$$\mathrm{RCo^{III}(chgH)_2py + Co^{II}(dmgH)_2py \rightleftharpoons RCo^{III}(dmgH)_2py + Co^{II}(chgH)_2py} \tag{1}$$

where chgH and dmgH are the conjugate bases of cyclohexanedionedioxime and dimethylglyoxime, respectively. Though it was reasonably suggested[2] that the cobaloxime(II) reagent was not directly comparable with conventional organic free radical reagents, such as the methyl radical, the reaction did demonstrate the capability of cobaloxime(II) as a leaving group in homolytic substitution and indicated that other homolytic displacement reactions might be both useful in organic synthesis and important in a number of biosynthetic reactions of organocobalamins.[3]

We here describe the first examples of homolytic displacement of cobalt(II) from organocobalt(III) complexes by conventional organic radicals.[4] Thus, allylbis(dimethylglyoximato)pyridinecobalt(III) (**1**) reacts with bromotrichloromethane at ambient temperature in chloroform to give near quantitative yields of 4,4,4-trichlorobut-1-ene (**2**).[5] The time necessary for the reaction varies from a few minutes to an hour; the reaction is noticeably faster in the case of impure samples of the allylcobaloxime containing traces of cobaloxime(II) species. The corresponding reaction takes several hours at 40 °C when carbon tetrachloride is used both as solvent[6] and as reagent; it is inhibited by added galvinoxyl but is markedly faster in the presence of added benzoyl peroxide (5% w/w) and in the presence of light.

Corresponding reactions of the substituted allylcobaloximes **3–6** with bromotrichloromethane and with carbon tetrachloride each gave only a single low molecular weight olefinic product and, in all cases for which a distinction can be made, the reactions were 100% regiospecific, giving the rearranged allyl product **7–10**, respectively. Small deviations from quantitative recovery of the monomeric olefin could be ascribed to partial oligomerization of the initial product. The inorganic product in each case was the bromo- or chlorobis(dimethylglyoximato)pyridinecobalt(III) complex.

$\mathrm{R(R')C{:}CR''{\cdot}CH_2Co(dmgH)_2py}$ + $\mathrm{XCCl_3}$
1, R = R′ = R″ = H   X = Br or Cl
3, R = Me; R′ = R″ = H
4, R = Ph; R′ = R″ = H
5, R = R′ = H; R″ = Me
6, R = R′ = Me; R″ = H

$$\rightarrow \mathrm{XCo(dmgH)_2py + CH_2{:}CR''{\cdot}CR(R')CCl_3} \tag{2}$$

2, R = R′ = R″ = H
7, R = Me; R′ = R″ = H
8, R = Ph; R′ = R″ = H
9, R = R′ = H; R″ = Me
10, R = R′ = Me; R″ = H

From the influence of initiators, inhibitors, and the nature of the reagent on the rates of the above reactions, we believe that they involve chain reactions in which trichloromethyl radicals and cobaloxime(II) complexes are the chain carriers[7] (eq 3-5). The main initiating species are probably allyl radicals and cobaloxime(II) species formed by either thermolysis or photolysis of small quantities of the reagent allylcobaloxime.[8,9] At this stage we cannot distinguish whether the reaction (4) is completely concerted with species **11** as a transition state, or a two-step reaction in which species **11** is a short-lived intermediate.

$$\text{initiator} + \mathrm{XCCl_3 \rightarrow Cl_3C\cdot} \tag{3}$$

$$\mathrm{Cl_3C\cdot + RCH{:}CH{\cdot}CH_2Co(dmgH)_2py \rightarrow Cl_3C{\cdot}CHR{\cdot}\dot{C}H{\cdot}CH_2Co(dmgH)_2py}$$

11

$$\rightarrow \mathrm{Cl_3{\cdot}CHR{\cdot}CH{:}CH_2 + Co(dmgH)_2py} \tag{4}$$

$$\mathrm{Co(dmgH)_2py + XCCl_3 \rightarrow Cl_3C\cdot + XCo(dmgH)_2py} \tag{5}$$

Similar reactions proceed with allylcobaloximes and other polyhalogenomethanes known to give polyhalogenomethyl radicals, though the yields of organic product decrease with increasing requirement for long reaction times.

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(4) This is also probably the first clear example of homolytic displacement of any transition metal from carbon.

(5) All reagents and products described have been characterized by ^{1}H NMR and elemental analysis.

(6) Under the reaction conditions the allylcobaloxime was only partially soluble in carbon tetrachloride, but this alone did not account for the slowness of the reaction.

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Manganese(II) and Manganese(III) 8-Quinolinol Complexes. Redox Model for Mitochondrial Superoxide Dismutase

Sir:

The discovery in 1969[1] that superoxide ion (O_2^-) is a common respiratory intermediate of aerobic organisms with its concentration controlled by the superoxide dismutase (SOD) enzyme has revolutionized the interpretation of biological oxidation-reduction processes. A subsequent discovery is that there is a manganese-containing version of superoxide dismutase as well as the originally discovered copper-zinc form from erythrocytes; the manganese SOD has been isolated from bacterial sources[2,3] and from mitochondria.[4] At present there is still controversy as to whether the manganese SOD contains one or two manganese atoms per enzyme molecule.[2,4] Unfortunately, because the enzyme is not well characterized and a crystal structure has not been reported as yet, the chemical properties are not known; i.e., the exact role of the manganese atom(s) in the enzyme, the oxidation state(s) of the manganese atom(s), the degree of association of the two manganese atoms if two are indeed present, the type of ligands coordinated to the manganese atom(s), and the stereochemistry around the metal(s).

The most recent report on the chemistry of this system indicates that the catalytic cycle can be represented by[5]

$$\mathrm{E + O_2^- \rightarrow E^- + O_2} \tag{1}$$

$$\mathrm{E^- + O_2^- \xrightarrow{H^+} E + H_2O_2} \tag{2}$$

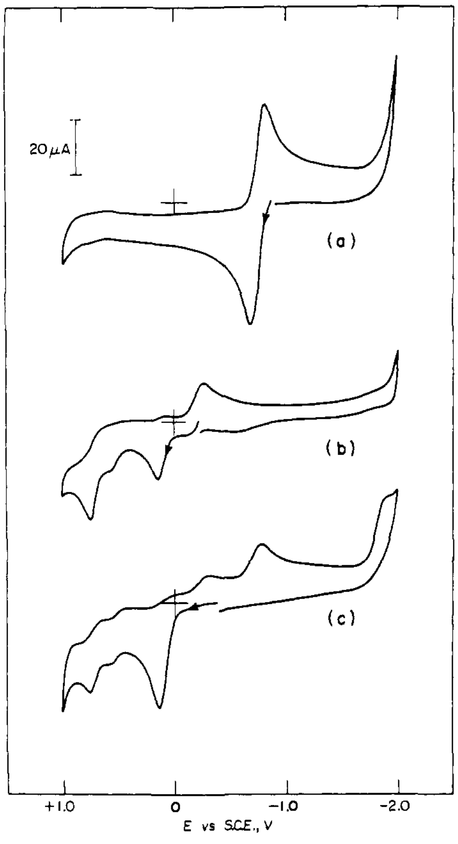

Figure 1. Cyclic voltammograms in 0.1 M TEAP–Me_2SO at a Pt electrode of (a) 1.32 mM O_2^-, (b) 1.00 mM $Mn^{II}Q_2{\cdot}2H_2O$, and (c) a mixture of 1.32 mM O_2^- and 1.00 mM $Mn^{II}Q_2{\cdot}2H_2O$. Scan rate, 0.1 V/s.

$$E^- + O_2^- \rightarrow E^{2-} + O_2 \quad (3)$$

$$E^{2-} + O_2^- \xrightarrow{H^+} E^- + H_2O_2 \quad (4)$$

Such a mechanism would require that the manganese exist in three different oxidation states if the enzyme contains only one metal atom per molecule. However, if the enzyme contains two metal atoms, only two formal oxidation states would be required. The goal of the present research is to identify manganese model complexes that will mimic the reactions of eq 1-4.

The manganese(II) 8-quinolinol complexes,[6,7] $Mn^{II}Q_2{\cdot}2H_2O$ and $Mn^{II}Q_3^-$, and the manganese(III) complex,[8] $Mn_2^{III}OQ_4(HQ)_2{\cdot}2CH_3OH$, in Me_2SO solution represent a system that undergoes oxidation-reduction chemistry which parallels much that is observed for mitochondrial superoxide dismutase. A self-consistent redox mechanism for these compounds appears in Table I. The $Mn^{II}Q_2{\cdot}2H_2O$ complex is not reducible but is reversibly oxidized at fast scan rates to $Mn^{III}Q_2^+$ (+0.16 V vs. SCE). Most of the oxidized species undergo a hydrolytic reaction with the residual water present in the solvent[12] to form $Mn^{III}Q_2(OH)$ and H^+. The H^+ ions that are formed attack unoxidized $Mn^{II}Q_2$ to form $Mn^{II}Q^+$ [13] and HQ. This reaction has been confirmed by experiments in which H^+ ion is added to solutions of $Mn^{II}Q_2$. The liberated HQ reacts with $Mn^{III}Q_2(OH)$ to form $Mn_2^{III}OQ_4(HQ)_2$ and H_2O. Controlled potential coulometry on $Mn^{II}Q_2$ at +0.25 V indicates that *n*, the number of moles of electrons transferred per mole of complex, is 0.5 instead of 1.0, which is consistent with the overall reaction

$$2Mn^{II}Q_2 + H_2O - 1.0e^- \rightarrow \tfrac{1}{2}Mn_2^{III}OQ_4(HQ)_2 + Mn^{II}Q^+ \quad (5)$$

$Mn_2^{III}OQ_4(HQ)_2$ is reduced, in the absence of acid, by a 1.0e⁻ per manganese process at −0.31 V to form $Mn^{II}Q_3^-$ and H_2O. This has been confirmed by controlled potential coulometry at −0.50 V. When H^+ ions are present, $Mn^{II}Q_3^-$ is converted to $Mn^{II}Q_2$ and HQ.

Table I. Redox Reactions and Voltammetric Peak Potentials for Manganese(II) and -(III) 8-Quinolinol Complexes[a]

	V vs. SCE		
	E_{pc}	E_{pa}	e^-/Mn
$Mn^{II}Q_2{\cdot}2H_2O \xrightleftharpoons{Me_2SO} Mn^{II}Q_2 + 2H_2O$[b]			
$2Mn^{II}Q_2 \rightleftharpoons Mn^{II}Q^+ + Mn^{II}Q_3^-$[c]			
$Mn^{II}Q_2 + Q^- \longrightarrow Mn^{II}Q_3^-$[d]			
$Mn^{II}Q_3^- + H^+ \longrightarrow Mn^{II}Q_2 + HQ$			
$Mn^{II}Q_2 \rightleftharpoons Mn^{III}Q_2^+ + e^-$	+0.11	+0.16	1
$Mn^{III}Q_2^+ + H_2O \longrightarrow Mn^{III}Q_2(OH) + H^+$			
$Mn^{II}Q_2 + H^+ \rightleftharpoons Mn^{II}Q^+ + HQ$			
$2Mn^{III}Q_2(OH) + 2HQ \longrightarrow Mn_2^{III}OQ_4(HQ)_2 + H_2O$			
$Mn_2^{III}OQ_4(HQ)_2 + 2e^- \rightleftharpoons 2Mn^{II}Q_3^- + H_2O$	−0.31	−0.16	1
$2Mn^{III}Q_3(\text{solid}) + H_2O \xrightleftharpoons{Me_2SO} Mn_2^{III}OQ_4(HQ)_2$			
$Mn_2^{III}OQ_4(HQ)_2 \rightleftharpoons Mn_2^{IV}OQ_4(HQ)_2^{2+} + 2e^-$	+0.70[e]	+0.75	
$Mn_2^{III}OQ_4(HQ)_2 + 2OH^- \longrightarrow Mn^{II}Q_3^- + Mn^{II}Q^+ + Q_2 + 2H_2O$			

[a] At a platinum electrode (scan rate, 0.1 V s^{-1}) in 0.1 M tetraethylammonium perchlorate–dimethyl sulfoxide (Me_2SO). [b] Cryoscopic molecular weight determination in Me_2SO indicates compound is 80% dissociated. [c] Cyclic voltammetry indicates that 1 mM solutions of $Mn^{II}Q_2{\cdot}2H_2O$ in Me_2SO contain about 10% $Mn^{II}Q_3^-$, and conductance measurements indicate that such solutions dissociate about 10% into a 1-to-1 electrolyte. [d] Q^- was prepared electrochemically in situ by the reduction of HQ. [e] Acetonitrile solution.

The $Mn_2^{III}OQ_4(HQ)_2$ complex is irreversibly oxidized at +0.75 V to form a manganese (IV) species which immediately oxidizes the solvent, the residual water present in the solvent, or its own ligands and forms a mixture of the two manganese(III) complexes again. The $Mn^{II}Q_2$ complex also is highly susceptible to nucleophilic displacement of the Q^- ligands by OH^- ions. In addition, $Mn^{II}Q_2$ reacts slowly with both O_2 and H_2O_2 to form $Mn_2^{III}OQ_4(HQ)_2$ and $Mn^{II}Q^+$.

Figure 1 illustrates cyclic voltammograms in Me_2SO solution at a platinum electrode for (a) 1.3 mM O_2^-, (b) 1 mM $Mn^{II}Q_2{\cdot}2H_2O$, and (c) a mixture of 1.3 mM O_2^- and 1 mM $Mn^{II}Q_2{\cdot}2H_2O$ 10 s after mixing. Clearly all of the O_2^- is decomposed within the time it takes to record the first cyclic voltammogram, and the complex is in its initial oxidation state and is not appreciably decomposed. The solution does not change color during the decomposition reaction. The increased peak current that appears to be associated with the oxidation of $Mn^{II}Q_2$ at +0.16 V probably is due to the coincident oxidation of the decomposition product, HO_2^-, to O_2. Some O_2 and H_2O_2 formation is evident from initial cathodic scans. More H_2O_2 and O_2 are released during the next 15 min. The catalytic properties of the system are complicated by the fact that the only source of protons for HO_2^- and H_2O_2 formation is H_2O. The OH^- ions thus generated attack the catalyst to form what appears to be an inactive species. When the catalyst is used at lower concentrations (0.5 mM or less), the decomposition of O_2^- is rapid at first but slows down rapidly, presumedly because of base-induced decomposition of the catalyst, and also because the increasing basicity of the media decreases the proton activity, which inhibits peroxide formation. In addition, the O_2 and H_2O_2 that are formed react with $Mn^{II}Q_2$ to form $Mn_2^{III}OQ_4(HQ)_2$.

$Mn_2^{III}OQ_4(HQ)_2$ and $Mn^{II}Q_3^-$ also react with O_2^- to give O_2 and H_2O_2, although somewhat more slowly. Based on our observations, a reasonable mechanism for the $Mn^{II}Q_2$ catalyzed disproportionation of O_2^- appears to be

$$\mathrm{Mn^{II}Q_2(H_2O)_2 + O_2^- \rightarrow Mn^{III}Q_2(O_2H)(H_2O) + OH^-} \quad (6)$$

$$\mathrm{Mn^{III}Q_2(O_2H)(H_2O) + O_2^- \xrightarrow{H_2O} Mn^{II}Q_2(H_2O)_2 + O_2 + HO_2^-} \quad (7)$$

secondary reactions

$$\mathrm{Mn^{II}Q_3^- + O_2^- \xrightarrow{H_2O} Mn^{III}Q_3(O_2H)^- + OH^-} \quad (8)$$

$$\mathrm{Mn^{III}Q_3(O_2H)^- + O_2^- \rightarrow Mn^{II}Q_3^- + O_2 + HO_2^-} \quad (9)$$

The most remarkable feature of this model is the apparent ability of a manganese(II) complex to reduce O_2^- to HO_2^-. Such a process, on the basis of the electrochemical peak potentials for the individual components, Figure 1, appears to be thermodynamically impossible. Apparently, eq 6 is favored as a result of the strong interaction of the product species, Mn^{III} and HO_2^- [14]

The apparent oxidation by O_2^- ion (generated from oxygen plus xanthine-xanthine oxidase or from illumination of spinach chloroplasts) of Mn(II) to Mn(III) in the presence of a pyrophosphate buffer system has been reported recently.[15] However, the authors conclude that the Mn(II)-pyrophosphate complex does not act as a disproportionation catalyst for O_2^- ions, and imply that the Mn(III)-pyrophosphate does not oxidize O_2^- ion but does oxidize H_2O_2. This is in sharp contrast to the results of the present study (eq 6-9).

Although the Fridovich mechanism (eq 1-4) invokes a third oxidation state for the enzyme to rationalize the kinetic results, there is another possible explanation. The slower catalytic state of the enzyme may simply be a different hydrolytic species.

Because protons catalyze the disproportionation of O_2^- ions and coordinated Me_2SO might serve as a proton source, the experiments of Figure 1 have been repeated in a pyridine solvent system. The results are qualitatively identical. Combination of 1 mM $Mn^{II}Q_2$ with 2 mM O_2^- immediately destroys all of the O_2^- and yields a solution that contains $Mn^{II}Q_2$, O_2, and H_2O_2 in amounts equivalent to 70-90% efficiency for eq 6-9.

Another possible interpretation of the results is that the $Mn^{II}Q_2$ complex acts as a Lewis acid to catalyze the disproportionation of O_2^- ions. However, when the experiment of Figure 1 is repeated with $Mg^{II}Q_2$ or $Zn^{II}Q_2$ substituted for $Mn^{II}Q_2$ the rate of decomposition for O_2^- is as slow as for Me_2SO solutions without added metal complexes (about 5-15% per hour). This supports the conclusion that $Mn^{II}Q_2$ acts as a redox catalyst.

The present study is being extended to determine what effects the ligands have on both the redox chemistry of the complexes and their ability to catalyze the decomposition of superoxide ion. In particular, ligands are being sought which will stabilize manganese(II) complexes toward nucleophilic displacement by OH^- ions and which will accelerate reaction 6. We also are trying to find a suitable buffer system to facilitate the formation of hydrogen peroxide and prevent the ultimate destruction of the catalyst. Such a system will make it possible to evaluate the kinetic parameters for the various reactions.

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(7) $Mn^{II}Q_3^-$ was prepared in situ in an electrochemical cell by the exhaustive controlled potential electrolysis of a 1 mM solution of $Mn^{III}Q_3 \cdot \frac{1}{2}H_2O \cdot CH_3OH$ in Me_2SO at −0.50 V vs. SCE.

(8) $Mn_2^{III}OQ_4(HQ)_2 \cdot 2CH_3OH$ was prepared by the reaction of air with a saturated solution of $Mn^{II}Q_2 \cdot 2H_2O$ in 50% CH_3OH/H_2O. The black crystals were filtered, washed with H_2O and CH_3OH, and dried in vacuo at room temperature for 2 h. Anal. Calcd for $Mn_2C_{56}N_6H_{46}O_9$. Mn, 10.39; C, 63.64; N, 7.95; H, 4.38. Found: Mn, 10.14; C, 63.70; N, 7.76; H, 4.30. Magnetic susceptibility measurements indicate that Mn(III) compounds with this stoichiometry are high-spin d^4 systems in the solid state ($\mu_{eff} = 5.02\ \mu_B$ by the Guoy method; spin-only value, 4.82 μ_B), but are diamagnetic in Me_2SO solutions ($\mu_{eff} \simeq 0.0\ \mu_B$ by the NMR method).[9] Because all known Mn(III)–Me_2SO complexes also are high-spin,[10] solvent effects sufficient to cause spin pairing are unlikely. The observed diamagnetism implies strong antiferromagnetic coupling of the type that is observed for other μ-oxobridged binuclear Mn(III) and Mn(IV) complexes,[11] and that the molecular form of the complex in solution is $[(HQ)Mn^{III}Q_2\text{–}O\text{–}Mn^{III}Q_2(HQ)]$.

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(13) $Mn^{II}Q^+$ probably reacts with water to form $Mn^{II}Q(OH) + H^+$. Neither manganese compound is electrochemically active.

(14) Several unsuccessful attempts have been made to isolate a Mn(III)–(8-quinolato)–peroxide complex. Combinations in Me_2SO with reaction stoichiometries of

$$\mathrm{6Mn^{II}Q_2 + 2O_2 + 3H_2O \rightarrow Mn_2^{III}OQ_4(HQ)_2 + 2Mn^{III}Q_2(HO_2) + 2Mn^{II}Q(OH)}$$

$$\mathrm{Mn^{II}Q_2 + H_2O_2 \xrightarrow[CPE]{+0.25\ V} Mn^{III}Q_2(HO_2) + H^+ + e^-}$$

have been studied by cyclic voltammetry. Both solutions exhibit an additional cathodic peak at −0.75 V (besides the peak at −0.31 V for $Mn_2^{III}OQ_4(HQ_2)$) which has the characteristic shape of H_2O_2 reductions in Me_2SO (−1.3 V) and may result from the reduction of $Mn^{III}Q_2(HO_2)$.

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Heats of Formation of $C_3H_5^+$ Ions. Allyl, Vinyl, and Cyclopropyl Cations in Gas-Phase Proton-Transfer Reactions

Sir:

Allyl cation intermediates in solution have been known for many years,[1] but the possibility of vinyl and cyclopropyl cation intermediates has recently attracted much interest. Vinyl cations now appear to be genuine intermediates in solvolysis reactions and electrophilic additions to allenes and acetylenes in solution.[2] Up to now, however, there have been no cases in which simple cyclopropyl cations have been unambiguously demonstrated as intermediates in solvolysis reactions,[3,4] since ring opening to an allyl cation appears to be concurrent with loss of the leaving group.[5] Theoretical calculations of the $C_3H_5^+$ energy surface[6] indicate that the 2-propenyl cation is at 17 kcal/mol higher energy than the allyl cation and rearranges to the allyl cation with a 17 kcal/mol barrier, while the cyclopropyl cation is some 39 kcal/mol higher in energy than the allyl cation with little or no barrier to rearrangement.[6b,d] We report here experimental evidence on the heats of formation of $C_3H_5^+$ ions and related allyl, vinyl, and cyclopropyl cations.