Inorg. Chem. **1988**, *27*, 1089–1095

in rejecting Cr^{III} as an important biologically active metal center during evolution. The natural abundance of chromium would also oppose its evolutionary selection.

Acknowledgment. We gratefully acknowledge support for this work through the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CHE8417751). Early synthetic efforts on this project were also carried out by L. W. Warner.

Registry No. 2-CH_3imH, 693-98-1; imH, 288-32-4; pyzH, 288-13-1; $[A_5Cr(pyzH)](tfms)_3$, 112793-26-7; $[A_5Cr(imH)](tfms)_3$, 112793-27-8; $[A_5Cr(2\text{-}CH_3imH)](tfms)_3$, 112793-29-0; $A_5Cr^{III}(1\text{-}CH_3imH)^{3+}$, 112793-30-3; $A_5Cr^{III}OH_2^{3+}$, 15975-47-0; $[A_5Cr(tfms)](tfms)_2$, 84254-61-5.

Supplementary Material Available: IR spectra of the imidazole and pyrazole complexes (Figure 1SM) and plots of pK_a versus $1/T$ (Figure 2SM) (2 pages). Ordering information is given on any current masthead page.

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Spin-Trapping Studies of the Reduction of O_2 and H_2O_2 by Titanium(III), Iron(II), and Ruthenium(II) Complexes

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Received September 25, 1987

The reductions of H_2O_2 and O_2 by $Ti(edta)(H_2O)^-$, $Ti(H_2O)_6^{3+}$, $Fe(edta)^{2-}$, $Fe(H_2O)_6^{2+}$, and $Ru(NH_3)_6^{2+}$ have been studied by the spin-trapping technique using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) and *N*-*tert*-butyl-α-phenylnitrone (PBN) radical traps. The resultant radical adducts $RDMPO^\bullet$ and $RPBN^\bullet$ have been characterized by ESR spectroscopy in agreement with literature values. $Ti(edta)(H_2O)^-$, $Fe(edta)^{2-}$, $Fe(H_2O)_6^{2+}$, and $Ru(NH_3)_6^{2+}$ reductions of H_2O_2 produce $HO^\bullet$ identified by the $HO\text{–}DMPO^\bullet$ and $HO\text{–}PBN^\bullet$ spectra. $HO^\bullet$ formed in these reductions may be intercepted by chemical mediators (CH_3OH, C_2H_5OH, $(CH_3)_2CO$, $(CH_3)_3COH$) to provide more long-lived secondary carbon-centered radicals, which are trapped by DMPO or PBN. Excellent spectral matches for $RDMPO^\bullet$ and $RPBN^\bullet$ species are obtained for the $Ti(edta)(H_2O)^-$, $Fe(edta)^{2-}$, $Fe(H_2O)_6^{2+}$, $Ti(H_2O)_6^{3+}$, and $Ru(NH_3)_6^{2+}$ reductants for H_2O_2 in the presence or absence of mediators. When O_2 is used as the oxidant for $Ru(NH_3)_6^{2+}$, this reaction known to proceed outer sphere via O_2^-, only the dismutation/reduction product ($HO^\bullet$) is trapped at pH 6.86. Both $HO_2^\bullet$ and $HO^\bullet$ are trapped at pH 2.57 in a 1.0:7.6 ratio. $Ti(edta)(H_2O)^-$ is known to be oxidized inner sphere by O_2 via coordinated O_2^-. No radical adducts for the $Ti(edta)(H_2O)^-/O_2$/radical trap system are observed with or without mediators in the solvent cage. The reduction of O_2 by either $Fe(edta)^{2-}$ or $Fe_2(ttha)^{2-}$ proceeds by an inner-sphere pathway in which the coordinated O_2^- survives long enough to attack an adjacent carboxylate moiety, forming a trappable ligand-based carbon-centered radical, or to attack sacrificial mediators in the solvent cage.

Introduction

The reduction of O_2 and H_2O_2 is an important chemical problem. Its ramifications are the central issue in the energy-transducing apparatus and protective enzymes for aerobic biochemical cells, the rate-controlling factors of many electrochemical fuel cells, and the wide class of chemical autoxidations of inorganic and organic substrates. A crucial question for the reactivity of O_2 and H_2O_2 with transition-metal centers is whether the processes proceed by inner- or outer-sphere paths. Inner-sphere reduction of H_2O_2 by labile metal centers frequently proceeds about 10^4 times faster than when H_2O_2 is restricted to an outer-sphere role.[1] Reduction of H_2O_2 by labile aqua transition-metal reductants such as $Fe(H_2O)_6^{2+}$, $Cr(H_2O)_6^{2+}$, or $Ti(H_2O)_6^{3+}$ proceeds predominantly by one-electron paths with formation of hydroxyl radical ($HO^\bullet$) as the initial product.[2-4] The reduction sequence for O_2 is typically more complicated in aqueous solution because any O_2^- that is formed by a one-electron pathway carries out a self-dismutation into O_2 and H_2O_2. Since the latter product is also chemically reactive, it is often difficult to discern between a reaction of one-electron steps involving O_2^- and a two-electron reduction forming H_2O_2 directly. This problem has been more frequently addressed by biophysical chemists in the study of biological redox reactions such as the electron transport chain in spinach chloroplasts[5] or in the characterization of bleomycin-type antitumor drugs and their chemical models.[6-9] The technique of spin trapping with DMPO or PBN has proven useful as a diagnostic tool in detection of intermediates that are produced in O_2 and H_2O_2 reductions from organic reagents. The technique has been reviewed previously by Janzen[9] and by Evans.[10] The use of spin-trapping reagents to study metal ion/peroxide redox reactions is less common in the literature,[11-13] but the tool was recently added to the mechanistic arsenal for inorganic chemists in the study of H_2O_2 reductions by $Fe(edta)^{2-}$, $Ti(edta)(H_2O)^-$, and $Ru(NH_3)_6^{2+}$.[14] Myser and Shepherd have used the DMPO spin trap in conjunction with parallel trapping agents to examine the mechanism of the O_2 oxidations of binuclear polyamino carboxylate complexes including $Fe_2(ttha)^{2-}$ [15] and $V_2O(ttha)^{2-}$.[16] These binuclear complexes of triethylenetetraaminehexaacetate, $ttha^{6-}$, have proven to be interesting comparison systems for the hemerythrin O_2-carrier enzyme[15] and for certain features of the

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superoxide dismutase enzyme.[16] The spin-trapping method provides a potentially important procedure for identification of radical intermediates created during inner-sphere reduction of O_2 and H_2O_2. These studies could provide evidence for many metal ion assisted oxidations and hydroxylations related to oxygenases and monooxygenases.[34] The study of these mechanisms for enzymatic processes and the simple chemical mimics of them is a very important, emerging research area. In this paper we report more detailed results that support the conclusions reached previously by Johnson and Shepherd[14] for the H_2O_2 oxidations of $Fe(edta)^{2-}$, $Ti(edta)(H_2O)^-$, and $Ru(NH_3)_6^{2+}$ and extent these studies to the O_2 oxidations of these reductants. The mechanism of the $Fe(edta)^{2-}/O_2$ reaction is particularly important in light of its use in DNA-nicking studies.[32] The results reported here are important in showing that the spin-trapping technique provides the proper trapped radical or the absence of radical species, depending on whether outer-sphere radical production or inner-sphere binding of the reduced oxygen species has occurred. These studies are particularly meaningful because the $O_2/Ru(NH_3)_6^{2+}$ reaction is known to occur by the one-electron outer-sphere path forming O_2^- [17] and the $O_2/Ti(edta)(H_2O)^-$ reaction is known to occur via a bound O_2^- intermediate.[18] The results lend considerable promise that DMPO and PBN traps will be useful as probes of intermediates in reactions of O_2 and H_2O_2 with a wide variety of inorganic transition-metal reductants and that spin trapping will be a profitable mechanistic tool for future use.

Experimental Section

N-tert-Butyl-α-phenylnitrone (PBN) and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) obtained from Aldrich were employed as radical-trapping agents by following the methods similar to those reported previously.[15,16] Solutions were prepared in glass bubblers attached to an Ar line. Oxygen removal was achieved by passage of Ar or N_2, scrubbed through Cr(II) solutions to remove O_2 impurities. The pressure in the glass bubbler was released to the atmosphere via a syringe needle placed into a rubber septum that sealed a 14/20 standard taper neck. The septum also provided entry for transferring or sampling reagents with a flushed gas-tight syringe carrying an appropriate needle (see below). Four bubblers were used. In the first bubbler 0.03 M stock solutions of the radical trap were prepared by dissolving in 10.0 mL of deionized water an appropriate weighed amount of PBN (~0.0532 g) or 0.033 mL of DMPO, sampled in an N_2 glovebag. In the second bubbler 3.0×10^{-3} M metal ion reducing agent solutions were prepared. Weighed solids of $TiCl_3$ and $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ were used to supply Ti^{3+} and Fe^{2+}. $Ru(NH_3)_6^{2+}$ was prepared as follows: 0.023 20 g of $Ru(NH_3)_6Cl_3$ was dissolved in 10.0 mL of distilled deionized water while the solution was vigorously deoxygenated with Ar gas. The solutions were handled in subdued lighting to prevent photodecomposition. Samples of the Ru(II) solutions were allowed contact only with Pt needles to avoid Fe impurities. Several Zn(Hg) chips were added to the $Ru(NH_3)_6Cl_3$ solution to effect the reduction to $Ru(NH_3)_6^{2+}$. Reduction was allowed to proceed for 15.0 min. A 5.0-mL aliquot of $Ru(NH_3)_6^{2+}$ solution was transferred to a bubbler containing 0.013 12 g of $Na_2H_2edta \cdot 2H_2O$ dissolved in 5.0 mL of phosphate buffer (pH 6.86, $\mu = 0.100$) preflushed with Ar. The concentrations of the stock $Ru(NH_3)_6^{2+}$ solution were $[Ru(NH_3)_6^{2+}] = 3.75 \times 10^{-3}$ M and $[H_2edta^{2-}] = 1.65 \times 10^{-3}$ M. H_2edta^{2-} is present to prevent precipitation of $Zn(OH)_2$: $[Zn(edta)^{2-}] \cong 1.88 \times 10^{-3}$ M. $Ru(NH_3)_6^{2+}$ was also prepared in HCl solution for studies in the pH range of 2–4. HCl was used to prevent oxidation of Ru(II) by ClO_4^-. $Fe(edta)^{2-}$ and $Ti(edta)(H_2O)^-$ were prepared by diluting the Fe^{2+} or Ti^{3+} stock solution into a purged solution containing the requisite amount of Na_2H_2edta for chelation. Transfer of either reagent was achieved with stainless steel needles and purged gastight syringes. Typical handling methods are described elsewhere.[18]

For studies at pH 6.86, 10 mL of phosphate buffer was used as the solvent, and for studies in solutions of a fixed $[H_3O^+]$, the solvent was 10 mL of 0.333 M $HClO_4$ (or HCl for $Ru(NH_3)_6^{2+}$) diluted to the necessary concentration. The third bubbler contained a solution of 3% H_2O_2, standardized by Ce(IV) titration. The reaction mixture was made in the fourth bubbler. A 0.50-mL aliquot of a 10.0 M solution of the substrate (methanol, ethanol, acetone, or other specified scavenger) was added to the bubbler and the Ar purge was started. The radical trapping solution (1.5 mL) was added by syringe followed by 1.5 mL of H_2O_2 solution. Finally, 1.5 mL of the metal ion solution was added, starting the oxidation reaction. A sample of the reaction mixture was transferred to a N_2- or Ar-purged flat quartz EPR cell and mounted in a Varian E-4 EPR spectrometer. Three to six minutes elapsed between the time the metal ion solution was added and the EPR spectrum was obtained. In the case of O_2 as the oxidant for $Ti(edta)(H_2O)^-$, $Fe(edta)^{2-}$, and $Ru(NH_3)_6^{2+}$, the delay time in obtaining the initial spectrum was reduced to ca. 60 s in order to search for any initially formed species that might undergo a rapid decay. No difference in the number of detectable species was observed at 1 min vs the more usual 3–6-min delay. The studies of Harbour, Chow, and Bolton[12] show that the HO• and HO_2• adducts of DMPO are sufficiently long-lived that detection under our conditions would be ensured. Studies with $Fe(edta)^{2-}$ oxidized by H_2O_2 were also carried out such that radicals could be detected within the first 2 min after mixing. No species in addition to those present after 3–6 min were observed. The free-radical spectra were obtained at room temperature in the X-band region (frequency ~9.395 GHz) with 100-kHz modulation and 0.50-G modulation amplitude to avoid saturation at 10.0 mV of microwave power. Repetitive scans of the EPR spectrum were obtained at 2.0-min intervals to observe any evidence of radical concentration decay with time. Some species were found to be stable, while others did decay with time as described in the text. The loss is typically less than 20% of the signal per 8.0-min sweep.

Table I. Spin Hamiltonian Parameters (Gauss) for Radicals Produced via H_2O_2 Oxidations^g

reductant	substrate	DMPO a_N	DMPO a_H	PBN a_N	PBN a_H
$Ti^{III}(edta)(H_2O)^-$	H_2O	15.0	15.0	16.5	3.3
	CH_3CH_2OH	16.2	23.2	16.4	3.5
	CH_3OH	16.2	23.0	16.1	3.9
	$(CH_3)_2CO$	16.1	23.8^a	NS^b	NS
$Fe^{II}(edta)^{2-}$	H_2O	15.0	15.0	...	...
	CH_3CH_2OH	16.0	23.2	16.35	3.5
	CH_3OH	16.0	23.0	16.4	4.0
	$(CH_3)_2CO$	15.0^c	15.0^c	NS	NS
	$CH_3(CH_2)_3OH$	...	...	16.4	2.75
	$(CH_3)_3COH$	—16.5^a	24.0^a	NS	NS
$Ti(H_2O)_6^{3+}$	CH_3CH_2OH			16.3	3.5
	CH_3OH			16.2	4.0
$Fe(H_2O)_6^{2+}$	H_2O			16.0	3.3
	CH_3CH_2OH	16.1	23.3	16.2^d	3.6^d
	CH_3OH	15.9	23.0	16.9	4.0
	$(CH_3)_2CO$			15.8^e	8.6^e
$Ru(NH_3)_6^{2+}$	H_2O	15.0	15.0	16.0	3.3
	CH_3CH_2OH	16.2	23.2	16.2	3.3
	CH_3OH	16.2	23.0	16.0	3.3
	$(CH_3)_2CO$	16.5^f	23.8^f		

^{a}OH• adduct; $a_N = a_H = 15.0$ g also detected. ^{b}NS = no signal detectable. ^{c}Only OH• adduct detected. ^{d}NH_2 adduct also observed from $Fe(NH_4)_2(SO_4)_2$ source. ^{e}Only NH_2• detected as a triplet of triplets. ^{f}HO• is the major species. ^{g}$[CH_3CH_2OH] = 1.73$ M, $[CH_3OH] = 2.46$ M, $[(CH_3)_2CO] = 1.36$ M, $[(CH_3)_3COH] = 1.00$ M; $[DMPO] = [PBN] = 9.0 \times 10^{-3}$ M; reducing agents ca. 9.0×10^{-4} M.

Results and Discussion

$Ti(edta)(H_2O)^-$ Reductant for H_2O_2. When 3.0×10^{-3} M $Ti(edta)(H_2O)^-$ was injected into the reaction mixture containing H_2O_2 and the DMPO radical trap, radical species were produced as shown in Figure 1A–D with the following species present: H_2O alone (spectrum 1A), ethanol (spectrum 1B), methanol (spectrum 1C), and acetone (spectrum 1D). All ESR spectra showed a slow decrease in amplitude with time. The spin Hamiltonian parameters for the isotropic coupling constants of a_N and a_H for the radical–DMPO adducts are given in Table I. Concentrations of reducing agents, traps, and mediators are given in the Table. Spectrum 1A clearly shows the HO• radical has been trapped due to the four-line spectrum of 1:2:2:1 intensity, which is characteristic of the HO–DMPO• adduct (literature values of $a_N = a_H = 15.0$ G[19] are given for HO–DMPO•). No additional species such as a carbon-centered radical due to the attack of HO• on coordinated $edta^{4-}$ was observed. Therefore, the HO• that is produced cleanly escapes the cage to be trapped by DMPO or to be reduced to HO^- by a second $Ti(edta)(H_2O)^-$ reductant.

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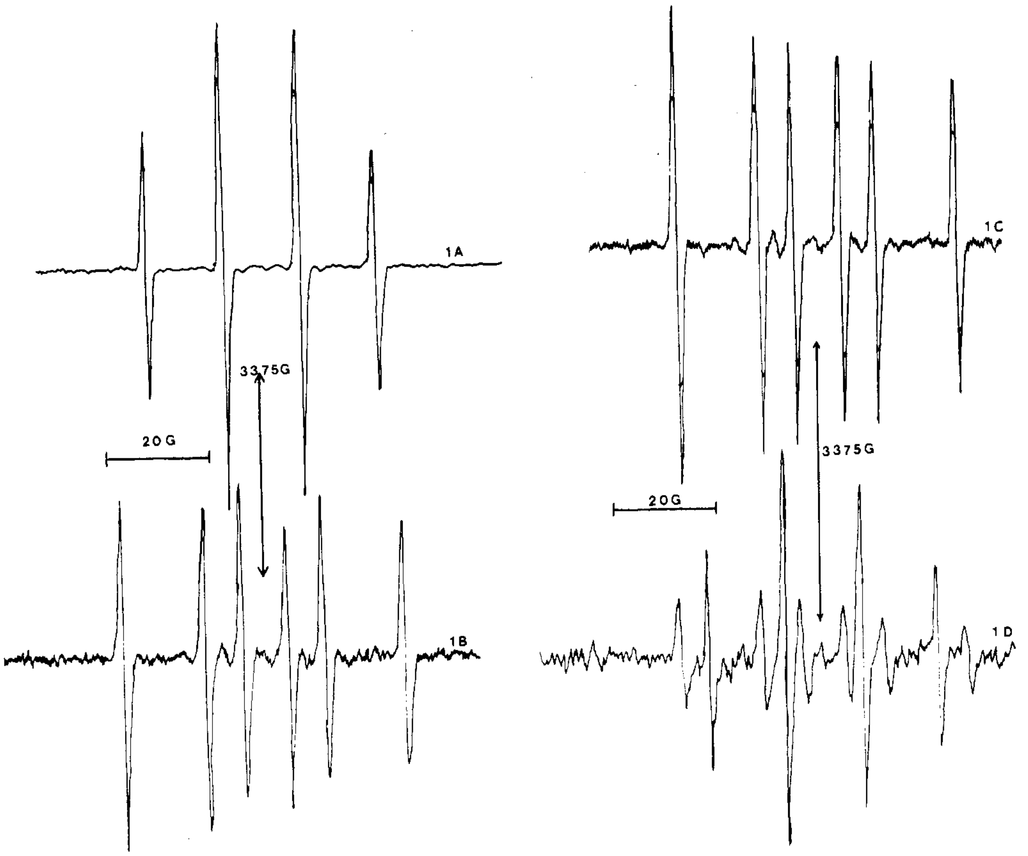
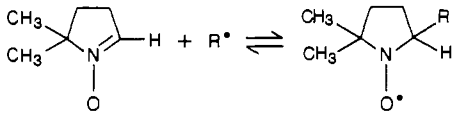


Figure 1. DMPO radical adducts generated by $Ti(edta)(H_2O)^-/H_2O_2$: (A) H_2O alone, 4.0-min scans, RG = 1.6×10^3; (B) C_2H_5OH added, 8.0-min scans, RG = 6.3×10^4; (C) CH_3OH added, 8.0-min scans, RG = 5.0×10^3; (D) $(CH_3)_2CO$ added, 8.0-min scan, RG = 2.0×10^4. All spectra were obtained at 9.475 GHz, with 0.50-G modulation amplitude and 10-mW microwave power at room temperature; RG = receiver gain; $[Ti(III)] \cong 3.0 \times 10^{-3}$ M, $[H_2O_2] \cong 0.30$ M, [mediators] $\cong$ 1.0 M.

The copious production of $HO^\bullet$ occurs via reaction 1 at pH $\geqslant 2$;[20] the trapping reaction for DMPO is shown for all radicals, $R^\bullet$, in reaction 2. The influence of the R group is indirect through modification of the a_N and a_H constants. It is sometimes useful for diagnostic purposes to convert reactive radicals such as $HO^\bullet$ or O_2^- into secondary, trappable, more long-lived carbon-centered radicals. Alcohols and acetone are frequently utilized for this purpose, as shown for ethanol in reaction 3. The carbon-centered radicals are reducing radicals and are very much less prone to reduction by the metal ion reductants than is $HO^\bullet$ or O_2^-. Therefore, the derivative $R^\bullet$ species survive longer for trapping.

$$Ti(edta)(H_2O)^- + H_2O_2 \rightarrow TiO(edta)^{2-} + HO^\bullet + H_3O^+ \quad (1)$$



(2)

$$HO^\bullet + CH_3CH_2OH \rightarrow CH_3\dot{C}HOH + H_2O \quad (3)$$

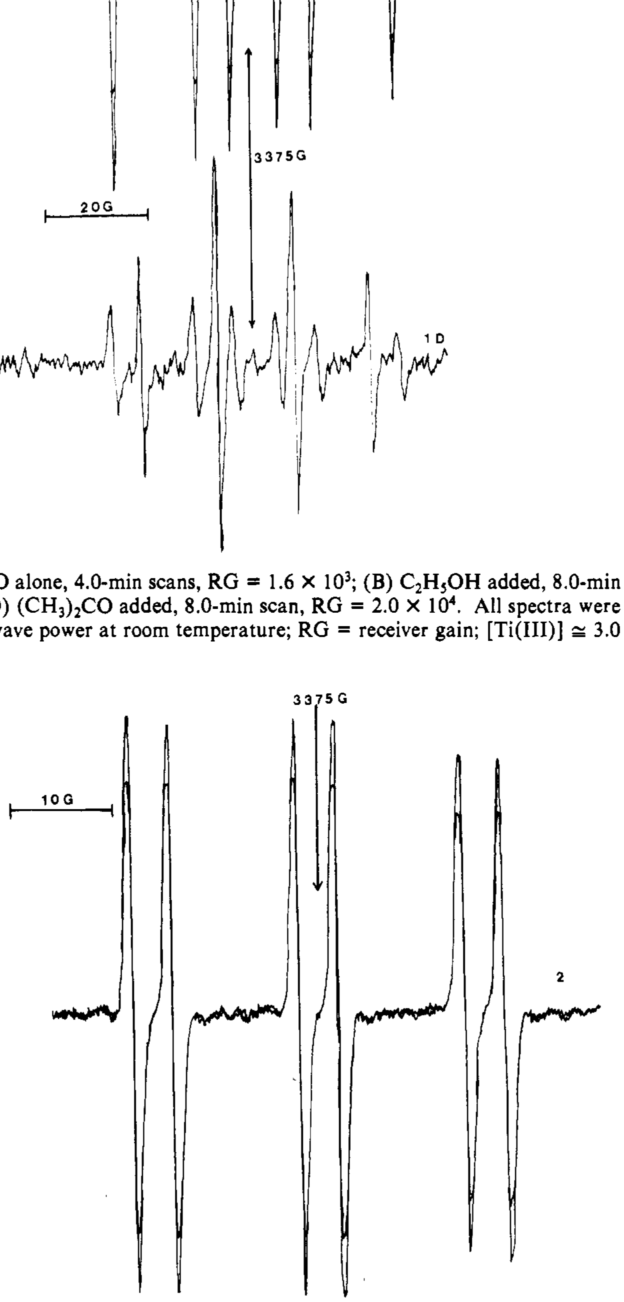


Figure 2. PBN radical adduct generated by $Ti(edta)(H_2O)^-/H_2O_2$ plus CH_3OH: 4.0-min scan, RG = 4.0×10^3, 9.476 GHz; all other settings as in Figure 1.

Finkelstein et al. have measured the rate constant for DMPO trapping of $HO^\bullet$ as 3.4×10^9 M^{-1} s^{-1},[25] compared to 1.85×10^9 for its H atom abstraction from ethanol, 8.6×10^8 from methanol, or 7.3×10^7 from acetone.[25,26] Rates with alcohols and acetone

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(24) Initially, our study suggested Ti^{IV} produced by the $Ti(H_2O)_6^{3+}/H_2O_2$ reaction caused a shift in the measured a_N and a_H values. This problem was shown to be an impurity problem with one batch of PBN trapping solution. When authentic Ti^{IV} as TiO^{2+} is mixed with the product trapping solution of radicals produced by the $Fe(H_2O)_6^{2+}/H_2O_2$ method with CH_3OH and CH_3CH_2OH, no change in a_N or a_H parameters is observed. Furthermore, a repeat of the $Ti(H_2O)_6^{3+}/H_2O_2$-generated radicals gave parameters identical with those of species generated by $Fe(H_2O)_6^{2+}$ alone or by $Fe(H_2O)_6^{2+}$ followed by addition of TiO^{2+}. The latter is present as TiO_2^{2+} due to the excess of H_2O_2 in the method and is detectable to the eye by its yellow color.

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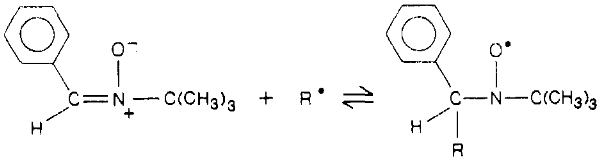
have been obtained in pulse radiolysis studies.[26] Comparison studies with O_2 as the oxidant instead of H_2O_2, which we will discuss, made it relevant to study the trappable radicals formed via reaction 3 with $HO^•$. The secondary radicals that were obtained for a useful series of alcohols and acetone are given in Table I. In all cases the observed radicals are the α-H atom abstracted radicals when produced with $HO^•$ generated from the $Ti(edta)(H_2O)^-/H_2O_2$ system. As shown in Table I the a_N and a_H parameters are reasonably close for the adducts of CH_3CHOH, $^•CH_2OH$, and $^•CH_2(CO)CH_3$, but the sensitivity of the ESR method is sufficient to distinguish these species with certainty. In the case of acetone (1.36 M) as the chemical trap for $HO^•$, the steps that form $^•CH_2(CO)CH_3$ and its trapping by DMPO (9.0×10^{-3} M) are competitive with the direct trapping of $HO^•$ by DMPO. This is consistent with the reported rate constants for $HO^•$ trapping by acetone and DMPO.[26] Both radical species are present for spectrum 1D; the $HO–DMPO^•$ adduct is trapped about twice as often as $^•CH_2(CO)CH_3$ under our conditions. The PBN trap is also active in scavenging $HO^•$ or its $R^•$ chemical equivalent via reaction 4. However, the variation in the a_N and a_H parameters is less with PBN than with the DMPO trap.


(4)

Therefore, the spectra appear to be nearly alike, as shown for the PBN–trapped $^•CH_2OH$ adduct in Figure 2. Trapping by PBN also appears to be kinetically slower than with the DMPO trap. PBN is known to be 10–100 times slower in trapping $R^•$.[10] In the case of acetone as the mediator, no signal is detectable with the PBN trap. This establishes that dimerization of $CH_2(CO)CH_3$ radicals and competitive reduction of $HO^•$ by $Ti(edta)(H_2O)^-$ proceed faster than trapping by PBN, whereas with the DMPO trap both $HO^•$ and $^•CH_2(CO)CH_3$ are detectable.

$Fe(edta)^{2-}$ Reductant for H_2O_2. When $Fe(edta)^{2-}$ was used as the reductant for H_2O_2, the same radical species were detected as with $Ti(edta)(H_2O)^-$ as the reducing agent. The relative amounts of the trapped radical show an increase of between 2-fold and 16-fold greater yield when $Fe(edta)^{2-}$ is the reductant compared to the case where $Ti(edta)(H_2O)^-$ is the reductant. The spin Hamiltonian parameters of the trapped radicals for both DMPO and PBN are given in Table I. The agreement in the parameters for the two methods is ±0.2 G for a_N and ±0.5 G for a_H. Due to the lack of sensitivity of the PBN trap to the identity of $R^•$, the spectra of all of the PBN adducts derived from $Fe(edta)^{2-}$ as the reductant for H_2O_2 again appear nearly identical with the spectrum shown in Figure 2 for the $Ti(edta)(H_2O)^-/H_2O_2/CH_3OH$ system. Therefore, the spectra have not been presented individually here. Excellent spectral matches are obtained by using DMPO as the trapping agent with either $Fe(edta)^{2-}$ or $Ti(edta)(H_2O)^-$ as the reductant for H_2O_2. When $Fe(edta)^{2-}$ at 1.02×10^{-3} M was oxidized by H_2O_2 in the presence of 3.33×10^{-2} M H_2edta^{2-} (pH 4.34) and either 2.00×10^{-2} or 5.00×10^{-3} M DMPO, no species other than $HO–DMPO^•$ was detected at the highest achievable receiver gain within the first 2 min. The effective concentration (0.133 M) of chemical trapping sites for H_2edta^{2-} is 4 times that of glycine ($k \sim 1.7 \times 10^7$ with $HO^•$). Thus, the effective trapping rate constant for H_2edta^{2-} with $HO^•$ should be greater than or equal to 7×10^7, comparable to the case for acetone. No signal other than that for $HO–DMPO^•$ was seen for $Fe(edta)^{2-}/H_2O_2$ with either of these potential mediators. This observation has important consequences for species that are trapped in the $Fe(edta)^{2-}/O_2$ reaction, which is described in a later section. If O_2^- is produced and either dismutes into O_2 or H_2O_2 or is reduced to H_2O_2, the resultant secondary reaction of H_2O_2 will yield $HO^•$, which is readily trapped by DMPO. $HO^•$ trapping is not attenuated kinetically by even high levels of H_2edta^{2-}. The absence of $HO–DMPO^•$ under similar conditions can be used to rule out outer-sphere production of O_2^- by $Fe(edta)^{2-}$ or related reagents. This is due in part to the fact that metal ion reductants generally react with $HO^•$ at rate constants between 10^7 and 10^{10} M^{-1} s^{-1}.[26] In the latter phase of any reaction that generates $HO^•$ while the pool of reducing agent is decreasing, DMPO at ca. 1×10^{-2} M has a distinct trapping advantage relative to $HO^•$ reduction.

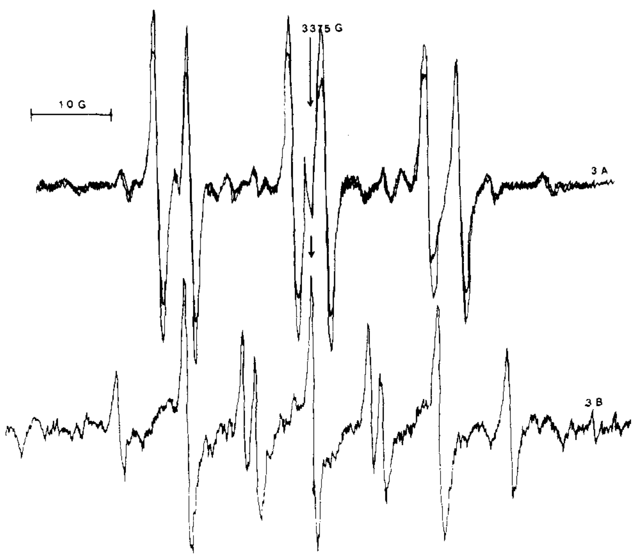


Figure 3. PBN radical adducts generated by $Fe(H_2O)_6^{2+}/H_2O_2$: (A) CH_3OH added, 8.0-min scan, RG = 5.0×10^3 at 9.476 GHz; (B) $(CH_3)_2CO$ added, 8.0-min scan, RG = 5.0×10^4 at 9.458 GHz; all other settings as in Figure 1.

$Fe(H_2O)_6^{2+}$ Reductant for H_2O_2. The radicals generated by the Fenton's reagent system ($Fe(H_2O)_6^{2+}/H_2O_2$) were examined with DMPO and PBN as the trapping agents. Nearly the same molar amounts of the radical adducts were obtained by using the $Fe(H_2O)_6^{2+}$ as the reducing agent as for $Ti(edta)(H_2O)^-$ with PBN. The source of $Fe(H_2O)_6^{2+}$ was the $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ salt. In the spectra with only H_2O present, or with CH_3OH or CH_3CH_2OH added, evidence of a minor secondary radical is present in the background spectrum, as shown in Figure 3A for the $^•CH_2OH$ adduct of PBN. The radical adducts exhibited the usual slow decay in intensity with 8.0-min field sweeps of 100 G. The nature of the second species was clearly shown when acetone was utilized as a mediator. Only a triplet of triplets with a_N = 15.8 G and a_H = 8.6 G was found at g = 2.0020. The logical interpretation of this pattern is that of the $^•NH_2$ adduct of PBN, which is presumably formed by the reaction of $HO^•$ or $R^•$ with NH_4^+ in the medium (see Figure 3B). In all other aspects the behavior of $Fe(H_2O)_6^{2+}$ as the reductant was the same as described previously for $Ti(edta)(H_2O)^-$ and $Fe(edta)^{2-}$. The values of a_N and a_H were also found to be invariant to added TiO^{2+} present in the form of the peroxo complex, TiO_2^{2+}.[24]

$Ti(H_2O)_6^{3+}$ Reductant for H_2O_2. The flow method has been used to characterize the ESR spectra and their a_H coupling constants in many organic radicals. In this method a Ti(III) salt is flowed together with H_2O_2 and the desired organic substrate through an EPR cavity. H atom abstraction generates the radical of interest whose spectrum is obtained at a steady-state flow rate. $Ti(H_2O)_6^{3+}$, formed from the aquation of $TiCl_3$, produced radicals with H_2O_2 having the same coupling constants as those generated via $Ti(edta)(H_2O)^-$, $Fe(edta)^{2-}$, or $Fe(H_2O)_6^{2+}$ with H_2O_2 in this work. These radicals underwent a decay at 2.0-min field sweeps, requiring 10 and 12 min for complete decay in the EPR cavity. Shiga has reported previously that different radicals are produced by $Ti(H_2O)_6^{3+}/H_2O_2$ than with $Fe(edta)^{2-}/H_2O_2$.[21] His results were interpreted as being due to α-abstraction by $HO^•$ generated from $Ti(H_2O)_6^{3+}$ and abstraction from more distant chain positions in ROH by the $Fe(edta)^{2-}/H_2O_2$ reagent. This difference was not seen in the present trapping experiments.[24]

$Ru(NH_3)_6^{2+}$ Reductant for H_2O_2. When $Ru(NH_3)_6^{2+}$ is prepared as described in the Experimental Section and combined with H_2O_2 in the presence of either the DMPO or PBN traps, the same

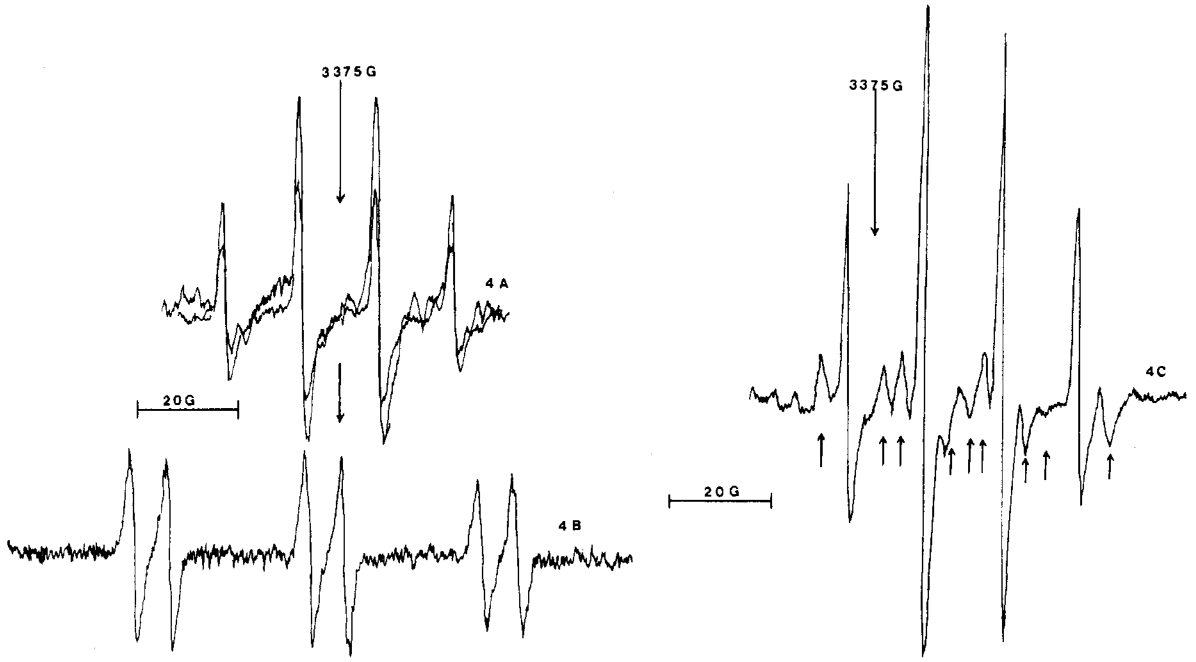


Figure 4. Radical adducts generated by $Ru(NH_3)_6^{2+}/O_2$: (A) DMPO trap, H_2O alone, pH 6.86, 8.0-min scans, RG = 6.3×10^4, 9.473 GHz; (B) PBN trap, H_2O alone, pH 6.86, 8.0-min scan, RG = 1.0×10^4, 9.482 GHz; all other settings as in Figure 1 (no H_2O_2); (C) DMPO trap, pH 3.60 (HCl), 8.0-min scan, RG = 4.0×10^4, 9.489 GHz; features of $HO_2^\bullet$ shown by arrows.

radicals are detected as have been described in the case of $Ti(edta)(H_2O)^-$ and $Fe(edta)^{2-}$. These species are produced in high yield compared to the $Ti(edta)(H_2O)^-$ reductant. The mechanism of the $Ru(NH_3)_6^{2+}/H_2O_2$ reaction is known to occur with a pathway associated with a large negative $\Delta S^\ddagger$ (−41.9 ± 4.3 eu).[14,22] The value of $\Delta S^\ddagger$ has prompted the suggestion that a seven-coordinate intermediate, $[Ru(NH_3)_6(H_2O_2)^{2+}]$, is formed during the reduction. Radical trapping has shown that a major pathway in this reaction involves the breakup of this intermediate into $Ru(NH_3)_6^{3+}$, OH^-, and $HO^\bullet$.[14]

$Ru(NH_3)_6^{2+}$ Reductant for O_2. Stanbury et al. have studied the autoxidation reactions of a series of Ru(II) complexes of the general formula $Ru(NH_3)_5L^{2+}$, where L = NH_3 or a pyridine base. The kinetic evidence has been interpreted as explained only by a one-electron outer-sphere reduction of O_2 forming O_2^-. The O_2^- is reduced further by a second 1 equiv of $Ru(NH_3)_5L^{2+}$.[17,30] When $Ru(NH_3)_6^{2+}$ was oxidized by O_2 in the presence of the radical traps in phosphate buffer (pH 6.86), we observed the 1:2:2:1 pattern of the $HO-DMPO^\bullet$ species ($a_N = a_H = 15.0$ G) with the DMPO trap (Figure 4a) and six-line, equal-intensity pattern of $a_N = 17.1$ G and $a_H = 3.7$ G with PBN as the trap (Figure 4B). The nearness of these parameters to those of the $HO^\bullet$ radical adducts as generated by $Ti(edta)(H_2O)^-$ and $Fe(edta)^{2-}$ indicates that only $HO^\bullet$ is trapped in the case of DMPO at pH 6.86. The rapid sequential reduction of O_2 through O_2^- and H_2O_2, and on to HO^- plus $HO^\bullet$, is implicated for this reagent. One may conclude that if O_2^- is formed by an outer-sphere reagent, its reduction is rapid enough that its $HO^\bullet$ generated partner is the one most likely to be trapped.

When $Ru(NH_3)_6^{2+}$ is oxidized by O_2 at pH 2.57 and 3.60 (HCl) in the presence of DMPO, two radicals are trapped in the ratio of 7.6:1.0. The major species is again the $HO-DMPO^\bullet$ radical. However, the lesser radical is seen to be the trapped $HO_2^\bullet$ adduct. A spectrum identical with that observed by Harbour et al.[12] for $HO_2-DMPO^\bullet$ is detected as lines secondary to those of the $HO-DMPO^\bullet$ radical (Figure 4C). In the pH range below 4.88, $HO_2^\bullet$ should be present from the outer-sphere one-electron reduction of O_2 (pK_a of $HO_2^\bullet$ = 4.88).[25] It has been shown previously that the rate of DMPO trapping of $HO_2^\bullet$ ($k = 6.60 \times 10^3$ M^{-1} s^{-1}) is significantly greater than for the case of O_2^- ($k = 10$ M^{-1} s^{-1}).[25] The trapping of O_2^- as $HO_2^\bullet$ in the $Ru(NH_3)_6^{2+}/O_2$ system would have a kinetic advantage in the acidic pH regime. However, the dismutation of $HO_2^\bullet$ is also much faster than for dismutation of O_2^-.[25,26] The results of replicate experiments show that 13% of the trapped radicals are $HO_2-DMPO^\bullet$ in the pH range of 2.57–3.60. Therefore, even at low pH, the major pathway for loss of O_2^- is dismutation via two $HO_2^\bullet$ radicals forming H_2O_2 and O_2. This is followed by a one-electron reduction of H_2O_2, which yields the trapped $HO^\bullet$. The high kinetic advantage of $HO^\bullet$ trapping vs $HO_2^\bullet$ trapping by DMPO causes a large signal for $HO-DMPO$ even though the $[HO^\bullet]$ is only 1.5×10^{-3}% of the $[HO_2^\bullet]$ when the signal ratio is 7.6:1.0. These results show that free O_2^- or $HO_2^\bullet$ is difficult to intercept by DMPO trapping when these are formed by metal ion reducing agents plus O_2 in the outer-sphere pathway. However, the absence of $HO-DMPO^\bullet$ in these systems can be taken as strong evidence for the absence of free O_2^- or $HO_2^\bullet$. H_2O_2, formed via either dismutation or reduction of O_2^- and $HO_2^\bullet$, is further reduced to $HO^\bullet$. $HO^\bullet$ is readily trapped by DMPO, as shown in Table I for $Ti(edta)^-$, $Fe(edta)^{2-}$, $Fe(H_2O)_6^{2+}$, $Ti(H_2O)_6^{3+}$, and $Ru(NH_3)_6^{2+}$ reductions of H_2O_2.

$Ti(edta)(H_2O)^-$ Reductant for O_2. Previous kinetic studies have shown that O_2 is reduced by $Ti(edta)(H_2O)^-$ by means of an inner-sphere reaction forming a bound superoxo intermediate, $Ti(O_2)(edta)^-$ ($k = 1.02 \times 10^4$ M^{-1} s^{-1}).[18] It was of interest to observe if the radical-trapping agents would intercept a *bound* superoxo moiety.[27] A $Co(III)-O_2$-complex was trapped with DMPO by Drago et al.[28] When $Ti(edta)(H_2O)^-$ was mixed with O_2 in the presence of DMPO, no radical of any kind was detectable within 60 s of the mixing. Under identical procedures with H_2O_2 present, copious amounts of the $HO-DMPO^\bullet$ adduct were identified at half the highest available receiver gain used to establish the absence of a signal with O_2 oxidation. No other radical species was detected for the O_2 oxidation of $Ti(edta)(H_2O)^-$ in the presence of C_2H_5OH as a potential additional scavenger. By this means it is shown that the $O_2/Ti(edta)(H_2O)^-$ reaction is 100% inner sphere and that the bound O_2^- complex does not react with either DMPO or an ethanol mediator in the solvent cage or dissociate giving free O_2^- (and $HO^\bullet$) on a time scale competitive

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(27) Results of the trapping of a Ru(II)–hydroperoxyl complex formed in the reaction of H_2O_2 with $Ru_2^{II}(ttha)^{2-}$ will be reported elsewhere. Coupling parameters similar to those observed by Drago et al.[28] have been found.

(28) Hamilton, D. E.; Drago, R. S.; Tester, J. *J. Am. Chem. Soc.* **1984**, *106*, 5353.

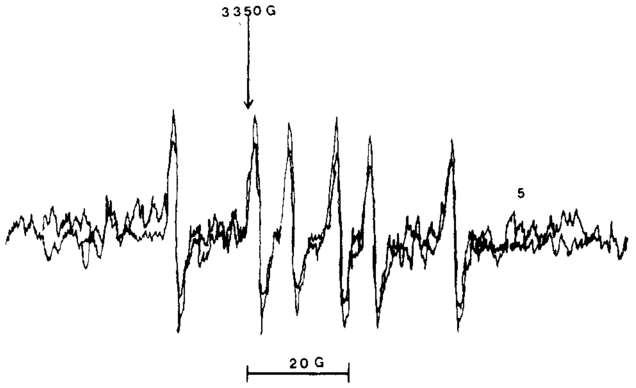


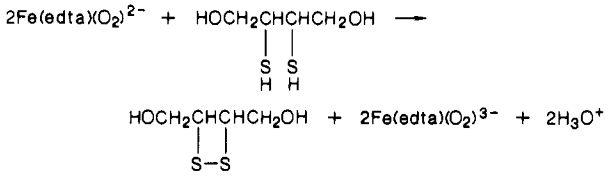
Figure 5. DMPO radical adduct generated by $\mathrm{Fe(edta)^{2-}/O_2}$: 30-s O_2 oxidation of $\mathrm{Fe(edta)^{2-}}$ followed by Ar purge, 4.0-min scans, RG = 4.0 × 10^4, 9.405 GHz, 0.80-G modulation amplitude; all other settings as in Figure 1 (no H_2O_2).

to its reduction to the bound peroxo product $\mathrm{Ti(O)_2(edta)^{2-}}$.

$\mathrm{Fe(edta)^{2-}}$ Reductant for O_2. The autoxidation of $\mathrm{Fe^{II}}$ polyamino carboxylates forms their $\mathrm{Fe^{III}}$ counterpart complexes in virtually quantitative yields. The $\mathrm{Fe_2(ttha)^{2-}}$ binuclear complex has been shown to reduce O_2 without the appearance of free $\mathrm{HO^\bullet}$, O_2^-, or H_2O_2.[15] The Udenfriend system for organic hydroxylations uses the $\mathrm{Fe^{II}(edta)^{2-}/O_2}$ system together with ascorbate as a sacrificial reducing agent.[33] The hydroxylation process has many of the properties of certain monooxygenase enzymes.[34] The active intermediate is reputed to be an $\mathrm{Fe^{III}(O_2^{2-})}$ (peroxo) intermediate formed by reduction of an $\mathrm{Fe^{III}(O_2^-)}$ (superoxo) precursor. A search for evidence of a superoxo intermediate and its ability to oxidize a sacrificial substrate was undertaken by using the DMPO spin-trapping procedure.

When O_2 was bubbled through a 3.0×10^{-3} M solution of $\mathrm{Fe(edta)^{2-}}$ at pH $\cong$ 6 for 30 s followed by a rapid purge of Ar to remove the excess O_2, which causes paramagnetic broadening of organic radicals, a six-line pattern (Figure 5) with $a_H = 22.8$ G and $a_N = 16.2$ G was obtained. A similar radical is generated by O_2^- from the photochemical oxidation of diethylenetriaminepentaacetate ($\mathrm{DTPA^{5-}}$) by O_2 with riboflavin.[29] These parameters are also very similar to those of the carbon-centered radicals that are found with alcohol mediators plus $\mathrm{HO^\bullet}$ as trapped by DMPO (see Table I under $\mathrm{Fe(edta)^{2-}}$ or $\mathrm{Ti(edta)(H_2O)^-}$ with H_2O_2 as the oxidant). The radical species trapped here must be due to either $\mathrm{HO^\bullet}$ or coordinated O_2^- abstraction of an H atom from coordinated edta, as the edta is the only source of organic species in the reaction medium. Other results implicate coordinated O_2^- as the active agent. O_2^- alone, provided by KO_2 as a salt and introduced into 0.10 M $\mathrm{H_2edta^{2-}}$ in the presence of DMPO, showed *only* $\mathrm{HO^\bullet}$ trapped by DMPO (no C-centered adducts). Therefore, free O_2^- will only carry out the dismutation steps generating $\mathrm{HO^\bullet}$. Neither O_2^- or $\mathrm{HO^\bullet}$ had sufficient activity to attack $\mathrm{H_2edta^{2-}}$ to give a C-centered radical in detectable yield. Furthermore, when $\mathrm{HO^\bullet}$ is generated in the presence of $\mathrm{Fe(edta)^{2-}}$ via H_2O_2 oxidation, no C-centered radical signal is detected. Therefore, the radical adduct shown in Figure 5 must originate within the cage of the original $\mathrm{[Fe(edta)(O_2)]^{2-}}$ intermediate.

The amplitudes of the radical production were identical for samples prepared by independent workers obtaining spectra 4 months apart. The C-centered radical production is quenched by addition of a sacrificial reducing agent, dithiothreitol (DTT). DTT is a well-known reducing agent used in many biochemical studies, particularly in the Dervan type ($\mathrm{Fe^{II}(edta)^{2-}/O_2}$-based) system used for DNA-nicking and footprinting procedures.[23,32] The spectrum of the Fe(III) peroxo complex[31] $\mathrm{Fe(edta)(O_2)^{3-}}$, $\lambda_{max} = 520$ nm, is observed. Absence of the C-centered radical when DTT is added indicates that eq 5 occurs more rapidly than the coordinated O_2^- will attack $\mathrm{edta^{4-}}$ within the complex. Presumably the ascorbate ion serves the same role in the Udenfriend reagent.



$$2\mathrm{Fe(edta)(O_2)^{2-}} + \mathrm{HOCH_2\underset{\underset{\displaystyle H}{\displaystyle S}}{C}H\underset{\underset{\displaystyle H}{\displaystyle S}}{C}HCH_2OH} \longrightarrow \mathrm{HOCH_2\underset{S-S}{CHCH}CH_2OH} + 2\mathrm{Fe(edta)(O_2)^{3-}} + 2\mathrm{H_3O^+} \quad (5)$$

When the $\mathrm{Fe(edta)^{2-}/O_2}$ reaction is carried out at pH 4.36 or in the presence of a large excess of free $\mathrm{H_2edta^{2-}}$, no radical is detected with DMPO. It is reasonable that the lower pH or source of a proton donor accelerates the loss of $\mathrm{Fe(edta)(O_2)^{2-}}$, presumably stabilizing the species toward sequential reduction to coordinated HO_2^-. At higher pH, reduction of coordinated O_2^- by $\mathrm{Fe^{II}(edta)^{2-}}$ is probably slower on electrostatic grounds. A longer lifetime of the $\mathrm{Fe(III)-O_2^-}$ intermediate will allow for attack of the ligand within the solvent cage, yielding a trappable radical related to the $\mathrm{DTPA^{5-}/O_2}$/riboflavin system.[29]

Support for this observation, that the inner-sphere O_2^- complex permits attack of the ligand structure within the intermediate in a small percentage of reduction events, has been found by earlier studies in the autoxidation of $\mathrm{Fe_2(ttha)^{2-}}$. $\mathrm{Fe_2(ttha)^{2-}}$ exists in solution in an extended-chain form such that the $\mathrm{Fe^{II}}$ centers are remote from each other and behave largely like separate $\mathrm{Fe(edta)^{2-}}$ units.[15] The results that are described here for the $\mathrm{O_2/Fe_2(ttha)^{2-}}$ and below for the $\mathrm{O_2/V_2O(ttha)^{2-}}$ systems[15,16] were supported by additional studies using SOD (superoxide dismutase) and CAT (catalase) enzymes to rule out any major component of outer-sphere O_2^- or H_2O_2 formation. O_2 oxidation of $\mathrm{Fe_2(ttha)^{2-}}$ in the presence of DMPO results in a trapped carbon-centered radical with spin Hamiltonian parameters $a_H = 22.8$ G and $a_N = 14.8$ G, which are very similar to the values found here for the $\mathrm{Fe(edta)^{2-}/O_2}$ reaction.[15] Furthermore, when $\mathrm{Fe_2(ttha)^{2-}}$ was autoxidized by O_2 in the presence of ethanol to mediate the DMPO trapping, a different radical with $a_H = 22.6$ G and $a_N = 16.0$ G was obtained, which is nearly the same as the $\mathrm{HO^\bullet}$ abstracted radical of ethanol ($\mathrm{CH_3CHOH}$) shown in Table I. The difference in behavior of the O_2^- inner-sphere complex for $\mathrm{Ti(edta)(H_2O)^-}$ compared to that for $\mathrm{Fe(edta)^{2-}}$ is probably due to the difference in the rates of reduction of the coordinated O_2^-, forming the peroxo products in competition with any tendency of the O_2^- to attack the nearby ligand, or to attack a sacrificial reagent such as ethanol mediator in the solvent cage.

The results that have been described elsewhere for the radical-trapping experiments of the $\mathrm{O_2/V_2O(ttha)^{2-}}$ system lend further support to the studies here.[16] As in the case of the Ti(III)edta reductant, very little radical is trapped with DMPO present alone when O_2 oxidizes $\mathrm{V_2O(ttha)^{2-}}$. A small amount of ethanol-mediated trapping of the O_2^- intermediate $\mathrm{[V^{III},V^{IV}O_2^-]}$ takes place.[16] An overall upper limit of 10% of the reduction events forming a carbon-centered ethanol radical was shown by DMPO trapping. This 10% reactivity may be due to the sum of several types of processes: (1) O_2^- abstraction from the ethanol mediator competitive with reduction of the coordinated O_2^-, (2) outer-sphere

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(29) (a) Reference 25. For a riboflavin/O_2 photooxidation of $\mathrm{Hedta^{3-}}$ see: Fife, D. J.; Moore, W. M. *Photochem. Photobiol.* **1979**, *29*, 43. (b) Buettner, G. R.; Oberly, L. W. *Biochem. Biophys. Res. Commun.* **1978**, *83*, 69.

(30) The reduction of O_2 on $\mathrm{Ru(NH_3)_6^{2+}}$ occurs much too rapidly to allow for loss of NH_3 to open a labile coordination position. See: (a) Shepherd, R. E.; Taube, H. *Inorg. Chem.* **1973**, *12*, 1392. (b) Pladziewicz, J. R.; Meyer, T. J.; Broomhead, J. A.; Taube, H. *Inorg. Chem.* **1973**, *12*, 639. (c) Reference 17.

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(32) (a) Sluska, J. P.; Horvath, S. J.; Bruist, M. F.; Simon, M. I.; Dervan, P. B. *Science (Washington, D.C.)* **1987**, *238*, 1129. (b) Dervan, P. B.; Sluka, J. P. In *Proceedings of the International Kyoto Conference on Organic Chemistry*; Elsevier: Amsterdam, 1986; Kodanska: Tokyo, 1986, p 307. (c) Taylor, J. S.; Schulze, P. G.; Dervan, P. B. *Tetrahedron* **1984**, *40*, 457.

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(34) Ochiai, E.-I. *Bioinorganic Chemistry, An Introduction*; Allyn and Bacon: Boston, MA, 1977; Chapters 7 and 10.

reduction of O_2 forming free O_2^-, which upon dismutation is converted to HO• and trapped by alcohol, and (3) dissociation of O_2^- from the inner-sphere complex. The latter two explanations would not account for the absence of HO-DMPO• trapping in the absence of the ethanol mediator. Therefore, these reactions must be inner sphere with coordinated O_2^- generating trappable radicals from substrates within the solvent cage.

Conclusion

Whenever HO• is formed during the reduction of H_2O_2 (inner sphere) or O_2 (outer sphere), the DMPO or DMPO/alcohol trapping systems detect the appropriate radicals as have been characterized for the $Ti(edta)(H_2O)^-/H_2O_2$ system and the $Ru(NH_3)_6^{2+}/O_2$ system. When O_2 reductions occur by inner-sphere pathways, the DMPO trapping shows a much lower yield or no detectable radical signal for the early transition-metal reductants. Unless a large pool of reducing agent is present, the superoxo intermediate $[Fe(edta)O_2]^{2-}$ may oxidize its own edta ligand in a small fraction of events, competitively with further reduction of the coordinated O_2^- complex. The attack of O_2^- on the ligand chelate system can be transferred to a more active sacrificial agent in the solvent cage such as DTT or ascorbate. This latter effect may be important in the Dervan-type DNA-nicking drugs,[23,32] which contain a $Fe(edta)^{2-}$ group tethered to a methidium intercalator or other DNA-sequence-specific binding agents. The present study shows that dithiothrietol rapidly reduces the $Fe(edta)(O_2)^{2-}$ intermediate to the Fe(III) peroxo complex. The 1e reduction of this complex should yield a pool of HO• while a 2e reduction yields a ferryl-oxo intermediate. These would be generated at a slow rate in the vicinity of a receptive DNA substrate to suffer nicking. The results found here for the additional $Ru(NH_3)_6^{2+}$, $Ti(edta)(H_2O)^-$, and $Fe(edta)^{2-}$ reductants show that the DMPO spin trap is a useful probe as to whether an inorganic autoxidation process occurs by an inner- or outer-sphere pathway. Absence of significant amounts of the HO-DMPO• adduct can be taken as evidence of an inner-sphere process in which coordinated O_2^- is further reduced by additional reducing equivalents of the reductant. In some cases, small amounts of radicals derived from attack of the ligand structure by O_2^- coordinated within the cage can also be deduced, leading to useful mechanistic information in conjunction with separate experiments involving the reactivity of free O_2^- or HO• and the free ligand.

Acknowledgment. This work was supported by the National Science Foundation through NSF Grant CHE-8417751 and by the donors of the Petroleum Research Fund, Administered by the American Chemical Society.

Registry No. DMPO, 40936-29-6; PBN, 3376-24-7; $Ti^{III}(edta)(H_2O)^-$, 74111-14-1; $Fe^{II}(edta)^{2-}$, 15651-72-6; $Ti(H_2O)_6^{3+}$, 17524-20-8; $Fe(H_2O)_6^{2+}$, 15365-81-8; $Ru(NH_3)_6^{2+}$, 19052-44-9; CH_3CH_2OH, 64-17-5; CH_3OH, 67-56-1; $(CH_3)_2CO$, 67-64-1; $(CH_3)_3COH$, 75-65-0; H_2O_2, 7722-84-1; O_2, 7782-44-7; O_2^-, 11062-77-4; HO•, 3352-57-6.

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Synthesis of $Cr(tacn)X_3$ Compounds (tacn = 1,4,7-Triazacyclononane). Photochemistry and Emission Properties of the Triisothiocyanate

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Received August 21, 1987

A series of $Cr(tacn)X_3$ compounds, where tacn = 1,4,7-triazacyclononane, has been prepared and characterized for X = Br, F, CN, and NCS. The latter two compounds emit in room-temperature solutions and were therefore explored as candidates for sensitization and quenching studies. The triisothiocyanate compound appears to be the most promising. Although it is insoluble in water, it dissolves in a number of nonaqueous solvents, emits strongly at 753 nm with a lifetime at 298 K of 27 μs in dmso, is quenched efficiently by a number of metal ions and complexes as well as by oxygen, and is thermally stable and relatively photostable, having a quantum yield for thiocyanate photosubstitution of about 0.05 in dmso, dmf, and acetonitrile. The emission of the compound is quenched by $Cr(en)_3^{3+}$, with a rate that is consistent with thermally activated energy transfer. Photolysis in aerated dmso of the triisothiocyanate leads to increased emission from the complex, a result of oxygen scavenging.

Introduction

There continues to be considerble interest in energy- and electron-transfer processes involving the excited states of transition-metal ions.[1-3] Analogous processes are involved in a number of important chemical and biological processes.

Research activity in this general area has included a large number of studies of energy transfer to and from chromium complexes.[4] These are particularly important to our understanding because of the well-defined spectroscopy of the chromium(III) quartet and doublet states,[5] which provide a system archetypal for many other less tractable systems. Studies of energy transfer involving chromium complexes are often hampered, however, by effects arising from the charges on the complexes, as well as by the high photolability of many of the molecules used to date.[6-8] The first of these problems can be particularly severe in studies in nonaqueous solvents, an unfortunate feature because these are otherwise excellent media in which to study the sensitization and quenching interactions between ground and excited states of organic molecules and metal complexes.[9]

It therefore appeared to us to be potentially useful to develop a series of uncharged Cr(III) complexes in which the overall ligand field and therefore the excited-state energy levels could be varied and to study their emission and photochemistry. This was in the hope that some useful new uncharged quenchers and sensitizers would emerge, compounds that would be useful in energy-transfer and quenching studies as well as interesting in their own photochemistry and photophysics. A promising candidate series was the triacido complexes of the tridentate ligand 1,4,7-triazacyclononane (tacn);[10] it was our expectation, based on current models of Cr(III) photochemistry,[11] that these molecules would be reasonably photostable, particularly where the acido ligand was of

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0020-1669/88/1327-1095$01.50/0