10^{-5} M H_2O_2, close to the expected value of 5.3×10^{-5} M.

Kinetics of Autoxidation of UO_2^+. All the experiments were conducted under pseudo-first-order conditions using either UO_2^+ or O_2 in large excess over the other reagent. The kinetics were unaffected by changes in $[H^+]$ in the range 5–10 mM or by addition of up to 1 mM UO_2^{2+}. The pseudo-first-order rate constants are plotted against the concentration of excess reagent in Figure 1. Once the stoichiometric factor of 2 is taken into account, the data can be fitted to a single line with a slope of 62.7 ± 2.0 M^{-1} s^{-1}, eq 2.

$$-d[UO_2^+]/dt = -2d[O_2]/dt = 62.7[UO_2^+][O_2] \qquad (2)$$

The reaction is expected to produce either $HO_2^\bullet/O_2^{\bullet-}$ ($pK_a = 4.69$)[12] or $UO_2(HO_2)^{2+}$ [13,14] as intermediates, as discussed in detail later. In the meantime, the term intermediate will stand for all the forms of superoxide irrespective of the protonation state or the degree of complexation to UO_2^{2+}.

The intermediate might either oxidize the second mole of UO_2^+ or disproportionate. In both cases, the overall stoichiometry would remain 2:1, but the measured rate constants would be up to twice as large in the first scenario, as shown in Schemes 3 and 4.

Scheme 3

$$UO_2^+ + O_2 \xrightarrow{k_U} UO_2^{2+} + \text{Int } (HO_2^\bullet/O_2^{\bullet-} \text{ or } UO_2(HO_2^\bullet)^{2+})$$

$$UO_2^+ + \text{Int} \xrightarrow{H^+,\text{ fast}} UO_2^{2+} + H_2O_2$$

$$-d[UO_2^+]/dt = -2d[O_2]/dt = 2k_U[UO_2^+][O_2]$$

Scheme 4

$$UO_2^+ + O_2 \xrightarrow{k_U} UO_2^{2+} + \text{Int } (HO_2^\bullet/O_2^{\bullet-} \text{ or } UO_2(HO_2^\bullet)^{2+})$$

$$\text{Int} \xrightarrow{\text{fast}} 0.5O_2 + 0.5H_2O_2$$

$$-d[UO_2^+]/dt = -2d[O_2]/dt = k_U[UO_2^+][O_2]$$

Effect of Cu^{2+}. In order to obtain information on the nature and fate of the intermediate, a series of experiments were conducted in the presence of aquacopper(II) ions. The couple $Cu^{2+/+}$ catalyzes the disproportionation of $HO_2^\bullet$ [15,16] as shown in eqs 3 and 4.

$$Cu^{2+} + HO_2^\bullet \rightleftharpoons Cu^+ + O_2\,(+H^+) \qquad (3)$$

$$Cu^+ + HO_2^\bullet \xrightarrow{H^+} Cu^{2+} + H_2O_2 \qquad (4)$$

It is not known whether Cu^+ and Cu^{2+} react with $UO_2(HO_2^\bullet)^{2+}$, but it is reasonable to propose that they do. Even if this is not the case, copper ions will still catalyze the disproportionation of $UO_2(HO_2^\bullet)^{2+}$ by reacting with equilibrium amounts of free $HO_2^\bullet/O_2^{\bullet-}$ produced in eq 5.[13,14]

$$UO_2^{2+} + HO_2^\bullet \underset{100\ s^{-1}}{\overset{1.5 \times 10^5\ M^{-1}\ s^{-1}}{\rightleftharpoons}} [UO_2(HO_2^\bullet)^{2+}] \qquad (5)$$

If the reaction between UO_2^+ and O_2 takes place as in Scheme 3 ($k_{obs} = 2k_U$), then Cu^{2+} should be able to compete with UO_2^+ for the intermediate and slow down the reaction. In the limit of high $[Cu^{2+}]$ the rate constant would become k_U. If, on the other hand, the autoxidation reaction proceeds as in Scheme 4, then Cu^{2+} should have no effect on the kinetics.

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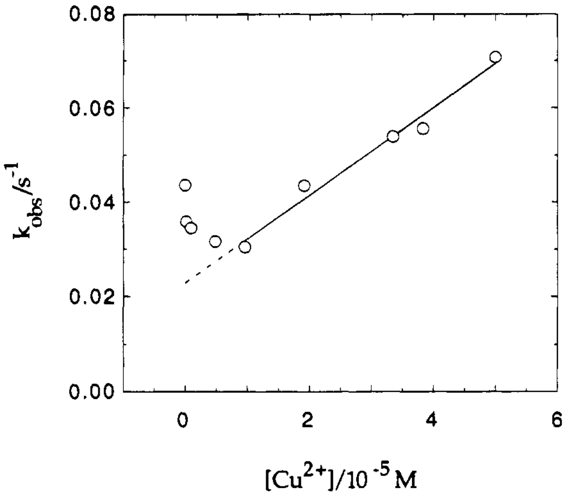

Figure 2. Plot of the observed rate constants against $[Cu^{2+}]$ for the reaction of UO_2^+ (0.01–0.1 mM) with O_2 (0.72 mM) in the presence of Cu^{2+} according to eq 10. At $[Cu^{2+}] \geq 0.01$ mM, the catalytic reaction of eq 6 dominates. The straight line defined by the data in this concentration regime has a slope $k_{cat} = 930$ M^{-1} s^{-1} and an intercept (0.0228 s^{-1}) that is only half the value measured in the absence of Cu^{2+}. At $[Cu^{2+}] < 0.01$ mM, the uncatalyzed autoxidation prevails, with Cu^{2+} and UO_2^+ competing for the intermediate. The observed rate constant for this path increases from $k_U[O_2]$ ($\alpha = 0$) to $2k_U[O_2]$ ($\alpha = 1$) as $[Cu^{2+}]$ decreases to zero.

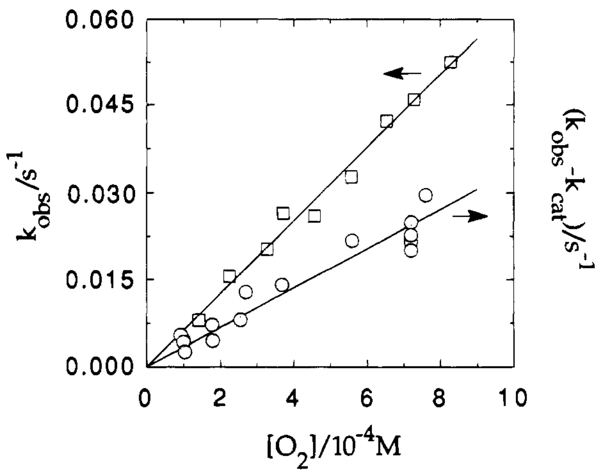

Figure 3. Kinetics of disappearance of UO_2^+ in the autoxidation reaction. The steeper line ($k = 62.9$ M^{-1} s^{-1}) represents the plot of the directly measured values of k_{obs} against $[O_2]$ in the absence of added Cu^{2+}. The rate constants obtained in the presence of Cu^{2+} were corrected for the catalytic path and also plotted against $[O_2]$. These data define the shallower line, $k = 33.9$ M^{-1} s^{-1}. The ratio of the two slopes is 1.86, close to the expected factor of 2.

Table 1. Summary of Kinetic Data for the Autoxidation of UO_2^+ and Related Reactions[a]

reaction	rate constant/M^{-1} s^{-1}
$UO_2^+ + O_2 \rightarrow UO_2(O_2)^+$	$k_U = 31.4 \pm 1.0$
$UO_2^+ + HO_2^\bullet \xrightarrow{H^+} UO_2^{2+} + H_2O_2$	$5 \times 10^5 < k_{U\text{-}int} < 5 \times 10^7$
$UO_2^+ + (NH_3)_5CoCl^{2+} \xrightarrow{5H^+}$ $UO_2^{2+} + Co^{2+} + 5NH_4^+ + Cl^-$	$k_{U\text{-}Co} = 10 \pm 1$
$UO_2^+ + Cu^{2+} \rightarrow UO_2^{2+} + Cu^+$	$k_{cat} = 930^b$ 900^c av 915 ± 15
$Cu^{2+} + HO_2^\bullet \xrightarrow{H^+} Cu^+ + H_2O_2$	$k_3 = 5 \times 10^{7\,d}$
$Cu^+ + O_2 \rightarrow Cu(O_2)^+$	$k_{-3} = 9.5 \times 10^{5\,e}$

[a] 25 °C, $[HClO_4] = 5$ mM, [2-PrOH] = 0.1–0.2 M. [b] O_2 used to scavenge Cu^+. [c] $(NH_3)_5CoCl^{2+}$ used to scavenge Cu^+. [d] Average of the values in refs 15, 16, and 21. [e] References 17 and 18.

The study of the effect of Cu^{2+} on the kinetics of reaction 1 was complicated by the occurrence of a direct reaction between Cu^{2+} and UO_2^+, eq 6. In effect, this reaction provides a pathway for catalyzed autoxidation owing to the rapid reaction of Cu^+ with O_2, regenerating Cu^{2+}, eq 7.[17,18] UO_2^+ is now consumed in two parallel reactions, autoxidation, eq 1, and catalyzed autoxidation, eqs 6 and 7.

$$Cu^{2+} + UO_2^+ \xrightarrow{k_{cat}} Cu^+ + UO_2^{2+} \tag{6}$$

$$Cu^+ \xrightarrow{O_2} Cu^{2+} \tag{7}$$

For a series of experiments using O_2 (0.72 mM) in a large excess over both UO_2^+ (0.01–0.1 mM) and Cu^{2+} (0.01–0.05 mM), a plot of k_{obs} vs $[Cu^{2+}]$ is linear with a slope $k_{cat} = 930$ M^{-1} s^{-1} and an intercept of 0.0228 s^{-1}, Figure 2. The latter value represents only 51% of that measured in the absence of Cu^{2+} (Figure 1), as would be expected if autoxidation takes place according to the mechanism in Scheme 3. The rate law for the stated conditions is given in eqs 8 and 9.

$$-d[UO_2^+]/dt = k_{obs}[UO_2^+] \tag{8}$$

$$k_{obs} = k_U[O_2] + k_{cat}[Cu^{2+}] \tag{9}$$

Additional data were collected at different concentrations of all three reagents, but always with O_2 in excess over UO_2^+. The measured rate constants were corrected for the contribution from the catalytic path ($k_{cat}[Cu^{2+}]$) and plotted against the concentration of O_2, Figure 3. For reasons that are not fully understood, the scatter was greater in experiments with added Cu^{2+}. This is particularly apparent in Figure 3, where each plotted value represents a difference between two comparable numbers. Also shown in Figure 3 are the rate constants for autoxidation that were measured in the absence of Cu^{2+}. The straight lines defined by the two sets of data have slopes 62.9 ± 1.2 M^{-1} s^{-1} ($[Cu^{2+}] = 0$) and 33.9 ± 1.3 M^{-1} s^{-1} ($[Cu^{2+}] \geq 0.01$ mM). The ratio of the two values, 1.86, is again close to 2 and confirms the earlier result that was obtained at a single O_2 concentration. The autoxidation of UO_2^+ is thus best described by Scheme 3 with $k_U = 31.4$ M^{-1} s^{-1}, Table 1.

As shown, even low concentrations of Cu^{2+} (≥0.01 mM) cut the rate constant by a factor of 2, indicating that UO_2^+ (0.01–0.10 mM) reacts with the intermediate more slowly than Cu^{2+} does. It should be possible to decrease the ratio $[Cu^{2+}]/[UO_2^+]$ to the point where the two metal ions compete for the intermediate. In this regime the rate constant for uncatalyzed autoxidation is $(1 + \alpha)k_U$, eq 10, where α represents the fraction of the intermediate that reacts with UO_2^+, $0 \leq \alpha \leq 1$, eqs 11 and 12. The rate constants for the reaction of the intermediate with Cu^{2+} and UO_2^+ are denoted $k_{Cu\text{-}int}$ and $k_{U\text{-}int}$, respectively.

As predicted, at low concentrations of Cu^{2+}, where the catalytic path is negligible, a decrease in $[Cu^{2+}]$ causes an increase in the observed rate constant, Figure 2. This is illustrated by the turnabout in the k_{obs} *vs* $[Cu^{2+}]$ plot at ≤0.01 mM Cu^{2+}.

The data were then fitted to eq 12, which contains the two unknown rate constants, $k_{Cu\text{-}int}$ and $k_{U\text{-}int}$. Because the kinetic data were obtained in experiments that had UO_2^+ as limiting reagent, the values of k_{obs} in eq 12 were calculated from the

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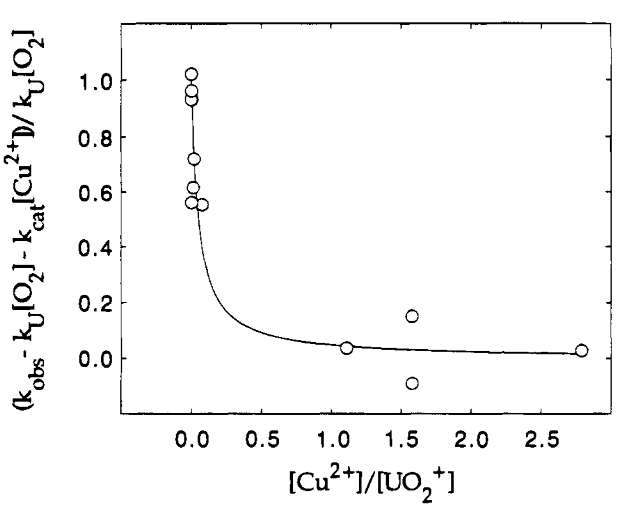

Figure 4. Plot of the left-hand side of eq 12 against the ratio $[Cu^{2+}]/[UO_2^+]$. The experiments had $[O_2]$ = 0.72 mM, $[UO_2^+]$ = 0.01–0.1 mM, and $[Cu^{2+}]$ = 0–5 mM.

$$k_{obs} = (1 + \alpha)k_U[O_2] + k_{cat}[Cu^{2+}] \qquad (10)$$

$$\alpha = \frac{k_{U\text{-int}}[UO_2^+]_{av}}{k_{U\text{-int}}[UO_2^+]_{av} + k_{Cu\text{-int}}[Cu^{2+}]} = \frac{1}{1 + \dfrac{k_{Cu\text{-int}}[Cu^{2+}]}{k_{U\text{-int}}[UO_2^+]_{av}}} \qquad (11)$$

$$\frac{k_{obs} - k_{cat}[Cu^{2+}] - k_U[O_2]}{k_U[O_2]} = \frac{1}{1 + \dfrac{k_{Cu\text{-int}}[Cu^{2+}]}{k_{U\text{-int}}[UO_2^+]_{av}}} \qquad (12)$$

first 20% of the reaction, and the concentrations of UO_2^+ were averaged over the same fraction of the reaction. The data fit, Figure 4, yielded the ratio $k_{Cu\text{-int}}/k_{U\text{-int}}$ = 20 ± 7.

Although far from ideal, the conditions chosen for these experiments were necessary to ensure that O_2 is the active oxidant and Cu^{2+} the catalyst. Had UO_2^+ been used in excess so as to keep its concentration essentially constant throughout each kinetic run, the direct UO_2^+–Cu^{2+} reaction (k_{cat} = 930 M^{-1} s^{-1}) would overshadow the UO_2^+–O_2 reaction (k_U = 31.4 M^{-1} s^{-1}). The data obtained under such conditions would not be useful in determining the reactivity of Cu^{2+} and UO_2^+ toward the intermediate produced in the UO_2^+–O_2 reaction.

The reaction of UO_2^+ with Cu^{2+} was presumed responsible for Cu^{2+} catalysis of the autoxidation of UO_2^+, and the rate constant k_{cat} = 930 M^{-1} s^{-1} was assigned to this step. To confirm this assignment, the kinetics of reaction 6 were studied directly under air-free conditions. From a single experiment using Cu^{2+} (0.05 mM) in excess over UO_2^+, a second-order rate constant of ~870 M^{-1} s^{-1} was calculated. However, when the range of concentrations was extended to higher $[Cu^{2+}]$, it became apparent that the plot of k_{obs} *vs* $[Cu^{2+}]$ is either nonlinear or has a nonzero intercept. A straight line drawn through the data has a slope of 600 M^{-1} s^{-1}, significantly less than 930 M^{-1} s^{-1} that was obtained under catalytic conditions. Also, added UO_2^{2+} slows down the air-free reaction but has no effect on the catalytic reaction.

We note that the reduction potentials[19] for the two couples involved, $Cu^{2+/+}$ (0.159 V) and $UO_2^{2+/+}$ (0.163 V), are comparable, which should lead to less than quantitative reaction and equilibration kinetics. Under such conditions, an excess of UO_2^{2+} should increase the rate constant, contrary to the observations. It is possible that Cu^+ reacts with both UO_2^+ and UO_2^{2+} and also that it disproportionates. It is difficult to predict what effect, if any, small (but unobserved) quantities of Cu^0 may have on the reaction.

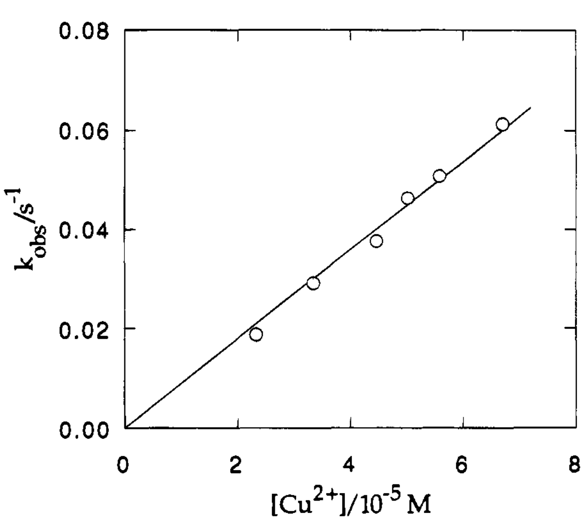

Figure 5. Plot of pseudo-first-order rate constants against $[Cu^{2+}]$ for the reaction of Cu^{2+} (0.02–0.07 mM) with UO_2^+ (0.1–0.2 mM) in the presence of 0.25–0.5 mM $(NH_3)_5CoCl^{2+}$ in Ar-saturated solutions. In these experiments Cu^{2+} is not consumed but instead acts as a catalyst for the UO_2^+– $(NH_3)_5CoCl^{2+}$ reaction.

We did not explore these possibilities further, because they do not bear on the study of the autoxidation of UO_2^+. In O_2-containing solutions all the Cu^+ is rapidly oxidized back to Cu^{2+}, and the rate constant calculated from the data in Figure 2 should be the true k_{cat}, if Cu^+ is indeed responsible for the complexities observed under air-free conditions. This hypothesis was tested by conducting the reaction of Cu^{2+} with UO_2^+ in the presence of $(NH_3)_5CoCl^{2+}$, another scavenger for Cu^+ ($k_{Cu\text{-}Co}$ = 4.9 × 10^4 M^{-1} s^{-1}).[20] The reaction was well behaved and obeyed first-order kinetics under conditions of excess Cu^{2+} and $(NH_3)_5CoCl^{2+}$. The observed rate constants were corrected for a small (2–12%) contribution from the direct oxidation of UO_2^+ by $(NH_3)_5CoCl^{2+}$ ($k_{U\text{-}Co}$ = 10 M^{-1} s^{-1} was determined in independent experiments). Such corrected rate constants showed no dependence on the concentrations of $(NH_3)_5CoCl^{2+}$, consistent with a scheme where the only role of $(NH_3)_5CoCl^{2+}$ is to reoxidize Cu^+ formed in reaction 6. The plot of the corrected rate constants against $[Cu^{2+}]$, Figure 5, is a straight line with a zero intercept and a slope of 900 M^{-1} s^{-1}, in excellent agreement with the value obtained in experiments on catalytic autoxidation of UO_2^+ (930 M^{-1} s^{-1}). This result establishes that the reaction of eq 6 is indeed rate determining in the Cu^{2+}-catalyzed autoxidation of UO_2^+.

Reaction of UO_2^+ with $HO_2^•/O_2^{•-}$. Several unsuccessful attempts were made to study the kinetics of this reaction. $HO_2^•/O_2^{•-}$ was generated by UV photolysis of H_2O_2 in O_2-saturated solutions containing formate and in air-free solutions containing large concentrations of H_2O_2. In the former case, the intermediates involved are $HO^• \rightarrow CO_2^{•-} \rightarrow HO_2^•/O_2^{•-}$, and in the latter, $HO^• \rightarrow HO_2^•/O_2^{•-}$. The chemistry involved is well-known[21] and will not be discussed here. Both methods failed in the presence of uranium ions, which form complexes with both

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H_2O_2 and HCO_2^-, resulting in a complex mixture of uranium species and inordinately large absorbances in the UV. Yet another method involved the photolysis of $Ru(bpy)_3^{2+}$ in the presence of MV^{2+} and O_2.[22] In this scheme UO_2^+ and $Ru(bpy)_3^{3+}$ compete for $HO_2^•$. Unfortunately, the kinetic behavior of the system was more complex than expected, presumably because of the direct reaction between the two competitors.

The ESR detection of $HO_2^•$ and/or $UO_2(HO_2^•)^{2+}$ in frozen solution was not successful, presumably because of the low steady state concentrations of these intermediates.

Discussion

The standard reduction potentials[19] and self-exchange rate constants are available for the couples $O_2/O_2^{•-}$ ($E° = -0.16$ V and $1 \le k_{self} \le 10$ M^{-1} s^{-1} [23,24]) and $UO_2^{2+/+}$ ($E° = 0.16$ V and $1 \le k_{self} \le 15$ M^{-1} s^{-1} [7]). With use of these parameters, one estimates $0.002 \le k_{13} \le 0.02$ M^{-1} s^{-1} for the thermodynamically unfavorable ($K = 4 \times 10^{-6}$) outer-sphere process of eq 13a. The measured rate constant for autoxidation, $k_U = 31.4$ M^{-1} s^{-1}, exceeds this value by more than 3 orders of magnitude, seemingly ruling out reaction 13a as a major pathway. More likely, the reaction yields initially a uranium–dioxygen intermediate, probably a superoxouranium(VI) complex, eq 13b, followed by rapid steps that ultimately consume an additional mole of UO_2^+.

$$UO_2^+ + O_2 \rightarrow UO_2^{2+} + O_2^{•-} \qquad (13a)$$

$$UO_2^+ + O_2 \rightarrow [U^{VI}O_2[O_2^{-•})]^+ \qquad (13b)$$

It is tempting to propose that the intermediate is the conjugate base of the known species that was previously generated from UO_2^{2+} and $HO_2^•$, eq 5.[13,14] If so, the rapid protonation of $[U^{VI}O_2(O_2^{•-})]^+$ will convert it to $[UO_2(HO_2^•)^{2+}]$. The acid concentration (0.1 M $HClO_4$) employed in the study of $[UO_2(HO_2^•)^{2+}]$[13,14] is admittedly higher than that in the present study (5–10 mM), but this change in pH is not expected to change significantly the nature of the species.

$[UO_2(HO_2^•)]^{2+}$ will oxidize the second mole of UO_2^+ either in a direct reaction, eq 14a, or by prior dissociation of $HO_2^•$, followed by UO_2^+–$HO_2^•$ reaction, eq 5 and 14b.

$$UO_2^+ + [UO_2(HO_2^•)]^{2+} \xrightarrow{H^+} 2UO_2^{2+} + H_2O_2 \qquad (14a)$$

$$UO_2^+ + HO_2^• \xrightarrow{H^+} UO_2^{2+} + H_2O_2 \qquad (14b)$$

At ≤ 0.05 mM UO_2^+, a rate constant $k_{14a} \ge 2 \times 10^7$ M^{-1} s^{-1} would be required for 90% of $[UO_2(HO_2^•)]^{2+}$ to react directly with UO_2^+ rather than dissociate ($k_{-5} = 100$ s^{-1}). In that case copper ions must also react with $[UO_2(HO_2^•)]^{2+}$, given that they compete for the intermediate 20 times more efficiently than UO_2^+ does. This ratio, and low concentrations of Cu^{2+} in these experiments (≤ 0.01 mM), would place the rate constant for the reaction of Cu^{2+} with $[UO_2(HO_2^•)]^{2+}$ at $\ge 2.5 \times 10^9$ M^{-1} s^{-1}, some 25–100 times faster than the reaction of Cu^{2+} with $HO_2^•$.[15,16] We consider this unlikely, because coordinated $HO_2^•$ should not be a more reactive *reductant* than the free radical. Thus, at least at ≤ 0.05 mM UO_2^+, we prefer a mechanism whereby $[UO_2(HO_2^•)]^{2+}$ dissociates to yield $HO_2^•$, which in turn reacts with UO_2^+.

The same argument, and using $k = 5 \times 10^7$ M^{-1} s^{-1} (an average of the published values) for the reaction of Cu^{2+} with $HO_2^•$,[15,16,21] leads us to conclude that the intermediate reacting with low concentrations of Cu^{2+} is also free $HO_2^•$, at least in the concentration range where the competition ratio $k_{Cu\text{-}int}/k_{U\text{-}int} = 20$ was determined. Under these conditions the mechanism is as given in Scheme 5.

Scheme 5

$$UO_2^+ + O_2 \xrightarrow{31.4} [U^{VI}O_2(O_2^{•-})]^+ \xrightarrow{H^+,\ fast} UO_2^{2+} + HO_2^• \qquad (V\text{-}1)$$

$$HO_2^• + Cu^{2+} \overset{-H^+}{\rightleftharpoons} Cu^+ + O_2 \qquad (3)$$

$$HO_2^• + UO_2^+ \xrightarrow{H^+} UO_2^{2+} + H_2O_2 \qquad (14b)$$

$$HO_2^• + Cu^+ \xrightarrow{H^+,\ 2.3 \times 10^9} Cu^{2+} + H_2O_2 \qquad (4)$$

We cannot rule out a direct reaction between $[UO_2(HO_2^•)]^{2+}$ and UO_2^+, eq 14a, in experiments with excess UO_2^+ (≤ 1 mM). Under such conditions, a rate constant required for this path to dominate completely over the dissociation of $HO_2^•$ is $\ge 1 \times 10^6$ M^{-1} s^{-1}. Similarly, a direct reaction between Cu^{2+} and $[UO_2(HO_2^•)]^{2+}$ may take place at high $[Cu^{2+}]$ (≥ 0.01 mM).

The ratio $k_{Cu\text{-}int}/k_{U\text{-}int}$ (20) does not simply reflect the relative reactivity of $HO_2^•$ toward Cu^{2+} and UO_2^+ in Scheme 5. Rather, $k_{Cu\text{-}int}$ represents the overall rate constant for catalytic disproportionation of $HO_2^•$ and thus depends on the rates of both reactions 3 and 4. Despite the smaller rate constant, reaction 3 is probably the faster of the two, given the concentration advantage of Cu^{2+}. The scheme is even more complicated by the involvement of another superoxometal complex, $Cu(O_2)^+$, an intermediate in reaction 3. Significant fractions of Cu^+ and $HO_2^•$ may,[17,18] and probably do, exist in the form of $Cu(O_2)^+$ under our experimental conditions, which makes the calculation of $k_{U\text{-}int}$ from $k_{Cu\text{-}int}/k_{U\text{-}int}$ unreliable. Indeed, calculations that treated Cu^+ and $HO_2^•$ as steady state intermediates but ignored $Cu(O_2)^+$ yielded unreasonably low values for $k_{U\text{-}int}$.

Still, the upper and lower limits for $k_{U\text{-}int}$ can be estimated. The reaction of UO_2^+ with $HO_2^•$ has to be much faster than disproportionation of $HO_2^•$ ($k = 1 \times 10^6$ M^{-1} s^{-1} at 5 mM H^+)[21] under conditions in Figure 1, i.e. $10^6[HO_2^•] < k_{U\text{-}int}[UO_2^+]$. From this inequality and treating $HO_2^•$ as a steady-state intermediate, we obtain $k_{U\text{-}int} > 5 \times 10^5$ M^{-1} s^{-1}. The other limit is set by the requirement that 0.01 mM Cu^{2+} react with the intermediate much faster than 0.01 mM UO_2^+ does, Figure 4. No matter how complicated the subsequent chemistry, the competition between Cu^{2+} and UO_2^+ has to favor Cu^{2+}. This leads to $k_{U\text{-}int} < 5 \times 10^7$ M^{-1} s^{-1}. Note that the rate constant at the midpoint of the range, 5×10^6 M^{-1} s^{-1}, is close to 3×10^6 M^{-1} s^{-1}, the value one calculates from $k_{Cu\text{-}int}/k_{U\text{-}int}$. Thus despite the complicated mechanism, it appears that the competition between the major species, Cu^{2+} and UO_2^+, at the very first branching point determines the course of the reaction.

Conclusions

The autoxidation of UO_2^+ takes place with a stoichiometry $[UO_2^+]$:$[O_2]$ = 2:1 and produces UO_2^{2+} and H_2O_2 quantitatively.

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The initial step has a rate constant $k_U = 31.4\ M^{-1}\ s^{-1}$ and produces $UO_2(HO_2^\bullet)^{2+}$, which dissociates rapidly to UO_2^{2+} and $HO_2^\bullet$. In the second, rapid step either $HO_2^\bullet$ or $UO_2(HO_2^\bullet)^{2+}$ oxidizes an additional mole of UO_2^+. Cu^{2+} exerts a dual effect on the reaction. When present at low concentrations ($<10^{-5}$ M), Cu^{2+} slows down the reaction by scavenging $HO_2^\bullet$ and/or $UO_2(HO_2^\bullet)^{2+}$ and changing the stoichiometry of autoxidation to 1:1. At concentrations above 1×10^{-5} M, Cu^{2+} catalyzes the reaction by opening a new pathway whereby UO_2^+ reduces Cu^{2+} to Cu^+, which is then rapidly reoxidized by O_2. Even in the absence of catalysis, the autoxidation of UO_2^+ is fast enough to make UO_2^{2+} a good candidate for catalyst in photocatalytic oxygenation reactions.

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