Iron(II)-Catalyzed Autoxidation of a Macrocyclic Cobalt(II) Complex

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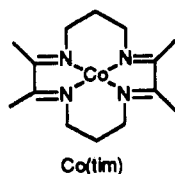Department of Chemistry, Iowa State University, Ames, Iowa 50011

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The otherwise very slow reduction of O_2 by $Co(tim)^{2+}$ (tim = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) in acidic aqueous media is efficiently catalyzed by iron(II) ions. The rate law shows first-order dependences on $Co(tim)^{2+}$, O_2, and Fe^{2+} but remains independent of halide and hydrogen ion concentrations. The catalytic autoxidation yields $Co(tim)^{3+}$ and involves the four-electron reduction of O_2 as indicated by the stoichiometry, which is independent of the reagent in excess. Moreover, the reduction of oxygen to water clearly bypasses the stage in which $Co(tim)^{2+}$ would reduce hydrogen peroxide, since this independently known reaction leads to other products. The small deviations from the exact model proposed, more evident at the 340-nm isosbestic point for $Co(tim)^{2+}$ and $Co(tim)^{3+}$, arise from a minor side reaction. The chemistry of the system is consistent with the formation of $[(tim)CoOOFe^{4+}]$ and $[(tim)CoOOH^{2+}]$ in succession.

Introduction

Metal activation of molecular oxygen is being studied extensively owing to its importance in industrial applications and in biological processes.[1-7] However, metal-catalyzed O_2 oxidations rarely utilize all four redox equivalents. Reactive intermediates complicate the schemes and may give consequent catalyst decomposition and loss of selectivity.

An example of a clean four-electron reduction of O_2 by Co-$(tim)^{2+}$, catalyzed by $Co(dmgBF_2)_2$,[8] was recently reported.[9] In this paper we report the kinetics of the autoxidation of $Co(tim)^{2+}$ catalyzed efficiently by an even simpler metal species, aqueous ferrous ion. We present a mechanistic interpretation of the catalysis and conclusive evidence that the reduction of dioxygen to water is a direct four-electron reaction, i.e., that it bypasses free hydrogen peroxide and radical intermediates.

Co(tim)

Experimental Section

The solvent used throughout was distilled water purified by passage through a Milli-Q Millipore system. $[Co(tim)(H_2O)_2](CF_3SO_3)_2$ was prepared as described previously.[9] Its stock solutions, usually 2 mM,

were kept under Ar and used the same day. The concentrations were determined spectrophotometrically at 545 nm (ϵ_{max} = 3450 L mol^{-1} cm^{-1}).[10]

Stock solutions of Fe^{2+}, *ca.* 1 M in 1 M $HClO_4$, were prepared from $Fe(ClO_4)_2 \cdot 6H_2O$ (Morton Thiokol) and kept under argon. To suppress the content of iron(III) from ~4% to below 0.2%, the stock solution was stirred with a ~20-mg piece of standard electrolytic iron (Hach Chemical Co.). This procedure could be used repeatedly, with the concentrations of the stock solution maintained by the addition of an adequate volume of 2 M $HClO_4$. Before each experiment the stock solution of Fe^{2+} was analyzed for iron(II) spectrophotometrically with 1,10-phenanthroline and for traces of Fe^{3+} by use of its reaction with $Co(tim)^{2+}$. Only when $[Fe^{3+}]$ was ≤0.2% of $[Fe^{2+}]$ was such an Fe^{2+} solution used.

Spectral and kinetic measurements were carried out by the use of Shimadzu UV 3101PC, UV 2101PC, or Perkin-Elmer diode array 3840 spectrophotometers. An oxygen electrode (portable dissolved oxygen meter, Model 16046, Hach Chemical Co.) was used to follow the kinetics of dioxygen consumption. Limited by the electrode properties, reproducible results could be obtained in the concentration range of 0.03–0.6 mM O_2 and for $k_\psi < 0.01$ s^{-1}. The temperature was controlled in all the measurements at 25.0 ± 0.2 °C. The usual $HClO_4$ concentration was 0.1 M, and the ionic strength was maintained with $LiClO_4$ at μ = 0.2 M except when varying the acidity.

The solubility of O_2 at 25 °C was taken as 1.27 mM in pure water and 1.21 mM in 0.1 M $HClO_4$ with an ionic strength of μ = 0.2 M.[11] The variations of concentrations of other solutes caused less than 1% change in O_2 solubility. Dioxygen concentrations lower than its saturation level were achieved by careful dilutions, without agitation, as described earlier.[9]

The stability of aqueous solutions of $Co(tim)^{2+}$ containing dissolved oxygen was reported previously.[9,12] The stoichiometry of the iron(III)-catalyzed O_2 oxidation of an excess of $Co(tim)^{2+}$ was determined spectrophotometrically. The exact excess concentration of the Co(II) complex for each run was calculated from its absorbance.

Data from at least three half-lives of the reaction were fitted to a first-order question. For the kinetic measurements the following concentration ranges were used: 0.05–4 mM $Co(tim)^{2+}$, 0.005–1.2 mM O_2, 0.2–17 mM Fe^{2+}, and 0.01–1 M $HClO_4$. The Fe^{2+} catalyst was present at a high concentration compared to the limiting substrate so that the reaction would proceed at a conveniently measurable rate.

Results

Preliminary Observations. The slow spontaneous autoxidation of $Co(tim)^{2+}$ and its intense optical absorption at 545 nm make it a convenient substrate for studies of catalytic autoxidation

(1) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.
(2) Drago, R. S. *Coord. Chem. Rev.* **1992**, *117*, 185.
(3) Bailey, C. L.; Drago, R. S. *Coord. Chem. Rev.* **1987**, *79*, 321.
(4) *Oxygen Complexes and Oxygen Activation by Transition Metals*; Martell, A. E., Sawyer, D. T., Eds.; Plenum: New York, 1988.
(5) *Metal Ion Activation of Dioxygen*; Spiro, T. G., Ed.; Wiley: New York, 1980.
(6) Niederhoffer, E. C.; Timmons, J. H.; Martell, A. E. *Chem. Rev.* **1984**, *84*, 137.
(7) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 140.
(8) Abbreviations used for the macrocyclic ligands: tim = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; $dmgBF_2^-$ = (difluoroboryl)dimethylglyoximate; aqua ligands are omitted hereafter.
(9) Marchaj, A.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1992**, *31*, 4860. The catalytic four-electron reduction of dioxygen by face-to-face cobalt porphyrins has been reported: Collman, J. P.; Denisevich, P.; Konai, V.; Marrocco, M.; Koval, C.; Anson, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 6027.

(10) Rillema, D. P.; Endicott, J. F.; Patel, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 394.
(11) *Solubility Data Series, Volume 7, Oxygen and Ozone*; Battino, R., Ed.; Pergamon Press: Oxford, England, 1981.
(12) Wong, C.-L.; Switzer, J. A.; Balakrishnan, K. P.; Endicott, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 5511.

processes. While searching for catalysts able to activate dioxygen, we have found that millimolar concentrations of Fe^{2+} in acidic medium increase the rate of autoxidation of $Co(tim)^{2+}$ by several orders of magnitude. Product spectra indicated that this catalytic reaction leads cleanly to $Co(tim)^{3+}$, according to the net reaction:

$$4Co(tim)^{2+} + O_2 + 4H^+ = 4Co(tim)^{3+} + 2H_2O \quad (1)$$
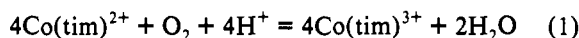
The rate turned out to be independent of acidity in the range of 0.01–0.17 M H^+, and it is unaffected by the addition of bromide ions up to 5 mM. A moderate increase in its rate with ionic strength was noted.

Besides the Co(II) complex, the other species present in solution, including the products, absorb negligibly around 545 nm. Thus visible spectrophotometry is a facile way to follow the catalytic autoxidation of $Co(tim)^{2+}$. The first experiments revealed a disturbing role of minute amounts of iron(III) in the Fe^{2+} reagent, which caused the direct oxidation of the cobalt(II) complex. Thus, even traces of Fe^{3+} needed to be removed from the stock solutions of Fe^{2+}.

Stoichiometry and Products. The stoichiometry of the autoxidation of $Co(tim)^{2+}$ catalyzed by Fe^{2+} was determined by the addition of O_2 to a 16-fold excess of the Co(II) complex. The change in $[Co(tim)^{2+}]$ was followed at 545 or 620 nm ($\epsilon_{620} = 311$ L mol^{-1} cm^{-1}). The data yielded $\Delta[Co(tim)^{2+}]/\Delta[O_2] = 3.6 \pm 0.1$. We ascribe the deviation from precisely 4.00 to a side reaction to be considered shortly. A stoichiometric ratio of 3.9 was observed earlier in the absence of a catalyst.[9]

The electronic spectrum of the product closely resembled that of authentic $Co(tim)^{3+}$, which was obtained independently by oxidation of $Co(tim)^{2+}$ with a small excess of Fe^{3+}. The initial and final (but not intermediate) absorbances of the reaction mixture are the same at the $Co(tim)^{2+/3+}$ isosbestic point ($\lambda_{iso} = 340$ nm, $\epsilon_{iso} = 698$ L mol^{-1} cm^{-1} at $\mu = 0.2$ M), indicating that the solution remaining *after* the catalytic autoxidation of $Co(tim)^{2+}$ did not contain any significant amounts of cobalt-containing products other than $Co(tim)^{3+}$.
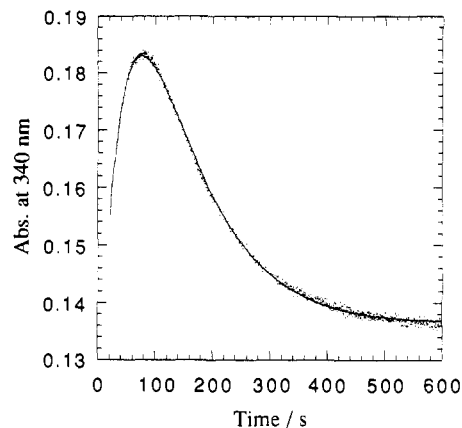
After completion of the autoxidation of $Co(tim)^{2+}$ with an excess of O_2 and millimolar concentrations of Fe^{2+}, the spectrum still indicated the presence of a few percent of the Co(II) substrate, consistent with the equilibrium given by the equation:

$$Co(tim)^{2+} + Fe^{3+} \rightleftharpoons Co(tim)^{3+} + Fe^{2+} \quad (2)$$
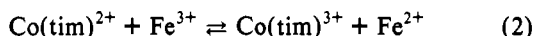
From the concentrations the equilibrium constant $K = 1.9 \times 10^3$ could be estimated, which is exactly as expected from the standard reduction potentials of Fe^{3+} ($E° = 0.771$ V) and $Co(tim)^{3+}$ ($E° = 0.564$ V).[13] This equilibrium, however, cannot entirely account for the discrepancy between the theoretical 4:1 stoichiometry of eq 1 and the 3.6:1 measured with relatively high concentrations of $Co(tim)^{2+}$.

Repetitive spectral scans as well as deviations from pseudo-first-order loss of $Co(tim)^{2+}$ when O_2 was present in large excess indicated minor but reproducible deviations. This was manifest most prominently at the 340-nm isosbestic, where the absorbance rose and then fell to its original value. We believe this side reaction to be the cause of the deviation from an exact 4:1 stoichiometry. Apparently a fraction of the oxidizing equivalents is used for covalent modifications of the ligand. A typical absorbance–time profile is shown in Figure 1. The intervening species is not an intermediate, however, although the two stages of absorbance change fit a biexponential equation. A species with an absorption spectrum similar to that of the 340-nm transient forms slowly and persists in aerated $Co(tim)^{2+}$ solutions, but disappears when Fe^{2+} is added.

On the other hand, the addition of Fe^{2+} after completion of the $Co(tim)^{2+}/H_2O_2$ reaction has only a minor effect on the spectrum

(13) Endicott, J. F.; Durham, B.; Glick, M. D.; Anderson, T. J.; Kuszaj, J. M.; Schmonsees, W. G.; Balakrishnan, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 1431.

Figure 1. A typical absorbance–time profile for the iron(II)-catalyzed autoxidation of $Co(tim)^{2+}$ observed at the $Co(tim)^{2+/3+}$ isosbestic point at 340 nm. The solution contained initial concentrations of 5.21 mM Fe^{2+}, 1.20 mM O_2, and 0.080 mM $Co(tim)^{2+}$. The solid line is the biexponential fit.

Conc. / 10^{-3} mol L^{-1}
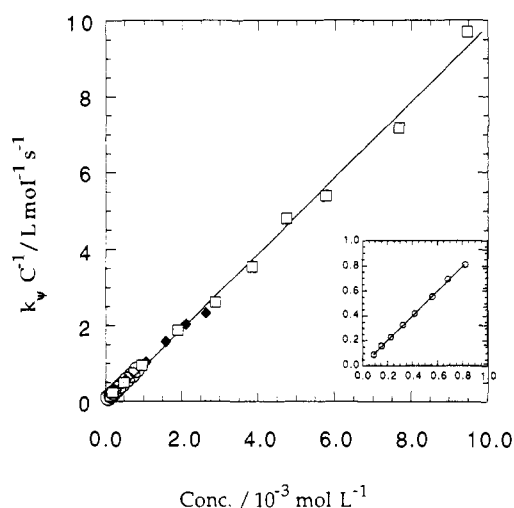
Figure 2. Dependence of the rate of the Fe(II)-catalyzed autoxidation of $Co(tim)^{2+}$ on various concentration variables. The ordinate represents the pseudo-first-order rate constant divided by one concentration, and the abscissa another concentration. Displayed are the following: $k_\psi/[Co(tim)^{2+}]$ against $[Fe^{2+}]$, open circles, in experiments with $[Co(tim)^{2+}]_0 \sim 1$ mM at $[O_2]_0 < 0.05$ mM—these are the experiments amplified in the inset; $k_\psi/[Fe^{2+}]$ against $[Co(tim)^{2+}]_0$ in experiments with $[Fe^{2+}] = 9.46$ mM and $[O_2] \cong 5$–50μM, shown as filled diamonds; $k_\psi/[Co(tim)^{2+}]$ against $[Fe^{2+}]$ for reactions followed with the oxygen electrode at ~ 3.7 mM $[Co(tim)^{2+}]$ and ~ 0.2 mM O_2, shown as open squares.

of the product. As has already been demonstrated,[14,15] the oxidation of $Co(tim)^{2+}$ by hydrogen peroxide occurs with a 1:1 stoichiometry and does not follow the Fenton mechanism or involve free hydroxyl radicals; rather, it occurs with partial destruction of the macrocyclic ligand. It is not surprising that an electron-transfer reagent (*i.e.*, Fe^{2+}) is unable to reverse the covalent ligand modification process.

Kinetics. Owing to the intervention of the highly absorbing transient, the most readily interpretable kinetic information was derived primarily from experiments with $[Co(tim)^{2+}]_0 \gg [O_2]_0$. Such experiments, when done spectrophotometrically, employed 5–50 μM O_2. Under these conditions the absorbance decrease obeyed first-order kinetics. The pseudo-first-order rate constants were directly proportional to both the catalyst and the Co(II) concentrations, as shown in Figure 2.

The disappearance of O_2, when it was limiting, was also followed directly with an oxygen-sensitive electrode. This method confirmed the first-order dependences on $[O_2]$ and $[Fe^{2+}]$ (Figure

(14) Heckman, R. A.; Espenson, J. H. *Inorg. Chem.* **1979**, *18*, 38.
(15) Martin, A. H.; Espenson, J. H. *J. Am. Chem. Soc.* **1977**, *99*, 5963.

Table I. Third-Order Rate Constants for the Iron(II)-Catalyzed Autoxidation of Co(tim)$^{2+}$ ^{a}

		$k''/10^3$ L^2 mol^{-2} s^{-1}, from dependencies on	
limiting reagent	kinetic monitoring	[Fe^{2+}]	[excess reagent]
O$_2$	Co(tim)$^{2+}$ at 545 nm	0.94(7)	1.02(6)
	O$_2$ electrode	0.86(9)	
	isosbestic at 340 nm	0.86(8)	1.10(22)
Co(tim)$^{2+}$	O$_2$ electrode	1.20(8)^b	
	isosbestic at 340 nm	0.87(10)^b	0.84(6)^b
av			0.96(0.10)

^{a} 25 °C, 0.10 M HClO$_4$, μ = 0.2 M. ^{b} After division by the stoichiometric ratio of 4.0.
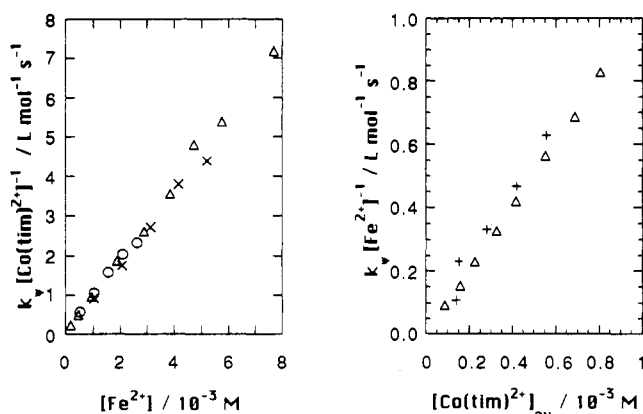
Figure 3. Comparison of the dependencies of the observed rate constants for the Fe(II)-catalyzed autoxidation of Co(tim)$^{2+}$ on [Fe^{2+}] (left) and on [Co(tim)$^{2+}$] (right) in experiments with limiting O$_2$. The data points refer to the first-order disappearance of [Co(tim)$^{2+}$] (545 nm, triangles) and [O$_2$] (oxygen electrode, circles), and to the kinetics at 340 nm, where biexponential fits yielded two sets of k_ψ values [the ones shown here (crosses and pluses) are those that coincide with the rate constants determined by the other methods].

2). The complete rate law is given in the equation:

$$-\frac{d[O_2]}{dt} = k''[Fe^{2+}][Co(tim)^{2+}][O_2] \quad (3)$$

The third-order rate constants from the individual series of the substrate disappearance kinetics with O$_2$ as the limiting reagent are included in Table I. Their average value is $k'' = (9.4 \pm 0.8) \times 10^2$ L^2 mol^{-2} s^{-1} at 25.0 °C.

Kinetic resolution of the biexponential pattern was also undertaken at the isosbestic point, 340 nm. The observed $A_{max} - A_\infty$ ranged between 0.002 and 0.047, dependent on concentrations. The biexponential fit yielded two pseudo-first-order rate constants. Determined with O$_2$ as the limiting reagent, both rate constants were proportional to [Fe^{2+}], whereas only one showed a dependence on [Co(tim)$^{2+}$]. The stage dependent on [Co(tim)$^{2+}$] has, in fact, the same kinetics as the overall single-stage process. Similarly, when Co(tim)$^{2+}$ was limiting, both pseudo-first-order rate constants were proportional to [Fe^{2+}], but only one depended linearly on [O$_2$].

The key step was identified by comparing the dependencies of the pseudo-first-order rate constants derived from both treatments on [Fe^{2+}] and on [excess reagent]. Figure 3 serves as an example of how such an assignment can be made on the basis of the dependencies on [Fe^{2+}] and [Co(tim)$^{2+}$]. Whenever compared this way, one of the rate constants for the biexponential kinetics could always be identified with the corresponding rate constant for substrate loss in the main reaction. The only rate constant from the biexponential fit that depended linearly on [Co(tim)$^{2+}$] led to the same third-order rate constant (1.10 × 10^3 L^2 mol^{-2} s^{-1}) as that from the single-exponential decay observed at 545 nm (1.02 × 10^3 L^2 mol^{-2} s^{-1}). From all of the data, the best-fit value

of the third-order rate constant is $k'' = (9.6 \pm 1.0) \times 10^2$ L^2 mol^{-2} s^{-1} at 25.0 °C.

In support of this assignment, an increase in [Co(tim)$^{2+}$] caused $A_{max} - A_\infty$ to increase at 340 nm, indicating that the concentration-dependent rate constant is the one to be associated with the main reaction.

It was also possible, although barely so, to use the oxygen-sensitive electrode to follow the consumption of excess O$_2$ in the Fe(II)-catalyzed autoxidation of Co(tim)$^{2+}$. These kinetic measurements yielded a value of the third-order rate constant of $(3.9 \pm 0.8) \times 10^3$ L^2 mol^{-2} s^{-1}. With these reversed concentrations, this value must be divided by a factor of 4 to obtain k'', to allow for the stoichiometric consumption ratio. Once that is done, all the data agree quite well. The values of the rate constants from the individual series of experiments are collected in Table I.

Regardless of the limiting reagent, the side reaction depended on Fe^{2+} only; Co(tim)$^{2+}$ is uninvolved. It is therefore a second-order reaction, characterized by $k = 2.7 \pm 0.4$ L mol^{-1} s^{-1}. The chemistry of this reaction is discussed later.

Attempts to fit the decreasing absorbance at 545 nm in experiments with a *large excess of O$_2$* to a biexponential equation led to less accurate results. The accuracy of the measurements at the isosbestic points was already limited by small absorbance changes (see above). At 545 nm, however, the side reaction is superimposed on the main process with its very large change. In fact, significant deviations from the first-order kinetics were observed only in oxygen-saturated solutions, where *up to* 0.5 mM Co(tim)$^{2+}$ ($A_{545} \approx 1.7$) can be used. At lower [O$_2$] and with Co(tim)$^{2+}$ still limiting, the deviation decreases and there is an almost first-order decrease of the absorbance. Nonetheless, it is clear from these data that the kinetics at 545 nm deviate perceptibly from a monoexponential function. The most logical interpretation is that they, too, arise from the same side reaction that is more prominently manifest at the isosbestic.

Discussion

Rate-Controlling Process. The form of the rate law for the main reaction reveals the composition of the transition state: [(tim)CoOOFe^{4+}]*. One can thus write this equation for the net activation process:[16]

$$Co(tim)^{2+} + O_2 + Fe^{2+} = [(tim)CoOOFe^{4+}]^\ast \quad (4)$$
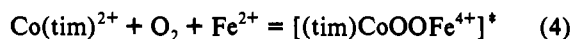
This process very likely takes place in a sequence of two steps—first, binding of oxygen by one metal in a prior equilibrium; second, its reaction with the other in the rate-controlling step. This conclusion will be explored further, to make it more specific. We believe that Co(tim)$^{2+}$ is the species that binds oxygen first, since numerous precedents are known, including many with tetraaza macrocycles. The binding of Co(tim)$^{2+}$ to O$_2$ is apparently very weak, however, since no direct evidence for it is known. If the scheme thus suggested is written in this notation:
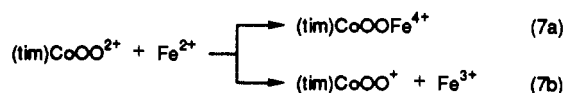
$$Co(tim)^{2+} + O_2 \underset{K_1}{\rightleftharpoons} (tim)CoOO^{2+} \overset{k_2[Fe^{2+}]}{\longrightarrow}$$

$$[(tim)CoOOFe^{4+}] \quad (5)$$
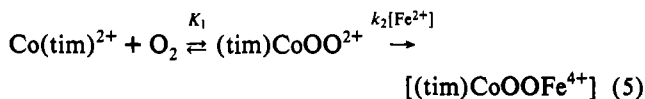
then the experimental rate constant is

$$-\frac{d[O_2]}{dt} = \frac{k_2 K_1 [Co(tim)^{2+}][O_2][Fe^{2+}]}{1 + K_1 C} \quad (6)$$

where C represents either O$_2$ or Co(tim)$^{2+}$, whichever is in excess. In any event the second denominator term is not evident in the kinetic data or in the absorption spectrum of Co(tim)$^{2+}$ when O$_2$ is introduced. Thus we can say that in all experiments 1 ≫

(16) Newton, T. W.; Rabideau, S. W. *J. Phys. Chem.* **1959**, *63*, 365.

$K_1\{[O_2] + [Co(tim)^{2+}]\}$, and $k'' = K_1 k_2$. Since the spectrophotometric experiments are sufficiently sensitive to allow us to say that <2% of oxygen binding occurs under the conditions used, we then have $K_1 < 20$ L mol^{-1} and $k_2 > 50$ L mol^{-1} s^{-1}. This is a reasonable value for k_2 when compared to those for the reactions of Fe^{2+} with CrO$_2^{2+}$ ($k = 4.5 \times 10^3$ L mol^{-1} s^{-1}) and Co([14]-aneN$_4$)O$_2^{2+}$ ($k = 1.1 \times 10^3$ L mol^{-1} s^{-1}). Assuming that k_2 is actually comparable to the values for CrO$_2^{2+}$ and Co([14]aneN$_4$)-O$_2^{2+}$, say $k_2 \sim 10^3$ L mol^{-1} s^{-1}, then $K_1 \sim 1$, and only 0.1% of the cobalt would be present as (tim)CoO$_2^{2+}$ in oxygen-saturated solutions.

The other possibility has Co(tim)$^{2+}$ reacting with FeO$_2^{2+}$. It leads to an unreasonably large value for the second-order rate constant, given[17] that the oxygen binding constant for FeO$_2^{2+}$ (Fe^{2+} + O$_2$ = FeO$_2^{2+}$) has to be much smaller than for (tim)-CoO$_2^{2+}$.

A μ-Peroxo Intermediate? The style in which the formula of the transition state (and, very likely, intermediate) was written in the preceding section suggests that a μ-peroxo species intervenes. Of course, the data do not in themselves require that; we might just as well have a reaction that leads directly to monometallic products. To cite just one possibility, consider these alternatives:

$$\text{(tim)CoOO}^{2+} + \text{Fe}^{2+} \longrightarrow \begin{cases} \text{(tim)CoOOFe}^{4+} & \text{(7a)} \\ \text{(tim)CoOO}^{+} + \text{Fe}^{3+} & \text{(7b)} \end{cases}$$

Since the reactions of Fe^{2+} with many radicals (e.g., Br$_2^{\bullet-}$, ROO$^{\bullet}$, and probably RS$^{\bullet}$)[18-20] occur by inner-sphere mechanisms, it seems a logical extension to suggest the same here, invoking reaction 7a. Moreover, there are ample precedents for dimetallic–μ-peroxo complexes,[21] which lend credence to the one interpretation. It is most reasonable to imagine reaction 7 as that of a radical center with Fe^{2+}. In this connection, we are viewing (tim)CoOO^{2+} as an analog of radicals such as HOO$^{\bullet}$ and ROO$^{\bullet}$.

What makes reaction 7a a particularly fascinating prospect is that this heterodimetallic complex is evidently much more stable than either of the homometallic analogs, FeOOFe^{4+} or (tim)-CoOOCo(tim)$^{4+}$. Or, if it is not of inherently greater stability, then at least it is more reactive. We can offer no reason for that stability ordering, since there are known any number of μ-peroxodicobalt complexes with different ligand systems consisting of other macrocycles or amines, etc.

One way of analyzing this further is to consider what is known independently about the reactions of η^1-superoxo complexes. A useful analogy may be found in the chemistry of the superoxo complex (H$_2$O)$_5$CrOO^{2+}.[22,23] It is rapidly but measurably reduced by mild electron donors, including Fe(H$_2$O)$_6^{2+}$.[23] Here, too, we can consider that the intermediate CrOOFe^{4+} may be formed; if so, its fate would be dissociation, since the resulting hydroperoxo complex has been identified:

$$\text{CrOO}^{2+} + \text{Fe}^{2+} \rightarrow \{\text{CrOOFe}^{4+}\} \xrightarrow{\text{H}^+} \text{CrOOH}^{2+} + \text{Fe}^{3+} \quad (8)$$
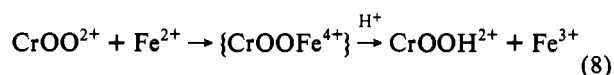
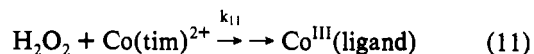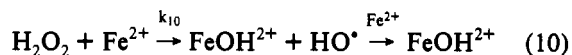We cannot rule out outer-sphere electron transfer between CrO$_2^{2+}$

and Fe^{2+}, however, particularly since the superoxochromium ion also reacts rapidly with Ru(NH$_3$)$_6^{2+}$.

This discussion brings out what is remarkable about this chemistry. Molecular oxygen is kinetically incompetent at converting Fe^{2+} to Fe^{3+}, despite thermodynamic considerations. Reaction of Cr^{2+} with O$_2$, however, opens a channel for the reaction, evidently by the formation of a *stable* complex (K_1 for Cr^{2+} + O$_2$ = CrO$_2^{2+}$ is *ca.* 10^{12} L mol^{-1}).[22] This complex is then able to function as an electron acceptor, as in reaction 8. With Co(tim)$^{2+}$, on the other hand, neither metal adducts to oxygen with a measurable binding constant. Despite that, the metals in binary combination are oxidized fairly rapidly under conditions where neither of them is separately.

Hydrogen Peroxide Is Not Formed. Whether or not the reaction between (tim)CoOO^{2+} and Fe^{2+} occurs by way of a μ-peroxo complex, it is not difficult to envisage free H$_2$O$_2$ as an intermediate. For example, the following reaction might occur:

$$\text{(tim)CoOOFe}^{4+} + 2\text{H}^+ \rightarrow \text{Co(tim)}^{3+} + \text{Fe}^{3+} + \text{H}_2\text{O}_2 \quad (9)$$
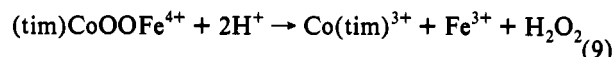
Several tests show that H$_2$O$_2$ is not formed. Were it formed, it may react with Fe^{2+} in a Fenton mechanism or with Co(tim)$^{2+}$ in a reaction of 1:1 stoichiometry that leads to a covalently-modified tim ligand:

$$\text{H}_2\text{O}_2 + \text{Fe}^{2+} \xrightarrow{k_{10}} \text{FeOH}^{2+} + \text{HO}^{\bullet} \xrightarrow{\text{Fe}^{2+}} \text{FeOH}^{2+} \quad (10)$$

$$\text{H}_2\text{O}_2 + \text{Co(tim)}^{2+} \xrightarrow{k_{11}} \rightarrow \text{Co}^{III}\text{(ligand)} \quad (11)$$

The rate constants at 25 °C are known: $k_{10} = 75$ L mol^{-1} s^{-1} [24] and $k_{11} = 164$ L mol^{-1} s^{-1}.[15] Some of the experiments were run under conditions where reaction 11 would be considerably faster than reaction 10, and *vice versa*. In both situations Co(tim)$^{3+}$ is the product, not the species otherwise formed in the reaction of free hydrogen peroxide. Moreover, addition of Fe^{2+} to a solution in which the Co(tim)$^{2+}$–H$_2$O$_2$ reaction had been conducted did not lead (to no surprise) to the covalently modified product being converted to Co(tim)$^{3+}$.

Subsequent steps are the rapid ones that are needed to complete the stoichiometry. As such, they play no role in the kinetic description and are not defined by the experiments that we have reported. Nonetheless, it seems useful to comment upon the possibilities in light of what is known in other reactions. First, consider the fate of the putative intermediate (tim)CoOOFe^{4+}. It might react directly with either of the electron donors, Fe^{2+} or Co(tim)$^{2+}$. If so, there must ultimately be consumed 3 mol of reagent, most likely in three successive steps. From a stoichiometric point of view, however, it matters not which reacts since regardless of whether Co(tim)$^{3+}$ or Fe^{3+}, or both, are formed; they will be equilibrated rather rapidly in reaction 2. Whereas such sequences are feasible, they do not seem to us the most plausible. In other circumstances both μ-peroxo complexes (and dialkyl peroxides, which we take as their analogs)[25] are rather slow to react with reducing metal complexes, probably for steric reasons.

If such reactions are too slow, the more labile metal ion may dissociate form the bimetallic complex. This is known to happen in closely related species, as in eq 8. Moreover, since this would be governed by the ligand substitution rate of aquairon(III) ion, it is reasonable that it can be complete on the time scale of this net reaction. We therefore propose that the following reaction is the next one:

$$\text{(tim)CoOOFe}^{4+} + \text{H}^+ = \text{(tim)CoOOH}^{2+} + \text{Fe}^{3+} \quad (12)$$
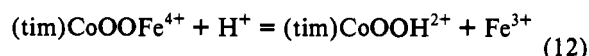
The cobalt complex resulting from this should show the reactivity of modified hydrogen peroxide. That is, it will react

(17) The species FeO$_2^{2+}$ formed in minor amounts in equilibrium with Fe^{2+} and O$_2$ was suggested as an intermediate in the reaction of Fe$_{aq}^{2+}$ and O$_2$. Indeed, the first part of the scheme is analogous to eq 6. George, P. *J. Chem. Soc.* **1954**, 4349.

(18) Thornton, A. T.; Lawrence, G. S. *J. Chem. Soc., Dalton Trans.* **1973**, 804.

(19) Butler, J.; Jayson, G. G.; Swallow, A. J. *J. Am. Chem. Soc.* **1992**, *114*.

(20) Huston, P.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1992**, *114*.

(21) Sykes, A. G.; Weil, J. A. *Prog. Inorg. Chem.* **1970**, *13*, 4-23.

(22) Brynildson, M. E.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 4579.

(23) Brynildson, M. E.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1988**, *27*, 2592.

(24) Wells, C. F.; Salam, M. A. *Trans. Faraday Soc.* **1967**, *63*, 120.

(25) Hyde, M. R.; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4463.

with $Co(tim)^{2+}$ and Fe^{2+} much as ROOH would (and, were it not for the ligand modification step unique to hydrogen peroxide, then analogous to it as well). Either or both metals reduce (tim)-$CoOOH^{2+}$—a subject under independent investigation with ([14]-$aneN_4)CoOOH^{2+}$.[26] The overall reaction is then all but complete save for the final adjustment of the electron-transfer reaction 2, as befitting the concentrations used in the given experiment.

Other Ions—Br⁻ and H⁺. The reaction rate is not altered by addition of bromide ions or by variation of [H⁺] over the range 0.01–0.2 M. This in itself is not remarkable, in that one would expect no effects on the reactions written. This deserves comment nonetheless, in that the oxidation of $Co(tim)^{2+}$ by O_2 when catalyzed by $Co(dmgBF_2)_2$ shows a first-order dependence on [Br⁻] and [H⁺].[9] In a detailed sense the two catalytic systems must function rather differently, although they have much in parallel. The need for Br⁻ in the one case but not the other is informative. In the one case, its role is that of an electron-transfer bridge between $Co^{II}L$ and a dicobalt–oxygen intermediate. It is needed in this case because neither cobalt of that intermediate can dissociate at a sufficient rate, both being substitutionally inert cobalt(III); moreover, the third $Co^{II}L$ is unable to attack directly the oxygen of LCoOOOCoL. No such redox catalysis of ligand dissociation is required for $(tim)CoOOFe^{4+}$, since the iron-(III) ion departs of its own accord at a sufficient rate. Indeed, the two sets of observations taken together support the mechanisms assigned for each more fully than either does alone.

(26) Wang, W.-D.; Espenson, J. H.; Bakac, A. Unpublished observations.