Inorg. Chem. **1992**, *31*, 4860-4863

Sixth-Order Kinetics in a Catalyzed Autoxidation of a Macrocyclic Cobalt(II) Complex

Adam Marchaj, Andreja Bakac,* and James H. Espenson*

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

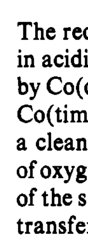
Received June 9, 1992

The 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 was studied in the presence of Br^-. This otherwise very slow reaction is strongly catalyzed by $Co(dmgBF_2)_2$ ($dmgBF_2$ = (difluoroboryl)dimethylglyoximate). The rate law shows a first-order dependence on $Co(tim)^{2+}$, O_2, Br^-, and H^+, and is second-order with respect to the catalyst. The catalytic autoxidation follows a clean 4:1 $Co(tim)^{2+}$:O_2 stoichiometry and yields the corresponding halocobalt(III) macrocycle. The reduction of oxygen to water clearly bypasses the hydrogen peroxide stage. The transition state is proposed and the mechanism of the sixth-order catalytic reaction is considered and discussed. It features O_2 binding and halide-bridged electron transfer. There is no evidence for involvement of the hydroxyl radical.

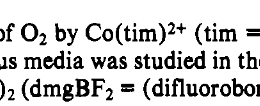
Introduction

In the search for catalysts able to activate dioxygen for homogeneous oxidations under mild conditions, cobalt(II) chelates have attracted perhaps the most attention. Their catalytic activity often involves the formation of cobalt-oxygen adducts,[1-3] which are better oxidants than O_2 itself. However, such adducts often tend to decompose by irreversible oxidation of the metal center or the chelate, leading to the loss of catalytic activity.

Neither of the two cobalt macrocycles used in this study, $Co(dmgBF_2)_2$[4-6] or $Co(tim)^{2+}$,[7,8] reacts with O_2 to a measurable extent at ambient temperature. Nevertheless, some qualitative observations showed that $Co(dmgBF_2)_2$ is an efficient autoxidation catalyst, implying that $Co(dmgBF_2)_2O_2$, present in undetectably small concentrations, is a powerful oxidant. This species is known to form at lower temperatures in aqueous solution[5] and in organic solvents.[5,6]



$Co(dmgBF_2)_2$



$Co(tim)^{2+}$

Interestingly, in order for the autoxidation to be catalytic, the oxygen adduct, $Co(dmgBF_2)_2O_2$, has to be reduced to $Co(dmgBF_2)_2$. This has been shown to be a net four-electron process in which water is produced. Reduction back to cobalt(II) in oxygen-containing solutions is quite remarkable in view of the fact that stoichiometric oxidations of mild reductants by other cobalt-dioxygen adducts, such as $Co(cyclam)O_2^{2+}$,[8-10] usually yield only oxidized cobalt products in aqueous solutions. The relatively high $E°$ value for the $Co(dmgBF_2)_2^{+/0}$ couple (0.65 V)[5] may be a key to the regeneration of $Co(dmgBF_2)_2$. Also, a common problem encountered with Co(II) catalysts is their oxidative degradation.[3,11] Fortunately, that is not a feature of the chemistry in this system.

The very slow disappearance of $Co(tim)^{2+}$ as a result of aerial oxidation was reported to be susceptible to catalytic effects.[8] It has been established for other cobalt(II) tetraazamacrocycles[8,9,12] that halides and H^+ catalyze the decomposition of their dioxygen adducts to Co(III) complexes. Halide ions are known as efficient bridging ligands for electron transfer in redox reactions involving macrocyclic complexes.[13-15] For $Co(tim)^{2+}$ the ratio of rate constants for inner- and outer-sphere reactions is $\sim 10^6$.[13,14]

Further indication of the role of halides in redox reactions of $Co(tim)^{3+/2+}$ complexes comes from their preparative procedures. The presence of halide ions is essential to obtain Co(III)-tim complexes from cobalt(II) salts by aerial oxidation. The complexes $Co(tim)X_2^+$ (X^- = Cl^-, Br^-) are intermediates in the preparation of other cobalt complexes of this macrocycle.[16-18] On

---

(1) (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press: New York, 1981. (b) Bailey, C. L.; Drago, R. S. *Coord. Chem. Rev.* **1987**, *79*, 321. (c) Skibida, I. P. *Russ. Chem. Rev. (Engl. Transl.)* **1985**, *54*, 875.

(2) Tan, S. F.; Leung, P. H.; Sin, W. C. *Transition Met. Chem. (Weinheim, Ger.)* **1991**, *16*, 542.

(3) (a) Nishinaga, A.; Yamazaki, S.; Matsuura, T. *Tetrahedron Lett.* **1986**, *27*, 2649; **1987**, *28*, 6309. (b) Nishinaga, A.; Yamato, H.; Abe, T.; Maruyama, K.; Matsuura, T. *Tetrahedron Lett.* **1988**, *29*, 6309. (c) Yamada, M.; Araki, K.; Shiraishi, S. *J. Chem. Soc., Chem. Commun.* **1988**, 530. (d) Tamagaki, S.; Kanamaru, Y.; Ueno, M.; Tagaki, W. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 165.

(4) Abbreviations used for the macrocyclic ligands: $dmgBF_2^-$ = (difluoroboryl)dimethylglyoximate, tim = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene, cyclam = 1,4,8,11-tetraazacyclotetradecane, hmc = *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, X^- = halide; aqua ligands are omitted hereafter.

(5) Bakac, A.; Brynildson, M. E.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 4108.

(6) (a) Nonaka, Y.; Hamada, K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3185. (b) Lance, K. A.; Goldsby, K. A.; Busch, D. H. *Inorg. Chem.* **1990**, *29*, 4537.

(7) Simic, M. G.; Hoffman, M. Z. *J. Am. Chem. Soc.* **1977**, *99*, 2370.

(8) Wong, C.-L.; Switzer, J. A.; Balakrishnan, K. P.; Endicott, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 5511.

(9) Wong, C.-L.; Endicott, J. F. *Inorg. Chem.* **1981**, *20*, 2233.

(10) Kumar, K.; Endicott, J. F. *Inorg. Chem.* **1984**, *23*, 2447.

(11) (a) Nishinaga, A.; Tomita, H.; Oda, M.; Matsuura, T. *Tetrahedron Lett.* **1982**, *23*, 339. (b) Corden, B. B.; Drago, R. S.; Perito, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 2903.

(12) Dreos, R.; Tauzher, G.; Costa, G.; Green, M. *J. Chem. Soc., Dalton Trans.* **1975**, 2329. dtct⁻ = 2,2-difluoro-5,6,12,13-tetramethyl-1,3-dioxa-4,7,11,14-tetraaza-2-boracyclotetradeca-4,6,11,13-tetraene(1-)-*N,N',N'',N'''*.

(13) Durham, B.; Endicott, J. F.; Wong, C.-L.; Rillema, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 847.

(14) Rotzinger, F. P.; Kumar, K.; Endicott, J. F. *Inorg. Chem.* **1982**, *21*, 4111.

(15) Endicott, J. F.; Wong, C.-L.; Ciskowski, J. M.; Balakrishnan, K. P. *J. Am. Chem. Soc.* **1980**, *102*, 2100.

(16) Jackels, S. C.; Farmery, K.; Barefield, E. K.; Rose, N. J.; Busch, D. H. *Inorg. Chem.* **1972**, *11*, 2893.

(17) Rillema, D. P.; Endicott, J. F.; Patel, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 394.

(18) Rillema, D. P.; Endicott, J. F. *J. Am. Chem. Soc.* **1972**, *94*, 8711.

0020-1669/92/1331-4860$03.00/0

the other hand, halides are to be avoided in the direct preparation of $Co(tim)^{2+}$ to prevent aerial oxidation.[19]

The indicated properties of $Co(tim)^{2+}$ and $Co(dmgBF_2)_2$ allow the autoxidation of the first complex to be catalyzed by the second one, especially in the presence of halides. The halide ions can play a double role in the mechanism of this process. First, they could serve as a bridge for electron transfer between $Co(dmgBF_2)_2O_2$ and $Co(tim)^{2+}$, and second, they are expected to stabilize the products as $Co(tim)X_n^{3-n}$ (n = 1 or 2) complexes. Indeed, we observed for each of the Co(II) macrocycles separately a nearly negligible oxidation in O_2-containing acidic aqueous solutions even when Cl^- or Br^- was present. Only when both $Co(tim)^{2+}$ and $Co(dmgBF_2)_2$ were present in solution did the autoxidation of $Co(tim)^{2+}$ take place rapidly. We thus undertook a study of the kinetics and mechanism of this reaction.

Experimental Section

The solvent used throughout was distilled water purified by passage through a Milli-Q Millipore system. $[Co(dmgBF_2)_2(H_2O)_2]$[5] and $[Co(tim)Br_2]Br$[16] were prepared as described previously.

$[Co(tim)(H_2O)_2](CF_3SO_3)_2$ was prepared by a variant of the method for $[Co(tim)Br_2]Br$.[16] Methanol (140 cm^3) was placed in a 2-necked flask and bubbled with a stream of argon. 1,3-Diaminopropane (6.8 cm^3, 0.08 mol) was added, followed by dropwise addition of trifluoromethanesulfonic acid (12 cm^3 of 60% aqueous solution of CF_3SO_3H; 0.08 mol). After this, 2,3-butanedione (7.1 cm^3, 0.08 mol) was added, followed *immediately* by 10.0 g of $Co(OAc)_2 \cdot 4H_2O$ (0.04 mol), and the solution was stirred under Ar for 4 h. At this time 4 cm^3 of deoxygenated H_2O and 18 cm^3 of 60% CF_3SO_3H were added. The MeOH was then partially removed by passing Ar through the solution for an additional 5 h. The reaction mixture was filtered under Ar, washed with 10:1 ether/methanol and then with ether, and dried; yield ~20%.

UV–visible spectra of each cobalt(II) macrocycle in aqueous solutions matched those reported earlier.[5,17,20] Trifluoromethanesulfonic acid, CF_3SO_3H, 98% (Aldrich) was purified by vacuum distillation and diluted as needed. Other chemicals (Fisher, Certified ACS, or Aldrich, analyzed) were used without further purification.

Spectral and kinetic measurements were carried out by the use of Cary 219, Perkin-Elmer diode array 3840, and Shimadzu UVPC 3101 spectrophotometers. The temperature was controlled in all the measurements at 25.0 ± 0.2 °C. The $HClO_4$ concentration (0.1 M) usually defined the ionic strength except when the acidity was varied, where μ = 0.5 M was maintained with $NaClO_4$ or $LiClO_4$. The data were identical irrespective of which perchlorate salt was used.

The solubility of O_2 at 25 °C was taken as 1.27 mM in pure water and 1.06 mM in 0.5 M $NaClO_4$.[21] The dioxygen concentration was usually kept at or close to its solubility limit when required to be constant. The variation of O_2 concentration was achieved by carefully mixing aqueous solutions saturated with oxygen, air, or argon. This was done in cells filled to capacity. The good linearity obtained for the dependence of k_ψ versus $[O_2]$, see later, confirms the accuracy of this method.

The stoichiometry of the O_2 oxidation of an excess of $Co(tim)^{2+}$ was determined spectrophotometrically. The kinetics of the catalytic reaction were studied under pseudo-first-order conditions with $Co(tim)^{2+}$ as the limiting reagent. Data from at least 2 half-lives of the reaction were fitted to a first-order equation. A typical catalytic system contained 0.1 mM $Co(tim)^{2+}$, 0.1 mM $Co(dmgBF_2)_2$, 0.1 M $HClO_4$, 1.27 mM O_2, and 5 mM NaBr. For the kinetic measurements the following concentration ranges were used: 0.01–1 mM $Co(tim)^{2+}$, 0.02 – 0.5 mM $Co(dmgBF_2)_2$, 0.02–0.4 M H^+, 0.307–1.26 mM O_2, and 1–10 mM Br^-. When possible background reactions consuming the Co(II) complexes were explored in control experiments, their slow and often complicated decays were followed to <20% completion and approximated by a first-order rate law, yielding k_0 values that are valid only for comparison purposes.

Results

General Observations. Each of the two cobalt(II) complexes is separately quite unreactive toward molecular oxygen in aqueous solution under normal conditions. Yet in solutions containing both complexes in the presence of O_2 the characteristic absorbance of $Co(tim)^{2+}$ disappears significantly faster than it does without the participation of $Co(dmgBF_2)_2$. The latter is recovered nearly quantitatively at the end of the reaction. Millimolar concentrations of bromide in an acidic medium accelerate this catalytic reaction, bringing its rate into a range convenient for kinetic study.

The intense absorption band of $Co(tim)^{2+}$ at 545 nm has ϵ_{max} = 3450 L mol^{-1} cm^{-1}.[17] Other species present in solution, including the products, absorb negligibly at this wavelength. This makes the visible spectrophotometry a facile analytical method for this complex. Each component of the catalytic system was tested for its effect on the observed A_{545} decay. As a catalyst, $Co(dmgBF_2)_2$ was supposed to remain at a steady concentration over the course of the reaction, so its stability under the conditions employed was checked as well. The following results were obtained in aqueous 0.1 M $HClO_4$ at 25 °C, for $[Co(tim)^{2+}]$ = 0.3 mM and $[Co(dmgBF_2)_2]$ = 0.2 mM.

$Co(tim)^{2+}$ was found to be practically stable (decomposition <1%/h) in deaerated solutions. Saturation with O_2 affected its decay only slightly, resulting in $k_0 = 5 \times 10^{-6}$ s^{-1}. Addition of 5 mM Br^- accelerated the oxidation significantly with rather complex kinetics. The first 20% of the reaction, approximated by a first-order rate law, yielded $k_0 = 8 \times 10^{-4}$ s^{-1}. The addition of $Co(dmgBF_2)_2$ to solutions of $Co(tim)^{2+}$ containing O_2, but not Br^-, caused a slow, acid-independent (pH 1–7) oxidation of $Co(tim)^{2+}$ ($k_0 = 6 \times 10^{-5}$ s^{-1}). Finally, when Br^- and $Co(dmgBF_2)_2$ were both added, $Co(tim)^{2+}$ was oxidized catalytically with $k_\psi = 1.6 \times 10^{-2}$ s^{-1}.

Deaerated solutions of $Co(dmgBF_2)_2$, although practically stable when neutral, decompose slowly at pH = 1 with a rate constant of $\sim 1 \times 10^{-4}$ s^{-1}, which is unaffected by O_2 or bromide when they are present separately. When the solution contained 5 mM Br^- and 1.27 mM O_2, the decay rate constant for $Co(dmgBF_2)_2$ increased to $\sim 7 \times 10^{-4}$ s^{-1}. This decay was not affected by the presence of $Co(tim)^{2+}$.

The disappearances of $Co(tim)^{2+}$ in the catalytic system and of $Co(tim)^{2+}$ and $Co(dmgBF_2)_2$ separately were acid dependent. However, only the catalytic oxidation of $Co(tim)^{2+}$ was consistently first-order with respect to $[H^+]$ in the range 0.01–1 M. The best separation between the catalytic reaction and the independent decay of the two cobalt complexes was achieved at $[H^+]$ = 0.1–0.3 M. For this reason 0.1 M remained the standard $HClO_4$ concentration for further experiments, setting the ionic strength as well.

Stoichiometry and Products. The stoichiometry of the autoxidation of $Co(tim)^{2+}$ catalyzed by $Co(dmgBF_2)_2$ was calculated from the change in $[Co(tim)^{2+}]$ upon addition of limiting amounts of O_2. The data yielded $\Delta[Co(tim)^{2+}]/\Delta[O_2] = 4.0 \pm 0.1$. A value of 3.9 was obtained in the absence of the catalyst. When O_2 was replaced by H_2O_2 the stoichiometry was $\Delta[Co(tim)^{2+}]$:$\Delta[H_2O_2]$ = 1.4:1 at 5 mM Br^-. In the absence of Br^- a ratio of 1:1 was reported.[22] The stoichiometric ratios for the H_2O_2 reaction were unaffected by the presence of $Co(dmgBF_2)_2$.

Other halides were also tried as alternatives for bromide in the catalytic system. At 5 mM Cl^- the catalytic autoxidation of $Co(tim)^{2+}$ was ~4 times slower than that at the same concentration of bromide. However, 5 mM I^- accelerated the reaction by more than 3 orders of magnitude. The iodide reaction was additionally complicated by oxidation of I^- to I_2.

The expected products of the catalytic autoxidation of $Co(tim)^{2+}$ are the halocobalt(III) complexes, $Co(tim)X_n^{3-n}$ (n = 1 or 2). Positive spectroscopic evidence for the formation of these weakly absorbing species was difficult to obtain due to the intense spectrum of the catalyst that decomposes slowly in acidic medium. After the autoxidation of $Co(tim)^{2+}$ in 5 mM Br^- in the absence of $Co(dmgBF_2)_2$ was allowed to reach >95% completion, the UV spectrum corresponded to a mixture of $Co(tim)Br_n^{3-n}$ complexes. This was determined by comparison with the spectrum of $[Co(tim)Br_2]Br$ dissolved in 5 mM Br^-. It should be noted that the halides coordinated to $Co(tim)^{3+}$ are quite labile in the presence

---

(19) Compare the method described in the Experimental Section with that reported for $[Co(tim)Br_2]Br$.[16]

(20) Endicott, J. F.; Lilie, J.; Kuszaj, J. M.; Ramaswamy, B. S.; Schmonsels, W. G.; Simic, M. G.; Glick, M. D.; Rillema, D. P. *J. Am. Chem. Soc.* **1977**, *99*, 429.

(21) *Solubility Data Series, Volume 7, Oxygen and Ozone*; Battino, R., Ed.; Pergamon Press: Oxford, England, 1981.

(22) Heckman, R. A.; Espenson, J. H. *Inorg. Chem.* **1979**, *18*, 38.

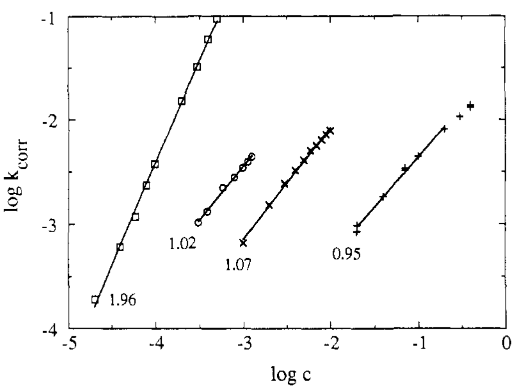


Figure 1. Plots of log k_{corr} for the catalytic autoxidation of $Co(tim)^{2+}$ against the logarithm of $[O_2]$ (circles), $[Br^-]$ (crosses), $[H^+]$ (pluses), and $[Co(dmgBF_2)_2]$ (squares) at 25.0 °C. The values of the slopes are also given. When not varied, the concentrations were as follows: $[Co(tim)^{2+}]$ = 0.1 mM, $[Co(dmgBF_2)_2]$ = 0.1 mM, $[HClO_4]$ = 100 mM, $[Br^-]$ = 5 mM, and $[O_2]$ = 1.27 mM (μ = 0.1 M) or 1.00 mM (μ = 0.5 M). All the data refer to μ = 0.1 M ($HClO_4$), except for the k_ψ vs $[H^+]$ points where μ = 0.5 M ($NaClO_4$ or $LiClO_4$). The three data points at $[H^+] \geq 0.3$ M were not used in the data fit; see text.

of even trace amounts of $Co(tim)^{2+}$,[13,17] which is usually found in solutions of the Co(III) complex.[17] From the spectral changes caused by the variation of the halide concentration, it was concluded that at 5 mM Br^- the Co(III) complex constitutes a mixture of ~75% $Co(tim)Br^{2+}$ and ~25% $Co(tim)Br_2^+$. Also, >95% of the monochloro and ~90% of the diiodo complexes were found in 5 mM Cl^- and 5 mM I^-, respectively.

Several experiments were performed to check whether free hydroxyl radicals were involved in the catalytic reaction. Methanol had no effect, and the addition of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) failed to yield the ESR-detectable OH-adduct. A qualitative test for radical species based on the induced polymerization of methyl methacrylate[23] gave negative results as well.

Kinetics. The catalytic autoxidation yielded linear first-order plots as long as the concentration of $Co(tim)^{2+}$ did not exceed significantly that of $Co(dmgBF_2)_2$. At $[Co(tim)^{2+}] \gg [Co(dmgBF_2)_2]$ the kinetics became more complex and resembled those recorded in the absence of the catalyst. For that reason large $[Co(tim)^{2+}]/[Co(dmgBF_2)_2]$ ratios had to be avoided.

The pseudo-first-order rate constants for the oxidation of $Co(tim)^{2+}$ depended on the concentration of each of the other species in solution. The kinetic order in each species was determined from a series of experiments using $Co(tim)^{2+}$ as a limiting reagent and varying the concentration of the species of interest. All the other concentrations were kept constant throughout each series of experiments. Figure 1 shows the results plotted as log (rate constant) against the logarithm of the concentrations of individual kinetic species. The rate constants were corrected for the background noncatalytic oxidation of $Co(tim)^{2+}$, $k_{cor} = k_\psi - k_0$. The slopes of the straight lines yielded a kinetic order of 1 for H^+, Br^-, and O_2 and 2 for the catalyst $Co(dmgBF_2)_2$. The exact values of the slopes were 0.95 ± 0.03, 1.07 ± 0.02, 1.02 ± 0.03, and 1.96 ± 0.03, respectively. The first order with respect to $Co(tim)^{2+}$ is established by the linearity of all the first-order plots when $Co(tim)^{2+}$ was used as a limiting reagent. The complete rate law is given in eq 1.

$$
\begin{aligned}
-d[Co(tim)^{2+}]/dt &= k_\psi[Co(tim)^{2+}] \\
&= k_0 + k_1[H^+][O_2][Br^-] \times \\
&\quad [Co(dmgBF_2)_2]^2[Co(tim)^{2+}] \qquad (1)
\end{aligned}
$$

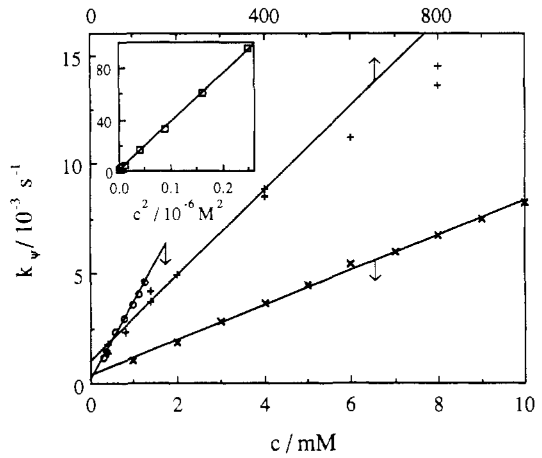


Figure 2. Plots of k_ψ for the catalytic autoxidation of $Co(tim)^{2+}$ versus $[O_2]$ (circles), $[Br^-]$ (crosses), $[H^+]$ (pluses), and $[Co(dmgBF_2)_2]^2$ (squares, inset). Conditions are as in Figure 1.

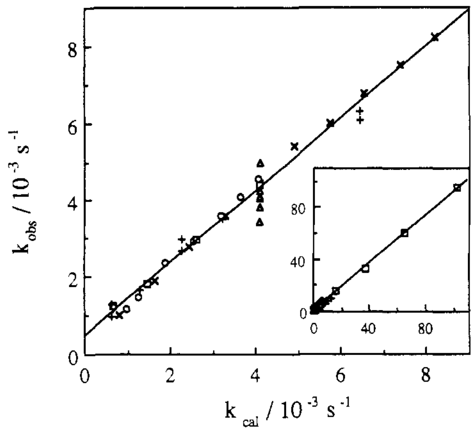


Figure 3. Comparison of the observed pseudo-first-order rate constants for the catalytic autoxidation of $Co(tim)^{2+}$ (k_{obs}) with those calculated (k_{cal}) using eq 1. The data points were obtained by varying $[O_2]$ (circles), $[Br^-]$ (crosses), $[H^+]$ (pluses), $[Co(dmgBF_2)_2]$ (squares), and $[Co(tim)^{2+}]$ (triangles). The inset shows all the points, including those outside the range of the main plot.

Figure 2 shows the plots of the uncorrected values of the rate constants, k_ψ, against $[H^+]$, $[Br^-]$, $[O_2]$, and $[Co(dmgBF_2)_2]^2$. The slopes of the lines yielded the corresponding pseudo-rate constants, which finally led to $k_1 = (6.46 \pm 0.39) \times 10^{11}$ L^5 mol^{-5} s^{-1}.[24] The small intercepts in Figure 2 represent k_0, the sum of all the noncatalytic pathways for the loss of $Co(tim)^{2+}$. The decomposition of $Co(dmgBF_2)_2$ is responsible for the deviations from the straight line at high $[H^+]$. Even small changes in $[Co(dmgBF_2)_2]$ have an effect owing to the second-order kinetic dependence on this reagent. The points at $[H^+] \geq 0.3$ M were thus not used in the data fit.

Although little mechanistic information can be drawn from the numerical value of the sixth-order rate constant, it could be used to assess the integrity of all the kinetic data acquired for the catalytic system. Indeed, all the observed k_ψ values[24] were found to form a straight line (Figure 3) when plotted against those calculated from eq 1 and the above value of k_1.

Discussion

The 4:1 stoichiometry for the reaction of $Co(tim)^{2+}$ with O_2, both in the presence and in the absence of $Co(dmgBF_2)_2$, rules out H_2O_2 as intermediate in these reactions. Earlier work[22]

---

(23) Saha, M. K.; Mukherjee, A. R.; Ghosh, P.; Palit, S. R. *J. Polymer. Sci.* **1967**, *C16*, 159. A variant of this method with Fe^{2+} was also used to test the catalytic reaction for H_2O_2 as an intermediate. The result was negative, in agreement with the stoichiometric determinations.

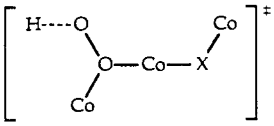
(24) The increase in ionic strength in these measurements caused by itself a slight rate increase. Thus, for the calculations of k_1 and for the plot in Figure 3 the k_ψ values were corrected to μ = 0.1 M. This was done by multiplying each of the k_ψ values obtained at μ = 0.5 M by the correction factor $f = k_\psi(\mu = 0.1\ M)/k_\psi(\mu = 0.5\ M) = 0.712$. This value was determined experimentally at 0.1 M H^+. The ionic strength affects the intercept k_0 and the slope k_ψ of Figure 2 to a similar extent.

showed that H_2O_2 oxidizes $Co(tim)^{2+}$ with a 1:1 stoichiometry. It was independently confirmed in this work that the reaction with H_2O_2 does not reach the 2:1 stoichiometry when H_2O_2 is used under typical conditions for catalytic autoxidation.

Even more telling is the effect of Br^- on the reactions of $Co(tim)^{2+}$ with O_2 and H_2O_2. Addition of 0.2 M Br^- causes the rate of oxidation by hydrogen peroxide to increase by only ~30%,[22] whereas 5 mM Br^- accelerates the autoxidation, both in the presence and in the absence of $Co(dmgBF_2)_2$, by more than 2 orders of magnitude. The moderate rate increase in the H_2O_2 reaction was attributed to the formation of an apparently more reactive bromocobalt(II) complex at high $[Br^-]$,[12,22] while the profound effect of bromide on the autoxidation is in accordance with the role of this anion as an electron-transfer bridge.[13,14]

In considering the mechanism of the catalyzed autoxidation, the following points need to be considered. (1) The reaction has an overall sixth-order rate law. (2) H_2O_2 is not produced in the course of the reaction. (3) $Co(dmgBF_2)_2^+$ is a strong oxidant that can readily oxidize $Co(tim)^{2+}$ to $Co(tim)^{3+}$ and has been shown independently to do so in this medium. (4) The autoxidation of $Co(tim)^{2+}$ in the absence of $Co(dmgBF_2)_2$ is also accelerated by Br^-.

The rate law indicates a transition state or an intermediate of a form $[CoOO(H)CoBrCo^{2+}]^{\ddagger}$, where two of the cobalt centers represent $Co(dmgBF_2)_2$



(abbreviated in equations as Co_B) and one $Co(tim)^{2+}$ (abbreviated as Co_T). A clear distinction between the two different cobalt macrocycles is not possible, although it is tempting to suggest that the central cobalt is Co(tim). This would be consistent with the initial μ-peroxo adduct being formed (eq 2) from $(dmgBF_2)_2CoO_2$ (a known species) and $Co(tim)^{2+}$, which does not bind O_2 appreciably and which, in the absence of $Co(dmgBF_2)_2$, is oxidized by O_2 only very slowly.

$$Co_BO_2 + Co_T^{2+} \rightarrow Co_BOOCo_T^{2+} \tag{2}$$

The initial μ-peroxo adduct would then react with the second molecule of $Co(dmgBF_2)_2$ in a reaction that is Br^- and H^+ catalyzed, eq 3.

$$Co_BOOCo_T^{2+} + Co_B \xrightarrow{Br^-,\, H^+} Co_BOO(H)Co_TBrCo_B^{2+} \tag{3}$$

The tricobalt species of eq 3 could react rapidly with a succession of three more molecules of $Co(tim)^{2+}$ to yield the final products, eq 4, or it could first decompose, possibly yielding hydroxyl radicals, as in eq 5. Subsequent oxidation of three more molecules of $Co(tim)^{2+}$ by $Co(dmgBF_2)_2^+$ and $^{\bullet}OH$ would again result in an overall 4:1 stoichiometry.

$$Co_BOO(H)Co_TBrCo_B^{2+} + 3Co_T^{2+} \xrightarrow{3H^+} 4Co_T^{3+} + 2Co_B + 2H_2O + Br^- \tag{4}$$

$$Co_BOO(H)Co_TBrCo_B^{2+} \xrightarrow{2H^+} Co_T^{3+} + 2Co_B^+ + {}^{\bullet}OH + Br^- + H_2O \tag{5}$$

The experimental evidence in favor of either reaction is not available, despite several attempts made in the course of this work. The failure of methanol to affect the kinetics is consistent with both eqs 4 and 5. Even if the $^{\bullet}OH$ radical had been formed and trapped by the alcohol, the resulting *C*-centered radical would be immediately captured by O_2 to yield the peroxy radical. It, in turn, would probably oxidize $Co(tim)^{2+}$,[25] which would leave both the kinetics and stoichiometry of the overall reaction unchanged.

Other experimental evidence, see Results, argues strongly against that involvement of $^{\bullet}OH$ radicals. This should not be too surprising, as one might expect that the complexity of the mechanism and the large number of species assembled in the transition state should have the advantage of being able to avoid the formation of such highly energetic species as $^{\bullet}OH$. Indeed, even the reaction of H_2O_2 with macrocyclic cobalt(II) complexes does not produce free hydroxyl radicals.[22] We thus favor reaction 4 over reaction 5 as a fast post-rate-determining step.

Although the individual mechanistic steps could not be observed independently, the proposed mechanism draws strong support from kinetic studies on oxygenation of other Co(II) macrocycles. For example, the oxygen binding constants for $Co(hmc)^{2+}$ increase significantly in the presence of halides[26] owing to a decrease in the rate of dissociation of oxygen from $XCo(hmc)O_2^+$ relative to that of $Co(hmc)O_2^{2+}$. Also, the conversion of $XCo(cyclam)O_2^+$ to final products is accelerated by halides and hydrogen ions.[8,9] The autoxidation of $Co(dtct)^+$ [12] follows a complicated rate law having a first-order dependence on $[O_2]$ and a two-term dependence on $[H^+]$. In fact, the catalysis by H^+ is observed routinely when O_2 is reduced to H_2O_2 and H_2O.

The bromide catalysis of the autoxidation of $Co(tim)^{2+}$ is probably the result of more than one effect. It may well be that the binding of oxygen in the early stages of the reaction is stronger in the presence of bromide, as in the case with $XCo(hmc)O_2^+$.[26] The subsequent redox steps are also expected to be catalyzed strongly by bromide, since halide ions are known to be excellent bridging ligands in electron transfer reactions.

We have ruled out the possibility that the oxidation of Br^- is an essential part of the scheme. The species involved appear unable to oxidize Br^-. Furthermore, even Cl^- catalyzes the reaction, and it is much more difficult to oxidize. Thus, $X^- \rightarrow X^{\bullet}$ or $X^- \rightarrow HOX$ transformations cannot be invoked. When the oxidation of halide is feasible, as in the case of I^-, then $Co(dmgBF_2)_2$ becomes an efficient catalyst for oxidation of halide, and the resulting halogen accumulates in solution. This clearly does not happen with chloride and bromide.

From a practical standpoint, two kinds of metal complexes are especially interesting in the realm of O_2 chemistry: (i) O_2 carriers, which bind but do not reduce O_2 (except for the charge transfer within the complex), and (ii) those complexes that oxidize H_2O (or reduce O_2) by four electrons. However, most of the known compounds fall between these two limits, such that O_2 carriers often get oxidized by O_2 and redox reactions involving O_2/H_2O utilize less than four electrons. This leads to the decomposition of the metal complex, formation of side products, and a general loss of activity in the system.

A clean four-electron reduction of O_2 reported in this work is encouraging. It appears that the relatively high and finely balanced values of $E°$ of the two cobalt complexes, with $E°$(catalyst) > $E°$(substrate), is an important feature of the system. Such values of $E°$ make it possible for $Co(dmgBF_2)_2^+$ to oxidize $Co(tim)^{2+}$ and thus close the catalytic loop. At the same time O_2 cannot oxidize $Co(tim)^{2+}$ directly, which reduces the number of reactive intermediates and side reactions and allows the majority of the reaction to be carried out in the catalytic four-electron process.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE-9007283). Some of the results were obtained with the use of the facilities of the Ames Laboratory.

---

[25] Mok, C. Y.; Endicott, J. F. *J. Am. Chem. Soc.* **1978**, *100*, 123.

[26] (a) Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1990**, *29*, 2062. (b) Marchaj, A.; Bakac, A.; Espenson, J. H. *Inorg. Chem.*, in press.