Kinetics of the Superoxide Radical Oxidation of [Cobalt sepulchrate](2+). A Flash Photolytic Study

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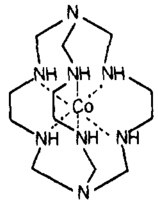
Abstract: The postulated formation of the superoxide radical anion, O_2^-, as an intermediate in the reaction of $Co(sep)^{2+}$ (sep = sepulchrate) with molecular oxygen has now been confirmed by a trapping reaction with Cu^{2+}. In the absence of Cu^{2+}, O_2^- oxidizes a second $Co(sep)^{2+}$ to $Co(sep)^{3+}$. The latter reaction, studied directly by use of the flash photolytic technique, has at 25 °C a rate constant of $(4.6 \pm 1.1) \times 10^7$ M^{-1} s^{-1}, independent of pH in the range 11.3–12.6. Nitrogen perdeuteration yields d(N)^6-$Co(sep)^{2+}$, which reacts with O_2 at the same rate but with O_2^- 2.1 times more slowly. The proposed mechanism of the O_2^- reaction consists of the hydrogen atom abstraction from a N–H bond of $Co(sep)^{2+}$ by O_2^-, followed by the rapid protonation of the products, Co^{III}(sep-H)$^{2+}$ and HO_2^-, to form $Co(sep)^{3+}$ and H_2O_2. In contrast, the reaction between $Co(sep)^{2+}$ and O_2, which shows no kinetic isotope effect, occurs by outer-sphere electron transfer.

A recent paper reported the kinetics of the autoxidation of cobalt sepulchrate[1,2] (henceforth $Co(sep)^{2+}$) in acidic aqueous solution.



$Co(sep)^{2+/3+}$

The structure of $Co(sep)^{2+}$, with the cobalt center encapsulated inside the saturated hexadentate ligand,[1] makes it unlikely that the oxidation proceeds by an inner-sphere pathway. The mechanism thus postulated[1] consists of an outer-sphere electron transfer as shown in eq 1, the rate-limiting step. The subsequent rapid

$$Co(sep)^{2+} + O_2 \underset{}{\overset{H^+}{\rightleftharpoons}} Co(sep)^{3+} + HO_2/O_2^- \qquad (1)$$

$$HO_2 \rightleftharpoons O_2^- + H^+ \qquad pK_a = 4.69^3 \qquad (2)$$

$$HO_2 + Co(sep)^{2+} \xrightarrow{H^+} Co(sep)^{3+} + H_2O_2 \qquad (3a)$$

$$O_2^- + Co(sep)^{2+} \xrightarrow{2H^+} Co(sep)^{3+} + H_2O_2 \qquad (3b)$$

$$2HO_2/O_2^- \xrightarrow{H^+} H_2O_2 + O_2 \qquad (4)$$

steps completing the reaction are one of the following alternatives: Either the superoxide radical rapidly oxidizes a second $Co(sep)^{2+}$, as in eq 3, or it undergoes self-reaction or disproportionation, as in eq 4. The overall stoichiometry and the final products are identical in the two cases, eq 5, which makes the alternatives

$$2Co(sep)^{2+} + O_2 + 2H^+ = 2Co(sep)^{3+} + H_2O_2 \qquad (5)$$

indistinguishable on the basis of the kinetics and product analysis data reported.

Either alternative is chemically reasonable. In acidic solutions the self-reaction of the superoxide radical (eq 4) is fast and pH dependent.[3] On the other hand, it has not been known whether $Co(sep)^{2+}$ reacts directly with either superoxide species. We can now document that oxidation of superoxide and not its disproportionation occurs as the second step. This article reports the direct determination of k_{3b} and considers the mechanism of both reactions, eq 1 and eq 3b.

We also demonstrate by a trapping reaction that the superoxide radical is indeed formed as an intermediate during the oxidation of $Co(sep)^{2+}$ by molecular oxygen, eq 1. The detailed analysis establishes that even in acidic solution reduction of superoxide (as HO_2, via eq 3a) occurs in preference to disproportionation. This analysis permits a lower limit to be set for the rate constant for the oxidation of $Co(sep)^{2+}$ by HO_2, eq 3a.

Experimental Section

Materials. Alkaline solutions of O_2^- for the preliminary experiments were prepared by irradiating oxygen-saturated solutions containing 0.004–0.04 M KOH, 2 M 2-propanol, 5×10^{-6} benzophenone, and 4×10^{-5} M EDTA with the 254-nm light in a Rayonet photochemical reactor as described previously.[4] Solutions of $Co(sep)^{2+}$ were prepared by dissolving a known amount of the solid $[Co(sep)](CF_3SO_3)_2$[1] in oxygen-free water under argon.

The N-perdeuterated cobalt(II) complex d(N)^6-$Co(sep)^{3+}$ was prepared by twice evaporating a solution of $[Co(sep)]Cl_3$ (1.0 g) in D_2O (20 mL) to dryness on a rotary evaporator. Independent ^1H NMR experiments showed that this was sufficient to effect complete conversion to the N–D form. The cobalt(II) complex was prepared by dissolving this sample in D_2O (30 mL) and reducing with amalgamated zinc. Proton exchange is expected to be much slower in the Co(II) complex (by ~10^6), and the enrichment of d(N)^6-$Co(sep)^{2+}$ should remain for the duration of the kinetics experiments.

^{13}C and ^2H NMR spectra of $Co(sep)^{3+}$ produced in the reaction of $Co(sep)^{2+}$ with O_2 in D_2O were run on samples prepared in the following way: $[Co(sep)]Cl_3$ (0.5 g) was dissolved in oxygen-free D_2O (40 mL, 99.75%) and reduced with amalgamated Zn under N_2. After complete reduction the solution was decanted from the Zn and oxidized with O_2. The reaction mixture was acidified, poured on a Dowex 50W-X2 cation exchange resin, and eluted with 1 M HCl to remove Zn^{2+}. The $Co(sep)^{3+}$ was eluted with 3 M HCl, the volume was reduced on a vacuum evaporator, precipitated with ethanol and ether, and dried over P_2O_5 under vacuum overnight. ^{13}C NMR spectra of saturated solutions in D_2O were recorded by use of JEOL JNB-FX 60 and JEOL FX-200 spectrometers. The ^2H NMR spectrum was recorded in H_2O on a Bruker CXP-200 spectrometer.

All other chemicals were of the highest purity available and were used as received. Triply distilled water was used throughout.

Flash Photolytic Experiments. In these experiments small aliquots of $Co(sep)^{2+}$ were injected into a 10-cm quartz spectrophotometric cell containing the thermostated, air-saturated solution of all the components necessary for the photochemical generation of O_2^-.[4] These solutions were then flashed within ~15 s after mixing. Owing to the relatively rapid reaction between oxygen and $Co(sep)^{2+}$, some of the latter complex was always oxidized in the 15-s interval, and the solutions flashed contained a mixture of $Co(sep)^{2+}$ and $Co(sep)^{3+}$. The latter complex shows high

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(1) Creaser, I. I.; Geue, R. J.; Harrowfield, J. MacB,; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016.
(2) Sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane.
(3) Bielski, B. H. J. *Photochem. Photobiol.* **1978**, *28*, 645.
(4) McDowell, S.; Bakač, A.; Espenson, J. H. *Inorg. Chem.*, **1983**, *22*, 847.

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absorptivity in the UV and it absorbed some of the flash light at the expense of benzophene. Depending on the relative concentrations of the two at the moment of the flash, variable amounts of O_2^- were produced.

The flash photolysis was conducted with unfiltered UV–vis radiation from fast-extinguishing xenon flash lamps in the Xenon Corp.'s Model 710 system.[5] A typical flash energy was 50 J. A Nicolet digitizing oscilloscope was used to record the transmittance change accompanying the reaction, which was monitored at the 480-nm maximum of Co(sep)$^{3+}$. Initial concentrations of Co(sep)$^{2+}$, O_2^-, and Co(sep)$^{3+}$ were calculated for each experiment from the absorbance changes observed in the two reactions and molar absorptivities at 480 nm of Co(sep)$^{2+}$ (8 M^{-1} cm^{-1}) and Co(sep)$^{3+}$ (190–207 M^{-1} cm^{-1}, pH dependent). The concentrations of Co(sep)$^{2+}$ and O_2^- at different times during the reaction were then calculated from the absorbance–time readings by standard procedures. The kinetic data obtained in this manner were fit to a second-order rate expression.

All the experiments were done at 25.0 ± 0.2 °C. No attempt was made to keep the ionic strength constant, and it varied with the concentration of KOH. Some preliminary experiments were done on a Canterbury SF-3A stopped-flow spectrophotometer. A Cary Model 219 spectrophotometer was used for spectral measurements and for monitoring the kinetics of the Co(sep)$^{2+}$–O_2 reaction.

Results

Co(sep)$^{2+}$–O_2^- Reaction. Owing to the rapid decomposition of the superoxide in acidic and neutral aqueous solutions,[3,4] all the experiments were done in alkaline solutions, pH 11.3–12.6. Under the experimental conditions, employed, the lifetime of the superoxide in this pH range varies from several minutes to approximately an hour.[3,4] Neither Co(sep)$^{3+}$ nor Co(sep)$^{2+}$ is appreciably deprotonated in this pH range on the basis of earlier observations,[1] although pK_a values have not been determined.

In a preliminary experiment an aliquot of a neutral aqueous solution of Co(sep)$^{2+}$ was added to an oxygen-saturated solution of O_2^- in a spectrophotometric cell, such that the concentrations upon mixing were [Co(sep)$^{2+}$] = 2.8 × 10^{-4} M, [O_2^-] = 1.5 × 10^{-4} M, [O_2] = 1 × 10^{-3} M, [2-propanol] = 2 M, pH 12.2 (KOH). The solution showed a large absorbance increase at 480 nm in the mixing time (5 s), corresponding to the formation of Co(sep)$^{3+}$. This was followed by a smaller and slower absorbance increase due to the formation of additional Co(sep)$^{3+}$ in the reaction of the excess Co(sep)$^{2+}$ with O_2. In an otherwise identical experiment, but omitting O_2^-, the absorbance increase in the mixing time was smaller and corresponded entirely to the initial stages of the Co(sep)$^{2+}$–O_2 reaction.

In another similar experiment O_2^- (1.5 × 10^{-4} M) was used in excess over Co(sep)$^{2+}$ (1.04 × 10^{-4} M), with other concentrations as above. The oxidation of Co(sep)$^{2+}$ was complete in the mixing time, and no additional absorbance change was observed over a period of several minutes. Under identical conditions the reaction between Co(sep)$^{2+}$ and O_2 takes ~20 s to go to completion.

Oxygen-free solutions of O_2^- were just as effective in oxidizing Co(sep)$^{2+}$. An oxygen-saturated solution of 2 M 2-propanol, 5 × 10^{-6} M Ph_2CO, and 4 × 10^{-5} M EDTA at pH 12.2 was irradiated at 254 nm to produce ~1.5 × 10^{-4} M O_2^-. This solution was then purged with a vigorous stream of Ar for ~10 min and then reacted with Co(sep)$^{2+}$ (1.01 × 10^{-4} M). The oxidation was again complete within mixing time.

Addition of up to 2 × 10^{-4} M H_2O_2 to the reaction solutions did not affect the rate of the Co(sep)$^{2+}$–O_2 reaction.[6] This is an important observation since hydrogen peroxide is the decomposition product of HO_2/O_2^- and thus always present in small amounts in aqueous solutions of the superoxide. It is also the final product of the oxidation of Co(sep)$^{2+}$ by molecular oxygen.

Flash Photolytic Experiments. Irradiation of aqueous, air-saturated solutions of Co(sep)$^{2+}$, Ph_2CO, 2-propanol, and EDTA, in the flash-photolysis instrument produced a rapid but measurable increase in absorbance, which we ascribe to the reaction of O_2^- with Co(sep)$^{2+}$, producing Co(sep)$^{3+}$. A subsequent slow absorbance increase is again caused by the oxidation of the excess of Co(sep)$^{2+}$ by oxygen. An illustration of a typical kinetic trace at 480 nm is shown in Figure 1.

To avoid a substantial amount of reaction between Co(sep)$^{2+}$ and O_2 prior to the flash, low initial concentrations of Co(sep)$^{2+}$ (<1.5 × 10^{-4} M) and air-saturated[7] solutions were used. Under

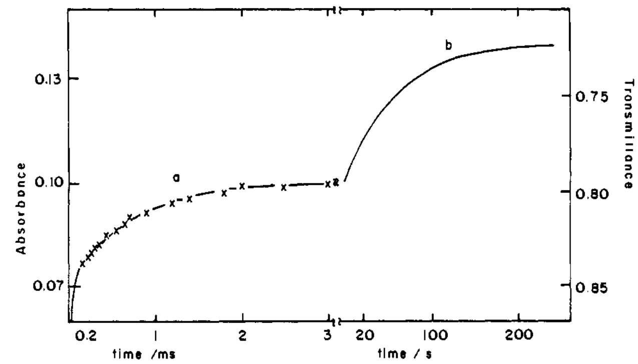

Figure 1. Absorbance–time dependence in the flash photolysis of air-saturated solutions containing Co^{II}(sep)$^{2+}$, 2 M 2-propanol, 5 × 10^{-6} M Ph_2CO, and 4 × 10^{-5} M EDTA. The two segments following the flash (duration ~0.15 ms) are shown: (a) The reaction of Co(sep)$^{2+}$ (3.46 × 10^{-5} M) with O_2^- (1.26 × 10^{-5} M), entry 2 from Table I. Crosses represent the experimental points. (b) The reaction of excess Co(sep)$^{2+}$ with oxygen observed after the reaction with O_2^- was completed. The absorbance was monitored at the 480-nm maximum of Co(sep)$^{3+}$.

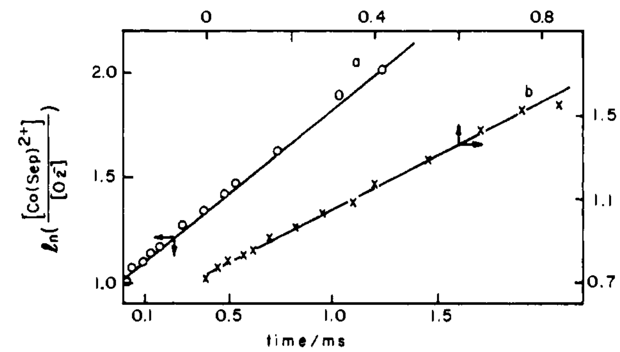

Figure 2. Two typical second-order kinetic plots for the reaction of Co(sep)$^{2+}$ with O_2^-. Plots a and b refer to entries 2 and 7 from Table I, respectively.

Table I. Kinetic Data for the Reaction of Co(sep)$^{2+}$ with Superoxide Radical Ions at 25 °C[a]

pH	10^5[Co(sep)$^{2+}$]$_0$/M	10^5[O_2^-]$_0$/M	$10^{-7}k$/(M^{-1} s^{-1})
11.3	4.12	1.07	4.79
11.3	3.46	1.26	3.76
11.3	3.30	1.88	6.06
11.3	2.89	1.18	6.37
11.4	5.56	1.51	3.80
11.4	4.17	2.03	3.98
11.4	3.58	1.75	5.65
11.6	7.82	2.18	3.20
11.6	5.40	2.10	3.88
11.6	5.35	1.84	3.20
11.6	3.62	2.82	5.28
12.6	5.62	1.70	5.87
12.6	3.56	2.90	4.17
11.5 (pD)	3.14	1.54	2.25[b]
11.5	5.15	1.41	2.18[c]
			av 4.6 ± 1.1

[a] All solutions were air-saturated ([O_2] = 2.5 × 10^{-4} M) and contained 1-2 M 2-propanol, 4 × 10^{-5} M EDTA, (5-10) × 10^{-6} M Ph_2CO, and (2-9) × 10^{-5} M Co(sep)$^{3+}$. [b] Using d(N)^6-Co(sep)$^{2+}$ in 92% D_2O). [c] Using d(N)^6-Co(sep)$^{2+}$ in H_2O.

(5) Ryan, D. A. Ph.D. Thesis, Iowa State University, 1981.
(6) This result is similar to the previous findings[1] in acidic aqueous solutions that the oxidation of Co(sep)$^{2+}$ by H_2O_2 occurs at least 10 times more slowly than its oxidation by molecular oxygen.

these conditions oxygen was always present in a large excess, a condition necessary for the formation of O_2^- to take place. The concentrations of O_2^- produced varied between 1.1 and 2.9×10^{-5} M, depending on the amount of Ph_2CO and $Co(sep)^{3+}$ initially present in solution. The fit to the second-order rate law of eq 6

$$-d[O_2^-]/dt = k_{3b}[O_2^-][Co(sep)^{2+}] \quad (6)$$

is shown in Figure 2; the rate constants are summarized in Table I. The rather large scatter is due primarily to the uncertainties in the initial concentrations. The rate constant k_{3b} is within the error independent[8] of pH in the range 11.3–12.6 and of the concentration of $Co(sep)^{3+}$. The average value is $k_{3b} = (4.6 \pm 1.1) \times 10^7$ M^{-1} s^{-1}.

In two experiments using low initial concentrations of $Co(sep)^{2+}$ ($<2 \times 10^{-5}$ M), the first rapid reaction was not followed by a slow step. This indicates that O_2^- was present in excess, such that no $Co(sep)^{2+}$ was left to react with oxygen. These kinetic traces could not be used to determine a rate constant, since the initial concentration of O_2^- was not known. Assuming, however, that $[O_2^-]$ was not very different from the experiments with higher ($[Co(sep)^{2+}] + [Co(sep)^{3+}]$), a rate constant of 10^7–10^8 M^{-1} s^{-1} can be estimated, in qualitative agreement with the value obtained with $Co(sep)^{2+}$ in excess.

Subsequent flashing of completely oxidized solutions of the cobalt sepulchrate complex caused a small absorbance increase, usually of the order of ~10% of the absorbance change produced in the first flash. At present we cannot fully explain this observation, although it seems likely that it involves the direct photochemistry of $Co(sep)^{3+}$. The reaction of O_2^- with $Co(sep)^{3+}$ has to be ruled out as a possibility, since mixtures of the two show a stable absorbance over extended periods of time.

^{13}C and ^{2}H NMR Spectra. The $Co(sep)^{3+}$ produced in the reaction of d(N)^6-$Co(sep)^{2+}$ with O_2 in D_2O exhibits identical ^{13}C NMR spectra, both coupled and decoupled, as that produced in an otherwise identical experiment using H_2O as solvent.[1] Specifically, there is no indication in the ^{13}C spectrum that any deuterium was incorporated into the methylene groups in the complex. Similarly, no signal attributable to a –CHD group was observed in the ^{2}H NMR spectrum of the complex produced by oxidation of $Co(sep)^{2+}$ by O_2 in D_2O.

Is O_2^- an Intermediate in the $Co(sep)^{2+}$–O_2 Reaction? The results just described show how authentic O_2^- reacts with $Co(sep)^{2+}$, but they do not address the question of O_2^- really being an intermediate in the oxygen reaction. That O_2^- is an intermediate is a plausible interpretation, but it was not verified earlier.[1] The acid-independent rate constant reported[1] for the oxidation of $Co(sep)^{2+}$ by molecular oxygen is $k_{1a} = 43 \pm 5$ M^{-1} s^{-1} at pH 1–3, a value that we confirm up to pH 7. Moreover, the reaction rate was shown to be photochemically insensitive at light levels present in the spectrophtometer, since intermittently interrupting the light beam impinging on the sample during a kinetic run was without effect.

To address the question stated, we studied the effect of small amounts of Cu^{2+} on the rate constant for the reaction of $Co(sep)^{2+}$ with O_2. The reaction of Cu^{2+} with O_2^- occurs at close to diffusion-controlled rates.[9] One therefore expects a kinetic effect of added Cu^{2+} if the superoxide radical is an intermediate in the reaction of O_2 with $Co(sep)^{2+}$. Assuming that reactions 1a and 3a take place in acidic solutions, the rate law of eq 7 will apply.

$$Co(sep)^{2+} + O_2 \xrightarrow{H^+} Co(sep)^{3+} + HO_2 \quad (1a)$$

$$Co(sep)^{2+} + HO_2 \xrightarrow{H^+, \text{ fast}} Co(sep)^{3+} + H_2O_2 \quad (3a)$$

$$-d[Co(sep)^{2+}]/dt = 2k_{1a}[Co(sep)^{2+}][O_2] \quad (7)$$

In the presence of Cu^{2+}, reaction 8 replaces reaction 3a, and the

$$Cu^{2+} + HO_2 \rightarrow Cu^+ + O_2 + H^+ \quad (8)$$

rate law changes to

$$-d[Co(sep)^{2+}]/dt = k_{1a}[Co(sep)^{2+}][O_2] \quad (9)$$

The Cu^+ produced in reaction 8 will be rapidly oxidized by O_2[10] and/or H_2O_2 to Cu^{2+}. In the two limiting cases the observed rate constant will change from $2k_{1a}$ (Cu^{2+} absent; HO_2 reacts as in eq 3a) to k_{1a} (Cu^{2+} present; HO_2 reacts as in eq 8).

The data in Table II show the effect of Cu^{2+} on the rate constant at pH ~4 and 1. In the presence of even small amounts of Cu^{2+} (3.8×10^{-4} M) at pH 3.8–4.5 the expected decrease in the rate

Table II. Kinetic Data for the Reaction of $Co(sep)^{2+}$ with Molecular Oxygen at 25 °C[a] in the Absence and Presence of Cu^{2+} Ions

$10^4[Cu^{2+}]$	pH	k/s^{-1}
	1-3	0.102 ± 0.004[b]
	2	0.0969
	7	0.102
	7	0.101[c]
	11.6	0.121
	12.6	0.144
2.23	1	(0.0753)[d]
3.80	1	(0.0820)[d]
3.80	4.5	0.0553[d]
3.80	4.5	0.0630[c]
7.60	4.2	0.0592[d]
7.60	4.2	0.0533[c]
11.3	4.0	0.0585[d]
18.9	3.8	0.0590[c]

[a] $[Co(sep)^{2+}] = (1.5-1.6) \times 10^{-4}$ M, $[O_2] = 1.26 \times 10^{-3}$ M (calculated from the data in: Linke, W. F. "Solubilities, Inorganic and Metal-Organic Compounds"; 4th ed.; American Chemical Society: Washington, D.C.; 1965); ionic strength = [KOH] (pH 11.6–12.6) or $3[Cu^{2+}] + [HClO_4]$ (pH 1–4.5). [b] Calculated from the data for six runs given in ref 1. [c] In the presence of 0.1 M t-BuOH. [d] From the first ~50% of the reaction. At pH 1 the Cu^{2+}–$Co(sep)^{2+}$ reaction contributes significantly to the overall rate constant (see text).

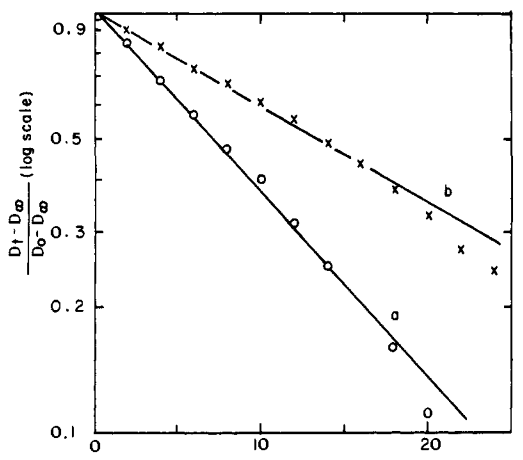

Figure 3. Effect of Cu^{2+} on the rate constant for the reaction of $Co(sep)^{2+}$ with oxygen. Plots a and b refer to entries 3 and 12 from Table II, respectively. The ratio of the rate constants for these two runs in 1.89.

(7) The use of O_2-saturated (rather than air-saturated) solutions was not feasible, because the reaction of O_2 with $Co(sep)^{2+}$ becomes too important. In the ~15-s delay time between the injection of $Co(sep)^{2+}$ into oxygenated solutions containing all other components and the time of the flash (see Experimental Section), most of the $Co(sep)^{2+}$ was oxidized to $Co(sep)^{3+}$. This not only reduced the amount of $Co(sep)^{2+}$ available for the reaction with O_2^-, but it also produced a high absorbance in the UV, thus preventing the photochemical formation of appreciable amounts of O_2^-.

(8) The variation of pH automatically involves a change in the ionic strength. Calculations using the Debye–Hückel equation show that the rate constant at pH 11.3 (0.002 M ionic strength) should be ~1.8 times faster than the rate constant at pH 12.6 (0.04 M ionic strength). The inherent experimental error prevents us from analyzing the data in enough detail to examine the effect of the ionic strength.

(9) (a) Rabani, J.; Klug-Roth, D.; Lilie, J. J. Phys. Chem. 1973, 77, 1169. (b) Brigelius, R.; Spottl, R.; Bors, W.; Lengfelder, E.; Saran, M.; Weser, U. FEBS Lett. 1974, 47, 72.

(10) Sellers, A. M.; Simic, M. G. J. Am. Chem. Soc. 1976, 98, 6145.

constant was observed. The simplest comparison is to note the value of k_{obsd} in the absence of Cu^{2+}, $(10.0 \pm 0.3) \times 10^{-2}$ s^{-1}, independent of pH 1.0–7.0, as compared to the value in its presence. For the latter we have chosen runs from Table I at pH 3.8–4.5 in the presence of 0.10 M *t*-BuOH, which have $k_{obsd} = (5.8 \pm 0.5) \times 10^{-2}$ s^{-1}, independent of $[Cu^{2+}]$, $(3.8 - 18.9) \times 10^{-4}$ M. The ratio of the rate constants is 1.7 ± 0.2, close to the ratio 2.0 predicted from eq 7 and 9. The effect of Cu^{2+} is illustrated in Figure 3.

The concentration of Cu^{2+} is, within certain limits, immaterial. Higher concentrations of Cu^{2+} could not be used, since we noted that a direct reaction occurs between Cu^{2+} and $Co(sep)^{2+}$; this process interferes, especially at pH <3. The first-order kinetic plots in the runs containing Cu^{2+} were linear to only ~50% reaction, after which the apparent rate constant became higher. The addition of 0.1 M *t*-BuOH, a good scavenger for HO· radicals, gave good first-order kinetic plots to ~75% of the reaction. The rate constants estimated from the first half of the runs without *t*-BuOH were identical within the error with the one evaluated in its presence (Table II).

Kinetic Isotope Effects. The rate constant for the reaction of $d(N)^6$-$Co(sep)^{2+}$ with O_2 is 37 ± 5 M^{-1} s^{-1}, virtually unchanged from that found for the parent complex. On the other hand, the reaction of the d^6-Co(II) complex with O_2^- (in H_2O or in 96% D_2O) has $k_{3b(D)} = 2.2 \times 10^7$ M^{-1} s^{-1}. The latter gives a small but significant kinetic isotope effect expressed as $k_{3b(H)}/k_{3b(D)} = 2.1$.

Interpretation and Discussion

The Involvement of a Superoxide Intermediate. Both the lack of an appreciable deuterium isotope effect and the kinetic effect of Cu^{2+} (Table II) fit very well into the mechanism proposed[1] for the oxidation of $Co(sep)^{2+}$ with oxygen. Outer-sphere electron transfer should yield O_2^- at a rate showing, as found, no appreciable kinetic isotope effect of N-deuteration. The kinetic factor of ~2 obtained at pH ~4 upon addition of Cu^{2+} strongly supports the involvement of the superoxide as a reaction intermediate. Importantly, the effect of Cu^{2+} is independent of the actual concentrations used. This is exactly as expected on the basis of the rate constants for the reactions of O_2^- with $Co(sep)^{2+}$ ($k_{3b} = 4.6 \times 10^7$ M^{-1} s^{-1}) and Cu^{2+} ($k_8 \sim 8 \times 10^9$ M^{-1} s^{-1}).[9a] It should be noted that both reactions of O_2^-, oxidation of $Co(sep)^{2+}$ and reduction of Cu^{2+}, occur more rapidly than superoxide disproportionation.

The deviation of the first-order plots from linearity in the latter stages of the reaction of $Co(sep)^{2+}$ with O_2 when Cu^{2+} is present is believed to arise from secondary reactions, such as the oxidation of Cu^+ with H_2O_2. The latter two species are formed in the scavenging reaction and in the oxidation of Cu^+ with O_2, respectively. The Cu^+–H_2O_2 reaction is likely to be fast and it probably produces reactive intermediates, such as OH radicals, which rapidly oxidize $Co(sep)^{2+}$ and thus speed up the overall reaction. The efficiency of *t*-BuOH in cleaning the kinetics lends credibility to the sequence of reactions proposed.

At pH 1 the proportion of the deprotonated form of the superoxide, O_2^-, is very low and the scavenging of the superoxide occurs by the reaction of HO_2 with Cu^{2+}. The rate constant for the HO_2 reaction is $k_{8a} \sim 10^8$ M^{-1} s^{-1},[9a] lower then k_8 for $Cu^{2+} + O_2^-$. At the lowest concentration of Cu^{2+} used (2.2×10^{-4} M) we calculate that scavenging at pH 1 should occur to ~70% extent, giving a rate constant $k_{obsd} = 0.065$ s^{-1}. The rate constant actually measured at pH 1 in the presence of Cu^{2+} (0.075 s^{-1}) is lower than in its absence (0.10 s^{-1}), but higher than predicted, because of the contribution of the direct Cu^{2+}–$Co(sep)^{2+}$ reaction, which we have examined only qualitatively. The interference by the direct reaction becomes more pronounced at the next higher concentration of Cu^{2+} (3.7×10^{-4} M), where an even higher value of the rate constant (0.082 s^{-1}) was measured. For that reason quantitative conclusions cannot be drawn from results obtained in the strongly acidic solutions. Despite that limitation, we conclude that O_2^- is the principal intermediate in the reaction of $Co(sep)^{2+}$ with O_2 under all pH conditions examined because the rate itself is pH independent.

Mechanisms of the O_2^- Reactions. The reducing behavior of the superoxide radical toward transition-metal complexes has been well established.[11] The oxidation of metal complexes, on the other hand, has been explored to a much lesser extent. Still, oxidations by O_2^- have been documented in several cases. The protonated form of the radical, HO_2, is a powerful oxidizing agent ($E° = 1.44$ V[11a] for HO_2/H_2O_2) and the oxidation of metal complexes takes place readily. Examples include $Fe(CN)_6^{4-}$,[12a] $Mo(CN)_8^{4-}$,[12b] $Ru(NH_3)_5(\text{isonicotinamide})^{2+}$,[13] Fe^{2+},[14] Cu^+,[9] Ce(III),[15] and some others.[11c] Oxidations by O_2^- are rarely encountered, despite its relatively strong oxidizing power ($E° = 0.89$ V[11a] for O_2^-/H_2O_2). The reason is the thermodynamic instability of the immediate product of electron transfer, O_2^{2-}. Oxidations of organic substrates by O_2^- thus often involve hydrogen ion[16] or hydrogen atom[17] transfer, which result in the formation of protonated products, HO_2 and HO_2^-, respectively. In the former case the cycle is completed by the oxidation of the deprotonated reductant by oxygen.

In the example at hand, reaction 3b, O_2^- is a very effective oxidant. The lack of a pH effect on the rate constant in the range studied (11.3–12.6) confirms that O_2^-, and not HO_2, is the actual oxidizing species.[18] Although $Co(sep)^{2+}$ is a strong reductant ($E°_{Co(sep)^{3+/2+}} = -0.26$ V),[1] an outer-sphere electron transfer for the reaction represented by eq 3b seems unlikely owing to the instability of O_2^{2-} mentioned.[19] In further support, we note the appreciable kinetic isotope factor of 2.1. Were the reaction of O_2^- with $Co(sep)^{2+}$ to proceed by outer-sphere electron transfer, a rate ratio near unity would be expected, just as was found for the reaction of O_2 with $Co(sep)^{2+}$.

Hydrogen atom abstraction from a C–H bond of either kind of methylene group clearly has to be ruled out as a possibility based on the NMR spectra of the oxygenation product. Both ^{13}C and ^2H spectra definitively show that no methylene hydrogen has been replaced by a deuterium when the reaction of $d(N)^6$-$Co(sep)^{2+}$ with O_2 was carried out in D_2O. In the event that hydrogen abstraction had taken place during the second step, the resulting $d(N)^6$-$Co^{III}(sep\text{-}H)^{2+}$ would rapidly pick up a deuterium ion from solvent producing $d(N)^6d(C)$-$Co(sep)^{3+}$. One out of every 12 carbons of the product of this step would have been deuterated, or $^1/_{24}$ of the entire product, considering that the first step, the oxygen reaction, is not an abstraction reaction.

We prefer the mechanism shown in eq 10–12, whereby O_2^-

$$Co(sep)^{2+} + O_2^- \rightarrow Co(sep\text{-}H)^{2+} + HO_2^- \quad (10)$$

$$HO_2^- + H^+ \rightleftharpoons H_2O_2 \quad (11)$$

$$Co(sep\text{-}H)^{2+} + H^+ \rightarrow Co(sep)^{3+} \quad (12)$$

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(18) The p*K*a for the reaction $HO_2 \rightleftharpoons H^+ + O_2^-$ is 4.69.[3] Note also that were HO_2 the reactive form of the superoxide radical in the pH range employed in this study, the rate constant for the reaction $HO_2 + Co(sep)^{2+} \rightarrow Co(sep)^{3+} + HO_2^-$ would have an impossibly high value of $\sim 10^{15}$ M^{-1} s^{-1}.

(19) This factor is very important in the chemistry of the superoxide radical as illustrated by the disproportionation reaction which shows a direct dependence on [H$^+$] even in very alkaline solutions.[3] The dominant pathway at pH >7 is the reaction $HO_2 + O_2^- \rightarrow HO_2^- + O_2$, $k_{4ab} = 5 \times 10^6$ M^{-1} s^{-1} while the reaction $2O_2^- \rightarrow O_2^{2-} + O_2$ is negligibly slow ($k_{4bb} < 0.3$ M^{-1} s^{-1}). This phenomenon is also responsible[11a] for the lack of superoxide self-reaction in aprotic solvents.

reacts by abstracting a hydrogen atom from one of the secondary amino groups of the sepulchrate ligand of $Co(sep)^{2+}$. This is followed by the rapid protonation of the products $Co^{III}(sep\text{-}H)^{2+}$ and HO_2^-. The observed isotope effect $k_H/k_D = 2.1$ is consistent with this mechanism, albeit smaller than the calculated maximum effect of ~ 8. The calculation of the latter is based on the assumption of half transfer in the transition state, with smaller values being consistent with greater or lesser degrees of transfer.[20] Kinetic isotope effects of similar magnitude have been observed before for the N–H exchange reactions using OH^- as a nucleophile in a related class of complexes.[21] Furthermore, hydrogen abstraction from a secondary amino group rather than a methylene group is consistent with the relative energies of the bonds involved.[22] Superoxide ion can abstract only weakly bound hydrogen atoms; in this case the N–H bond is effectively weakened by the internal electron-transfer process converting $Co^{II}\text{-}\dot{N}R_2$ to $Co^{III}\text{-}\ddot{N}R_2$.

A similar hydrogen atom transfer mechanism for the oxidation of some transition-metal complexes by C-centered radicals has recently been proposed.[23] Larger isotope effects were observed in such cases ($k_H/k_D \sim 6$ for hydrogen-atom abstraction from O–H bonds), and still larger effects (~ 20) were found[24] for C–H hydrogen abstraction from 2-propanol using Ru(IV) oxo complexes. Evidently the processes of electron transfer and atom abstraction are more intimately connected in these cases than they are in the reaction between $Co(sep)^{2+}$ and O_2^-. The comparatively small isotope effect found for the latter reaction implies that the N–H bond either is little stretched or is almost broken at the point where electron transfer occurs during the reaction of eq 10.

Reactions of HO_2. Although the rate of the $Co(sep)^{2+}$–HO_2 reaction in acidic solutions has not been measured, several observations pertinent to the reaction of $Co(sep)^{2+}$ with oxygen indicate that HO_2 also reacts rapidly. Steady-state calculations show that the $Co(sep)^{2+}$–O_2^- reaction will remain significantly faster than the superoxide self-reaction even in solutions as acidic as pH 3, but finally becoming much slower than the superoxide self-reaction at pH <1.5. If HO_2 were unreactive toward $Co(sep)^{2+}$, a gradual change in the mode of superoxide reactivity from eq 3b to 4 in the pH range $\sim$1.5–3 would lead to a change in the rate constant for the $Co(sep)^{2+}$–O_2 reaction. Ultimately, a kinetic factor of 2 would be observed at the pH extremes, the same as in the presence of Cu^{2+}. The data in Table II and that reported previously[1] conclusively show that this is not the case. The rate constant is within the error unchanged in the pH range 1–7. The value is somewhat higher in very alkaline solutions. The latter increase must, however, have a different origin,[25,26] since it occurs at the opposite end of the pH scale than predicted by the calculations were the HO_2/O_2^- self-reaction ever to become an important reaction. The scavenging effect of Cu^{2+} at pH 1, although not as clean as at pH $\sim$4 for the reasons mentioned, also strongly indicates that the oxidation of $Co(sep)^{2+}$ by HO_2 takes place more rapidly than the superoxide disproportionation. This leads to an estimated lower limit for the rate constant, $k_{3a} > 3 \times 10^5$ M^{-1} s^{-1}. Such a value is not at all unexpected since HO_2 is actually a more powerful oxidant than O_2^-.

Reduction of $Co(sep)^{3+}$; Equilibrium Considerations. The oxidized complex $Co(sep)^{3+}$ was found to be completely unreactive toward O_2^-. From the known reduction potentials for O_2/O_2^- (−0.16 V),[11a] O_2/HO_2 (+0.12 V),[11a] and $Co(sep)^{3+/2+}$ (−0.26 V),[1] the equilibrium constant for reactions 1a and 1b can be calculated.

$$Co(sep)^{2+} + O_2 \rightleftharpoons Co(sep)^{3+} + O_2^- \qquad K_{1b} \qquad (1b)$$

$$Co(sep)^{2+} + O_2 \xrightleftharpoons{H^+} Co(sep)^{3+} + HO_2 \qquad K_{1a} \qquad (1a)$$

The values are $K_{1b} \approx 50$ and $K_{1a} \approx 2.5 \times 10^6$. From the requirement $K_1 = k_1/k_{-1}$, we calculate the values of k_{-1b} and k_{-1a} as ~ 1 M^{-1} s^{-1} and $\sim 1 \times 10^{-5}$ M^{-1} s^{-1}. Obviously, the reactions of $Co(sep)^{3+}$ with O_2^- or HO_2 are much too slow to be observed at any pH due to the fast competing reactions of the superoxide disproportionation and the reactions with $Co(sep)^{2+}$. Consistent with this, the reaction of O_2 with $Co(sep)^{2+}$ is unaffected by accumulation or addition of $Co(sep)^{3+}$ simply because under all conditions the rate of reaction 3 would always be very much larger than that for the reverse of eq 1.

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Registry No. $Co(sep)^{2+}$, 63218-22-4; O_2^-, 11062-77-4; deuterium, 7782-39-0.

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(25) A referee reminded us that the reactions of Ru(II) complexes [e.g., $Ru(NH_3)_6^{2+}$, *cis*-$Ru(NH_3)_4(isn)(H_2O)^{2+}$] with O_2 are precisely *doubled* in rate by addition of Fe^{2+},[13] contrasted with the exact *halving* of the rate of reaction of $Co(sep)^{2+}$ with O_2 caused by Cu^{2+} (In both cases, the phenomenon is independent of $[Fe^{2+}]$ and $[Cu^{2+}]$ within certain ranges.) The former comes about because Fe^{2+} catalyzes the otherwise slow oxidation of a further 2 mol of Ru(II) by H_2O_2, thus increasing twofold the rate of Ru(II) consumption. The effect of Cu^{2+} is to intercept the superoxide intermediate formed from $Co(sep)^{2+} + O_2$, preventing the oxidation of a second $Co(sep)^{2+}$ by HO_2/O_2^-.

(26) The increase in the rate constant at high pH values could be due to a partial deprotonation of one of the secondary amino groups of the sepulchrate ligand.