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Oxidation of Tris(1,10-phenanthroline)iron(II) by Chlorine Dioxide

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Abstract: The reaction of $[Fe(phen)_3]^{2+}$ with ClO_2 has been investigated in aqueous solution at 25.0 °C and at an ionic strength of 0.10 M ($NaCF_3SO_3$). The equilibrium quotient for formation of $[Fe(phen)_3]^{3+}$ and ClO_2^- was determined spectrophotometrically to be $(1.98 \pm 0.22) \times 10^{-3}$. Since the product ClO_2^- is a weak base, it was possible by mass action to drive the reaction in the uphill direction in acidic media. In the reverse direction the kinetics were immeasurably rapid, but in the uphill direction the kinetics were slow enough to be measured by using a stopped-flow spectrophotometer. The kinetics were consistent with a mechanism involving reversible bimolecular electron transfer followed by protonation of the ClO_2^-. The rate constant for electron transfer was calculated as 4.5×10^4 M^{-1} s^{-1}. Applying the cross relationship of Marcus theory leads to an effective self-exchange rate constant of 7.8×10^1 M^{-1} s^{-1} for the ClO_2/ClO_2^- couple.

The redox chemistry of small molecules in aqueous solution is of general interest but is imperfectly understood. The simplest redox reactions involve transfer of a single electron with no bond formation or cleavage. Small molecules do participate in electron-transfer reactions, but the reactions are usually obscure because of the high reactivity of the free-radical intermediates. Reactions involving the chlorite/chlorine dioxide redox couple are unique because chlorine dioxide is stable.[1] A further simplification can be introduced by constraining chlorine dioxide to be reduced by a substitution-inert coordination complex. Electron-transfer reactions of this type may be termed outer sphere, although they may involve strong interactions between chlorine dioxide and the ligands. Marcus theory is the current perspective from which such reactions are discussed.[2]

A literature search for outer-sphere electron-transfer reactions involving the ClO_2/ClO_2^- couple turned up only one study. This was a brief study of the reduction of ClO_2 by $[Fe(phen)_3]^{2+}$ (phen = 1,10-phenanthroline).[3] Shakhashiri and Gordon demonstrated that the reaction was outer sphere and fast, in contrast with the slow inner-sphere reduction of chlorite. They measured a rate constant of 1.86 ± 0.13 M^{-1} s^{-1} at 35 °C and an ionic strength of 1 M (Na_2SO_4). As a starting point in a broader investigation of reactions of ClO_2 we have reinvestigated the reaction with $[Fe(phen)_3]^{2+}$. We have confirmed Shakhashiri and Gordon's conclusion that the reaction is fast and outer sphere, but we have also found that the rate constant is more than 4 orders of magnitude faster than they reported.

Experimental Section

Reagents. $Fe(ClO_4)_2 \cdot 6H_2O$ was obtained from Alfa Products and 1,10-phenanthroline monohydrate was obtained from Aldrich. $NaClO_2$ (practical flakes) was obtained from MCB Reagents and $K_2S_2O_8$ was obtained from Baker Chemicals. Triflic acid (HCF_3SO_3) was obtained from 3M (Fluorochemical Acid FC 24). All reagents except the HCF_3SO_3 were used without further purification. The concentrated HCF_3SO_3 was distilled under vacuum and diluted to appropriate concentrations. $NaCF_3SO_3$ was prepared by neutralizing HCF_3SO_3 with Na_2CO_3; the resulting crystals were recrystallized from hot water. Distilled deionized water was used for all dilutions and experiments.

Synthesis of $[Fe(phen)_3](CF_3SO_3)_2$. The triflate salt of the $[Fe(phen)_3]^{2+}$ complex was prepared by mixing 0.3 g of ligand in 10 mL of methanol with 0.2 g of $Fe(ClO_4)_2 \cdot 6H_2O$ in 2 mL of H_2O. $[Fe(phen)_3](CF_3SO_3)_2 \cdot xH_2O$ was precipitated by the addition of 15 mL of a saturated aqueous solution of $NaCF_3SO_3$. After cooling for several hours the black chunky crystals were collected, washed with ethanol and ether, and placed in a vacuum desiccator. After several days in the vacuum desiccator the material effloresced, and the dehydrated product $[Fe(phen)_3](CF_3SO_3)_2$ was obtained as a red powder. Anal. Calcd for $C_{38}F_6FeH_{24}N_6O_6S_2$: C, 51.02; H, 2.70; N, 9.39. Found: C, 50.85; H, 2.66; N, 9.48.

Synthesis of ClO_2. Aqueous solutions of ClO_2 were prepared in the following way.[4] To a three-neck flask 5 g of $NaClO_2$ and approximately 10 mL of H_2O were added. Approximately 1.5 g of $K_2S_2O_8$ was dissolved in 50 mL of H_2O. The $K_2S_2O_3$ solution was added dropwise to the reaction flask through an addition funnel. A stream of N_2 was bubbled through the dark brown reaction mixture, and the product gas was passed through a tube containing $NaClO_2$ flakes to absorb any chlorine gas. The ClO_2 was collected by bubbling the product gas into H_2O in an amber bottle. The reaction was run away from all direct light and behind an explosion shield. The ClO_2 solution was stored in the dark in a refrigerator.

Analytical Methods. Stock solutions of HCF_3SO_3 were standardized by titration with 0.1 N tris(hydroxymethyl)aminomethane, and stock solutions of $NaCF_3SO_3$ were standardized by passing an aliquot down a Dowex cation-exchange column in the acid form and titrating the elluent with 0.1 N NaOH. Acid concentrations in the reaction mixtures were determined by measuring the pH with a Corning 130 pH meter and then converting the pH readings to concentrations by using a calibration curve constructed from standard solutions. The concentrations of $[Fe(phen)_3]^{2+}$ and ClO_2 were determined spectrophotometrically with Cary 210 and Cary 17 spectrophotometers; these determinations used for $[Fe(phen)_3]^{2+}$ $\epsilon_{510} = 1.11 \times 10^4$ M^{-1} cm^{-1}[5] and $\epsilon_{360} = 750$ M^{-1} cm^{-1}[6] and for ClO_2 $\epsilon_{360} = 1.20 \times 10^3$ M^{-1} cm^{-1}.[1] ClO_2 does not absorb significantly at 510 nm.

Chlorine dioxide solutions were tested for the presence of ClO_2^- by bubbling with argon to remove all ClO_2 and examining spectrophotometrically. For ClO_2^- at 260 nm $\epsilon \sim 140$ M^{-1} cm^{-1}.[1] Solutions were found to be stable for at least 20 days.

Handling of Solutions. All solutions of ClO_2 were protected from light. Solutions of $[Fe(phen)_3]^{2+}$ were prepared in $NaCF_3SO_3$ media shortly before each experiment in order to minimize the effects of acid hydrolysis. Since the reaction mixtures were generally acidic, the acid was added to the ClO_2 solutions before mixing. All solutions were permitted to contact only glass, platinum, Teflon, and the polyethylene syringes. The temperature was maintained at 25.0 ± 0.1 °C by using a Forma 2095 refrigerated circulating water bath.

Kinetic Methods. Kinetic data were collected with a stopped-flow apparatus having a Beckman DU as a light source and monochromator and an Aminco-Morrow mixer. The signal from the photomultiplier was amplified and filtered, and then it was digitized and stored by using a Biomation 805 waveform recorder. Data were transferred from the Biomation to the departmental PDP 11/70 computer via a locally designed interface. Computer programs within the PDP 11/70 were used to convert the data to absorbance units and then to obtain least-squares fits of the proposed rate laws. Rate constants were obtained from the slopes of the linear equations 10 and 14, weighting the data as the reciprocal of the square root of the ordinate. The fits were generally good for 3 half-lives.

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Table I. Equilibrium Quotient Results[a]

$[\mathrm{Fe(II)}]_0$, M	$[\mathrm{Fe(II)}]_\infty$, M	$[\mathrm{ClO_2}]$, M	$[\mathrm{H^+}]$, M	10^3K_{eq}[b]
8.73×10^{-6}	5.01×10^{-6}	3.32×10^{-4}	0.053	2.07
7.94×10^{-6}	3.70×10^{-6}	6.79×10^{-4}	0.040	1.98
7.43×10^{-6}	3.77×10^{-6}	6.85×10^{-4}	0.026	2.07
7.99×10^{-6}	4.68×10^{-6}	6.66×10^{-4}	0.013	1.98
10.3×10^{-6}	5.22×10^{-6}	4.28×10^{-4}	0.100	1.68
10.3×10^{-6}	5.36×10^{-6}	5.70×10^{-4}	0.044	2.23
4.97×10^{-6}	2.50×10^{-6}	3.38×10^{-4}	0.045	1.98
5.40×10^{-6}	3.51×10^{-6}	1.82×10^{-4}	0.043	1.58

[a] 25.0 °C, $\mu = 0.1$ M ($\mathrm{NaCF_3SO_3}$). [b] Average $K_{eq} = (1.98 \pm 0.22) \times 10^{-3}$.

Results

An initial investigation of the system at 25 °C with an ionic strength of 0.1 M ($\mathrm{NaClO_4}$) met with difficulties. Attempts to measure the equilibrium quotient led to inconsistent results. The apparent equilibrium quotient showed extreme sensitivity to an increase in ionic strength. The effects were ultimately traced to a visually imperceptible precipitation of the perchlorate salt of the iron(III) complex. Subsequent studies in triflate ($\mathrm{NaCF_3SO_3}$) media gave much more reasonable results because of the high solubility of $[\mathrm{Fe(phen)_3}](\mathrm{CF_3SO_3})_3$.

Stoichiometry and Equilibrium. The reaction was presumed to have the stoichiometry

$$\mathrm{Fe(phen)_3}^{2+} + \mathrm{ClO_2} \rightleftarrows \mathrm{Fe(phen)_3}^{3+} + \mathrm{ClO_2}^- \qquad K_{eq} \quad (1)$$

but $[\mathrm{Fe(phen)_3}]^{3+}$ and $\mathrm{ClO_2}^-$ were not specifically observed. Spectrophotometric determinations of $[\mathrm{Fe(phen)_3}]^{2+}$ and $\mathrm{ClO_2}$ were, however, performed. It was found that in acidic media with an excess of $\mathrm{ClO_2}$ only partial oxidation of $[\mathrm{Fe(phen)_3}]^{2+}$ occurred, and this was attributed to the reversibility of the reaction. A further complication arose from the significant basicity of chlorite (K_a for chlorous acid is 0.017 M).[7] A value of K_{eq} was determined by mixing solutions of $[\mathrm{Fe(phen)_3}]^{2+}$ with $\mathrm{ClO_2}$ that were initially free of $[\mathrm{Fe(phen)_3}]^{2+}$ and $\mathrm{ClO_2}^-$ and observing the consumption of $[\mathrm{Fe(phen)_3}]^{2+}$. There was always a least a 30-fold excess of $\mathrm{ClO_2}$. Equilibrium quotients were calculated using eq 2 under

$$K_{eq} = \frac{([\mathrm{Fe(phen)_3}^{2+}]_0 - [\mathrm{Fe(phen)_3}^{2+}]_\infty)^2}{[\mathrm{Fe(phen)_3}^{2+}]_\infty[\mathrm{ClO_2}](1 + [\mathrm{H^+}]K_a^{-1})} \quad (2)$$

a variety of conditions and are listed in Table I. In obtaining these values the published acidity of chlorous acid was used. Chlorite undergoes disproportionation in acidic media, but the reaction is second order in [chlorite].[7] At the low chlorite concentrations prevailing in our studies disproportionation was not expected to be a problem. Indeed, on the time scale of the measurements the system was found to be stable.

The consistent values for K_{eq} under a variety of conditions is good evidence that the stoichiometry is as written in eq 1. Conclusive evidence for this is that K_{eq} is calculated as 2.5×10^{-3}, using published reduction potentials of 0.936 V for $\mathrm{ClO_2}$[8] and 1.09 V for $[\mathrm{Fe(phen)_3}]^{3+}$;[9] this calculated K_{eq} within the uncertainty of the reduction potentials is equal to our measured value of $(1.98 \pm 0.22) \times 10^{-3}$. It should be noted that the reaction, as written, is thermodynamically uphill. By working in acidic media with excess $\mathrm{ClO_2}$ it can be driven sufficiently far to the right to make measurements.

Kinetics. Attempts to measure the kinetics of the oxidation of $\mathrm{ClO_2}^-$ by $[\mathrm{Fe(phen)_3}]^{3+}$ failed; even at the lowest concentrations of reactants the reaction was complete within the dead time of the stopped flow. The reverse reaction, of $\mathrm{ClO_2}$ with $[\mathrm{Fe(phen)_3}]^{2+}$, was found to be slow enough to be observed, with half-lives between 8.0 and 31.5 ms. In this direction the reaction is uphill and could not be driven by mass action to completion. As a result, the kinetics were found to be complex because the reaction was relaxing to an equilibrium determined both by the $\mathrm{p}K_a$ of $\mathrm{HClO_2}$ and the reduction potential of $\mathrm{ClO_2}$.

Table II. Kinetic Results[a]

run	$[\mathrm{Fe(phen)_3}^{2+}]_0$, M	$[\mathrm{ClO_2}]$, M	$[\mathrm{H^+}]$, M	no. of runs	k_{-1}, $\mathrm{M^{-1}\ s^{-1}}$ [d,e]
1	1.03×10^{-5}	5.70×10^{-4}	0.053	1	2.57×10^7
2	5.40×10^{-6}	1.82×10^{-4}	0.052	2	2.33×10^7 (0.11)
3	9.08×10^{-6}	7.78×10^{-4}	0.104	4	1.83×10^7 (0.04)
4	9.22×10^{-6}	9.85×10^{-5}	0.104	4	2.49×10^7 (0.22)
5	9.51×10^{-6}	4.58×10^{-4}	0.022	4	2.29×10^7 (0.28)
6	1.88×10^{-5}	1.74×10^{-4}	0.021	4	2.21×10^7 (0.10)
7	9.22×10^{-6}	4.13×10^{-4}	0.052	5	2.34×10^7 [b] (0.26)
8	9.22×10^{-6}	4.70×10^{-4}	0.051	5	1.75×10^7 [c] (0.28)

[a] 25.0 °C, $\mu = 0.1$ M ($\mathrm{NaCF_3SO_3}$). [b] 1.78×10^{-6} M added $\mathrm{Fe(ClO_4)_2}$. [c] 9.69×10^{-5} M added 1,10-orthophenanthroline. [d] Average $k_{-1} = (2.29 \pm 0.26) \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$. Not including runs with added Fe^{2+} or ligand. [e] Average deviation in parentheses.

The rate constants for the reaction were obtained by fitting the time dependence of the reaction to the integrated rate law, which was derived from the following mechanism:

$$\mathrm{ClO_2} + \mathrm{Fe(phen)_3}^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ClO_2}^- + \mathrm{Fe(phen)_3}^{3+} \qquad K_{eq} \quad (3)$$

$$\mathrm{ClO_2}^- + \mathrm{H^+} \rightleftharpoons \mathrm{HClO_2} \qquad K_a^{-1} \quad (4)$$

This mechanism leads to the differential rate law

$$\frac{-\mathrm{d}[\mathrm{Fe(phen)_3}^{2+}]}{\mathrm{d}t} = \frac{k_{-1}}{1 + ([\mathrm{H^+}]/K_a)}\{[\mathrm{Fe(phen)_3}^{2+}](2[\mathrm{Fe(phen)_3}^{2+}]_0 + K_{eq}[\mathrm{ClO_2}]_0 (1 + ([\mathrm{H^+}]/K_a))) - [\mathrm{Fe(phen)_3}^{2+}]^2 - [\mathrm{Fe(phen)_3}^{2+}]_0^2\} \quad (5)$$

when $\mathrm{ClO_2}$ is in sufficient excess over $[\mathrm{Fe(phen)_3}]^{2+}$ to have an effectively constant concentration during any kinetic run, and no $\mathrm{ClO_2}^-$ or $[\mathrm{Fe(phen)_3}]^{3+}$ is initially present.

Defining

$$\Delta\mathrm{Fe(II)} \equiv [\mathrm{Fe(phen)_3}^{2+}] - [\mathrm{Fe(phen)_3}^{2+}]_\infty \quad (6)$$

and

$$K'_{eq} = K_{eq}[\mathrm{ClO_2}]_0(1 + ([\mathrm{H^+}]/K_a)) \quad (7)$$

and noting that

$$[\mathrm{Fe(phen)_3}^{2+}]_\infty = [\mathrm{Fe(phen)_3}^{2+}]_0 + (K'_{eq} - q^{1/2})/2 \quad (8)$$

where

$$q = (4[\mathrm{Fe(phen)_3}^{2+}]_0 + K'_{eq})K'_{eq} \quad (9)$$

leads to the integrated rate law

$$\ln\left(\frac{\Delta\mathrm{Fe(II)}(q^{1/2} - K'_{eq}) - q + K'_{eq}q^{1/2}}{-\Delta\mathrm{Fe(II)}(q^{1/2} + K'_{eq})}\right) = k'_{-1}(q)^{1/2}t \quad (10)$$

where

$$k'_{-1} = \frac{k_{-1}}{1 + ([\mathrm{H^+}]/\mathrm{K_a})} \quad (11)$$

The individual kinetic runs were fit with eq 10 by using our measured value of K_{eq} and converting the absorbance data to $[\mathrm{Fe(phen)_3}^{2+}]$ using $\epsilon = 1.11 \times 10^4\ \mathrm{M^{-1}\ cm^{-1}}$ at 510 nm. The values of k_{-1} were obtained under a variety of conditions but with $\mathrm{ClO_2}$ always in at least 10-fold excess, and they are given in Table II. For any given set of conditions the calculated rate constants fluctuated by as much as ±15% from run to run; the tabulated

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(9) Interpolated at $\mu = 0.1$ M from the data in: Schilt, A. A. "Analytical Applications of 1,10-phenanthroline"; Pergamon: New York, 1969; Table 9, p 107.

k_{-1} values are generally averages of four runs. This large uncertainty arose from the very rapid kinetics and the small overall absorbance changes ($\Delta A = 0.01$–0.06). The data in Table II span reasonably large ranges in concentration of H^+, ClO_2, and $[Fe(phen)_3]^{2+}$, but the k_{-1} values are constant within the considerable uncertainty of the individual runs. The entries in Table II for reactions performed with added ligand or $Fe^{2+}{}_{aq}$ show that these species have not interfered significantly in the reaction.[10] This is taken to be good evidence that eq 10 and hence the proposed mechanism correctly describe the reaction. Since $k_1 = K_{eq}k_{-1}$, we find a value of k_1 of 4.5×10^4 M^{-1} s^{-1}.

An alternative mechanism was considered in which a proton was included in the activated complex:

$$Fe(phen)_3{}^{2+} + H^+ + ClO_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Fe(phen)_3{}^{3+} + HClO_2 \qquad K_{2eq} \quad (12)$$

$$HClO_2 \rightleftharpoons H^+ + ClO_2{}^- \qquad K_a \qquad (13)$$

This mechanism has the integrated rate law

$$\ln\left(\frac{\Delta Fe(II)(q'^{1/2} - K''_{eq}) - q' + K''_{eq}(q')^{1/2}}{-\Delta Fe(II)(q'^{1/2} + K''_{eq})}\right) = k'_{-2}(q')^{1/2}t \qquad (14)$$

with $q' = (4[Fe(phen)_3{}^{2+}]_0 + K''_{eq})K''_{eq}$, $k'_{-2} = k_{-2}/(1 + (K_a/[H^+]))$, and $K''_{eq} = K_{2eq}[ClO_2]_0([H^+] + K_a)$. This rate law is of the same form as that in eq 10, but the concentration dependences are different. As a result, the time-dependent fits were just as good as those obtained by using eq 10. However, the values of k_{-1} so obtained varied from 3.26×10^6 M^{-1} s^{-1} for run 3 to 2.1×10^7 M^{-1} s^{-1} for run 5. Medium effects should be most pronounced in a comparison of runs 3 and 5 since between these runs the acidity is varied almost to the full extent of the ionic strength. It is well recognized that spurious terms can appear in rate laws when Na^+ is largely replaced by H^+, consistent with Harned's rule.[11] These effects at $\mu = 0.1$ M may perturb the proton activity by as much as 10%. It is not clear whether these effects are significant in the fit of our data to eq 10, but it is clear that the 6.6-fold variation in rate constants obtained for runs 3 and 5 when eq 14 is used is not consistent with medium effects. Thus, the alternative mechanism (eq 12 and 13) can be rejected with confidence.

Discussion

This investigation was initiated with the intent of obtaining kinetic data on a very simple electron-transfer reaction of a small molecule. It was somewhat ironic that such a complex kinetics analysis ensued. However, we believe we have met the goal of obtaining a rate constant for an outer-sphere electron-transfer reaction of a small molecule for which the free-energy change is accurately known.

The reaction is much faster than previously reported, and it could not have been measured by using the relatively slow mixing techniques of that study.[3] One might hope that Marcus's theory of electron transfer could be used to spot errors of this magnitude. The cross relationship of Marcus's theory can be expressed[12] as

$$k_{11} = \left(\frac{k_{12}}{W_{12}}\right)^2 \frac{1}{k_{22}K_{12}f_{12}}$$

$$W_{12} = \exp\left(\frac{-(w_{12} + w_{21} - w_{11} - w_{22})}{2RT}\right)$$

$$\ln f_{12} = \frac{\left(\ln K_{12} + \frac{w_{12} - w_{21}}{RT}\right)^2}{4\left(\ln\left(\frac{k_{11}k_{22}}{Z^2}\right) + \frac{w_{11} + w_{22}}{RT}\right)} \qquad (15)$$

$$w_{ab} = \frac{(4.23 \times 10^{-8})Z_AZ_B}{a(1 + (2.38 \times 10^7)a(\mu)^{1/2})}$$

where k_{11} is the self–exchange rate constant for the $ClO_2/ClO_2{}^-$ couple, k_{22} is the self-exchange rate constant for the $[Fe(phen)_3]^{3+}/[Fe(phen)_3]^{2+}$ couple, K_{12} is the equilibrium constant for the electron-transfer reaction, Z is the collision rate constant, taken to be 1×10^{11} M^{-1} s^{-1}, and a is the center-to-center distance between the relevant reactants when touching. Since ClO_2 is uncharged, w_{11} and w_{12} are zero, but w_{21} and w_{22} are significant in the calculation. k_{11} appears in the calculations of f_{12}, and so k_{11} is calculated from eq 15 iteratively.

Using eq 15 and Shakhashiri and Gordon's rate constant gives a self-exchange rate of about 10^{-7} M^{-1} s^{-1} for the $ClO_2{}^-/ClO_2$ couple. This calculation uses estimated "radii" for $[Fe(phen)_3]^{3+}/[Fe(phen)_3]^{2+}$ and $ClO_2/ClO_2{}^-$ of 6 and 1.5 Å, respectively, and a self-exchange rate constant of 5×10^8 M^{-1} s^{-1} for the $[Fe(phen)_3]^{3+}/[Fe(phen)_3]^{2+}$ couple.[13] Our recent experience with applying eq 15 to outer-sphere redox reactions has resulted in self-exchange rates of $\sim 10^2$ M^{-1} s^{-1} for the $O_2/O_2{}^-$ couple[14] and 10^{-2} M^{-1} s^{-1} for the $NO_2/NO_2{}^-$ couple.[15] Since the changes in bond angle and bond length for the $ClO_2{}^-/ClO_2$ couple are 6.5° and 0.10 Å, while for the $NO_2/NO_2{}^-$ couple the changes are 19° and 0.05 Å,[16] a slightly faster rate for the $ClO_2{}^-/ClO_2$ couple couple might be expected. A value of 10^{-7} M^{-1} s^{-1} is clearly anomalous.

Using eq 15 and our rate constant gives a value of 7.8×10^1 M^{-1} s^{-1} for the effective self-exchange rate constant for the $ClO_2/ClO_2{}^-$ couple. This number is consistent with our prior experience with small molecules. Dodgen and Taube in 1949 reported direct measurements of the electron exchange reaction between ClO_2 and $ClO_2{}^-$ using isotopic tracer methods.[17] Their experiment 8 showed almost complete exchange in 21 s when 1.3×10^{-4} M $ClO_2{}^-$ and 4.5×10^{-5} M ClO_2 were mixed. Using the McKay equation[2] leads to an estimate of the rate constant of 4×10^2 M^{-1} s^{-1}. Dodgen and Taube cautioned that the actual rate constant may be considerably greater, and so 4×10^2 M^{-1} s^{-1} should be regarded as a lower limit. The near equivalence between our effective self-exchange rate and Dodgen and Taube's result is quite likely coincidental. Gordon and Emmenegger have reported that mixtures of $ClO_2{}^-$ and ClO_2 show spectroscopic evidence for formation of $Cl_2O_4{}^-$ with an equilibrium constant of 1.6 M^{-1}.[18] This complex may provide a pathway for electron transfer involving strong overlap; therefore the direct rate constant may be much greater than the effective rate constant calculated by the cross relationship. Investigations of other outer-sphere reactions involving the $ClO_2/ClO_2{}^-$ couple are under way with the objective of determining whether the effective self-exchange rate is of general significance.

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(10) To ensure that there were no complications due to attack of the polyethylene syringes, duplicate runs were made with all-glass syringes at $[H^+] = 0.092$ M, $[ClO_2] = 2.0 \times 10^{-4}$M, and $[Fe(II)] = 9.5 \times 10^{-6}$ M. The variation in the values obtained for the rate constants between the two syringe types was less than 10%. This variation is within the range normally observed for duplicate runs.

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Registry No. $[Fe(phen)_3]^{2+}$, 14708-99-7; $[Fe(phen)_3](CF_3SO_3)_2$, 85152-70-1; ClO_2, 10049-04-4.

Vanadium(V) Peroxo Complexes. New Versatile Biomimetic Reagents for Epoxidation of Olefins and Hydroxylation of Alkanes and Aromatic Hydrocarbons

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Abstract: Novel covalent vanadium(V) oxo peroxo complexes of general formula $VO(O_2)(O{-}N)LL'$ [type I, O–N = pyridine-2-carboxylate (Pic), pyrazine-2-carboxylate; L, L′ = H_2O, MeOH, monodentate or bidentate basic ligands] and anionic complexes with the general formula $[VO(O_2)(Pic)_2]^-A^+L$ [type II, $A^+ = H^+$, PPh_4^+; L = H_2O, hexamethylphosphoric triamide (HMPT)] were synthesized and characterized by physicochemical methods and X-ray crystallography. The crystal structure of $VO(O_2)(Pic)\cdot 2H_2O$ (Ia) revealed a pentagonal-bipyramidal environment, with a significant hydrogen bonding between the peroxo moiety and the equatorial water molecule. Protonated type II complexes ($A^+ = H^+$) are dissociated in an aqueous solution and have an acidic nature ($pK_a = 1.8$) but are undissociated in a nonprotic solution, with a presumably peracid-like oxohydroperoxo structure. While relatively stable in solid state and protic solvents vanadium(V) peroxo complexes decompose in nonprotic solvents, the most unstable ones being the complexes Ia and IIb. Upon decomposition or reaction with hydrocarbons, complex Ia lost one oxygen atom and produced an oxo bis(μ-oxo) vanadium(V) dimeric complex IIIa which reacted with HMPT to give a trigonal-bipyramidal vanadium(V) *cis*-dioxo complex $VO_2(Pic)(HMPT)$ (IIIb) characterized by an X-ray crystal structure. Vanadium peroxo complexes are effective oxidants in nonprotic solvents under mild conditions. They transform olefins to epoxides and cleavage products in a nonstereoselective fashion (*cis*-2-butene gave a mixture of cis and trans epoxides). More interestingly, they hydroxylate aromatic hydrocarbons to phenols and alkanes to alcohols and ketones. Complex Ia oxidized benzene to phenol with a 55% yield, without any primary deuterium isotope effect ($k_H/k_D = 1$). Toluene was mainly hydroxylated at the ring positions with a 70% NIH shift value. Alkanes are much less readily hydroxylated than aromatics, this reaction occurring with a relatively low isotope effect ($k_H/k_D = 2.8$) and a significant amount of epimerization at the hydroxylated carbon atom. This reactivity, which appears very different from that of Mo peroxo complexes, was tentatively attributed to a radical $V^{IV}{-}O{-}O\cdot$ species generated from peracid-like forms, which adds to double bonds and aromatic nucleus and abstracts hydrogen atoms from alkanes to give a carbon radical intermediate. These observations are discussed in the context of proposed "oxenoid" mechanisms and enzymic cytochrome P_{450} monooxygenases.

The synthesis of well-defined transition-metal peroxides and the study of their oxidizing properties toward organic substrates provide a heuristic approach to the understanding of catalytic oxidation reactions.[3] In contrast to molybdenum peroxo complexes, which are well established as epoxidation reagents,[4] vanadium(V) peroxo complexes have never been studied as such with regard to their oxidizing properties. In fact, the well-characterized V(V) peroxo complexes, e.g., $[(Dipic)VO(O_2)\cdot H_2O]^-NH_4^+$ **1**,[5] $[VO(O_2)_2NH_3]^-NH_4^+$ **2**,[6] and related complexes,[7] are anionic species and generally insoluble in organic solvents. However, vanadium compounds have been widely used as catalysts for the oxidation of olefins by H_2O_2 or ROOH.[3d,e] They are generally less efficient and selective catalysts than molybdenum compounds for the epoxidation of unactivated olefins,[8] but highly active and stereoselective for allylic alcohols.[9] Interestingly, cyclohexene is mainly oxidized to cyclohex-1-en-3-ol and cyclohex-1-en-3-one by H_2O_2 in the presence of V_2O_5.[10]

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