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Kinetics of Aqueous Outer-Sphere Electron-Transfer Reactions of Superoxide Ion. Implications concerning the O_2/O_2^- Self-Exchange Rate Constant

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The kinetics and mechanism of the reactions of aqueous superoxide ion and several Co(III) amine complexes and ferrocenium ion are reported. The initial and rate-limiting step (and the only step for the ferrocenium ion reaction) is outer-sphere electron transfer from superoxide ion to the metal complex. Second-order rate constants at 25.0 °C are 31.3, 23.8, and 16.4 $M^{-1}\ s^{-1}$ for $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, and Co(*trans*-1,2-cyclohexanediamine)$_3^{3+}$, respectively, and $8.6 \times 10^6\ M^{-1}\ s^{-1}$ for $Fe(C_5H_5)_2^+$. For the Co(III) reactions, several physical (temperature, pH) and chemical (isotopic labeling of complex and solvent, choice of counteranion, presence and absence of dioxygen) effects were investigated. Dioxygen has a marked effect upon the Co(III) reactions, resulting in second-order rate constants that are greater by a factor of 2 under anaerobic conditions than under aerobic. This dioxygen effect is explained by the competing reactions of the Co(II) amine complexes produced in the electron-transfer step with O_2 or O_2^-. The Marcus cross-relation permits calculation of a parameter that might be interpreted as the $O_2(aq)/O_2^-$ self-exchange rate constant from data for these and other reactions, but widely variant values are obtained, 10^{-8}–$10^{5.7}\ M^{-1}\ s^{-1}$. This phenomenon is attributed to the very different solvation of dioxygen and superoxide ion.

Introduction

The superoxide radical anion is an important intermediate in some chemical and biochemical reactions of molecular oxygen.[1-4] Direct studies of the rates and mechanisms of O_2^- reactions in aqueous solution have heretofore required the use of highly specialized instrumentation such as pulse or stopped-flow radiolysis[5] or vacuum-UV photolysis,[6] which has tended to limit the number and types of reactions investigated. With the advent of a new method[7] for preparing aqueous solutions of O_2^-, a number of additional opportunities became available. We undertook to investigate *directly* the relatively slow reaction between O_2^- and $Co(NH_3)_6^{3+}$ and analogues and also the much faster reduction of ferrocenium ion by O_2^-:

$$Co(NH_3)_6^{3+} + O_2^- \rightarrow Co(NH_3)_6^{2+} + O_2 \qquad (1)$$

$$Fe(C_5H_5)_2^+ + O_2^- \rightarrow Fe(C_5H_5)_2 + O_2 \qquad (2)$$

The specific objectives were (1) to demonstrate the applicability of this method of O_2^- generation to a variety of chemical systems, especially ones deemed likely to react via the outer-sphere mechanism, (2) to add to the relatively limited store of kinetic data concerning electron-transfer reactions of aqueous superoxide, and (3) to provide additional data that might resolve the ongoing controversy[8-16] concerning the O_2/O_2^- self-exchange rate constant, k_{11}. Values of k_{11} ranging from 10^{-7} to $10^7\ M^{-1}\ s^{-1}$ have been calculated by application of the Marcus theory equation to the respective reactions of O_2^- with ferricyanide ion,[11] ruthenium–amine complexes,[13-15] and quinones;[8-10] numerous intermediate values were obtained in other systems, as discussed elsewhere[13-16] and considered later in this paper.

Experimental Procedures

Materials. Literature methods were used to prepare the following compounds: $[Co(NH_3)_6]Cl_3$,[17] $[Co(NH_3)_6](ClO_4)_3$,[17] $[Co(ND_3)_6]Cl_3$,[18] $[Co(en)_3]Cl_3$,[19] $[Co(en)_3](ClO_4)_3$,[19] $[Co(chxn)_3]Cl_3{\cdot}H_2O$[20] (chxn = *trans*-1,2-diaminocyclohexane), and $[Fe(\eta^5\text{-}C_5H_5)_2]PF_6$.[21] 2-Propanol (Aldrich Gold Label), benzophenone (Eastern Organic), and Na_2EDTA (Mallinckrodt) were used as received. It was necessary to use highly purified chemicals and solvents and thoroughly cleaned glassware to avoid the introduction of catalysts for superoxide disproportionation. Distilled water was passed through a Millipore-Q filtering system. All gases (O_2, N_2, and Ar) were passed through 5 M KOH to remove trace CO_2 impurities.

Techniques. The reactions of O_2^- with the Co(III) complexes are slow, and typically took a minute or so to reach completion. They were studied by separately generating O_2^- inside an already thermostated quartz spectrophotometer cell. Approximately 30 s of photolysis using medium-pressure mercury lamps in a Rayonet chamber was required. If desired, the residual O_2 was removed at this point by a vigorous stream of inert gas. After further thermostating, the concentration of O_2^- was determined spectrophotometrically at a wavelength of 245 (max), 260, or 270 nm (ϵ 2350, 1990, and 1480 $M^{-1}\ cm^{-1}$, respectively). The reaction was initiated by syringe injection of a solution of the Co(III) complex in 1 M 2-propanol. The final solution composition consisted of 4–6 μM Ph_2CO, 1.0 M 2-propanol, and $\sim$20 μM Na_2EDTA, at pH 11.3–11.9 (KOH). The progress of the reaction was measured by recording the decrease in absorbance at λ 245–270 nm, the wavelength used in a particular experiment being chosen to avoid too large a background absorption by the given Co(III) solution. The final solutions showed stable spectra corresponding essentially to the excess of the Co(III) complex because the cobalt products absorb much less in comparison. The kinetic measurements were made with $[Co(III)]_0 >> [O_2^-]_0$. The Co(III) reactions followed pseudo-first-order kinetics. The data were analyzed by using a nonlinear least-squares computer program to evaluate the pseudo-first-order rate constant k_{obsd} from the relation $D_t = D_\infty + (D_0 - D_\infty)\exp(-k_{obsd}t)$, where D = absorbance. Except for the case of $Co(NH_3)_6^{3+}$, where a slow drift of the experimental "end point"

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(1) (a) McCord, J. M.; Fridovich, I. *J. Biol. Chem.* **1968**, *243*, 5753. (b) Knowles, P. F.; Gibson, J. F.; Pick, F. M.; Brick, F.; Bray, R. C. *Biochem. J.* **1969**, *111*, 53.

(2) McCord, J. M.; Fridovich, I. *J. Biol. Chem.* **1969**, *244*, 6049.

(3) Michelson, A. M.; McCord, J. M.; Fridovich, I. "Superoxide and Superoxide Dismutases"; Academic Press: New York, 1977.

(4) Sawyer, D. T.; Valentine, J. C. *Acc. Chem. Res.* **1981**, *14*, 393.

(5) (a) Bielski, B. H. J.; Gebicki, J. M. *Adv. Radiat. Chem.* **1970**, *2*, 177. (b) Bielski, B. H. J. *Photochem. Photobiol.* **1978**, *28*, 645. (c) Ilan, Y. A.; Meisel, D.; Czapski, G. *Isr. J. Chem.* **1974**, *12*, 891. (d) Bielski, B. H. J.; Richter, H. W. *J. Am. Chem. Soc.* **1977**, *99*, 3019.

(6) (a) Holroyd, R. A.; Bielski, B. H. J. *J. Am. Chem. Soc.* **1978**, *100*, 5796. (b) Gebicki, J. M.; Bielski, B. H. J. *Ibid.* **1982**, *104*, 796.

(7) McDowell, M. S.; Bakač, A.; Espenson, J. H. *Inorg. Chem.* **1983**, *22*, 847.

(8) Willson, R. L. *Trans. Faraday Soc.* **1971**, *67*, 3020.

(9) Patel, K. B.; Willson, R. L. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 814.

(10) Meisel, D. *Chem. Phys. Lett.* **1975**, *34*, 263.

(11) Zehavi, D.; Rabani, J. *J. Phys. Chem.* **1972**, *76*, 3703.

(12) Faraggi, M. *J. Phys. Chem.* **1976**, *80*, 2316.

(13) Stanbury, D. M.; Mulac, W. A.; Sullivan, J. C.; Taube, H. *Inorg. Chem.* **1980**, *19*, 3735.

(14) Pladziewicz, J. R.; Meyer, T. J.; Broomhead, J. A.; Taube, H. *Inorg. Chem.* **1973**, *12*, 639.

(15) Stanbury, D. M.; Haas, O.; Taube, H. *Inorg. Chem.* **1980**, *19*, 518.

(16) Creaser, I. I.; Geue, R. J.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016.

(17) Bjerrum, J.; McReynolds, J. P. *Inorg. Synth.* **1946**, *2*, 216.

(18) Prepared in situ by stirring $[Co(NH_3)_6]Cl_3$ for 10 min in D_2O; at pH 11.6 the H/D exchange is complete within 1 min (Basolo, F.; Palmer, J. W.; Pearson, R. G. *J. Am. Chem. Soc.* **1960**, *82*, 1073).

(19) Work, J. B. *Inorg. Synth.* **1946**, *2*, 221.

(20) Beattie, J. K.; Binstead, R. A.; Broccardo, M. *Inorg. Chem.* **1978**, *17*, 1822.

(21) Yang, E. S.; Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1975**, *79*, 2049.

0020-1669/84/1323-2232$01.50/0

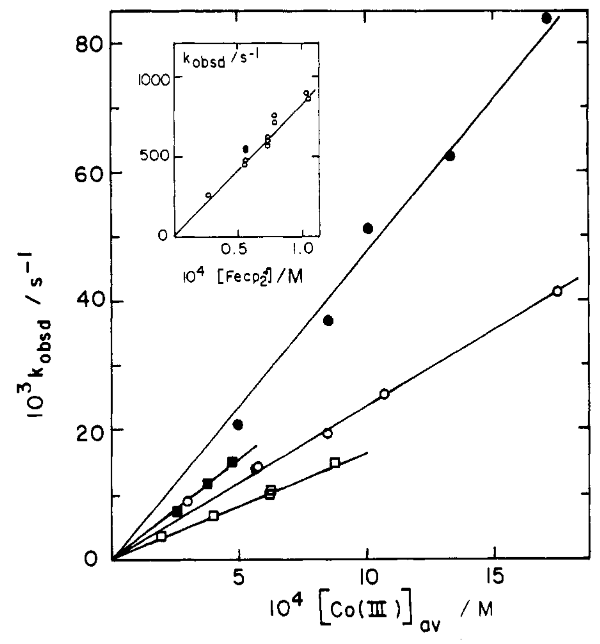

Figure 1. Linear dependence of the pseudo-first-order rate constant at 25.0 °C on the average concentration of the reagent in excess. The data shown refer to $Co(en)_3^{3+}$ (circles) and $Co(chxn)_3^{3+}$ (squares); open symbols refer to experiments in O_2-saturated solutions and filled symbols to N_2-saturated solutions. The inset is an analogous plot for the ferrocenium ion reaction.

absorbance was noted owing to secondary reactions, observed and least-squares-fit values of D_∞ agreed very well.

The reduction of $Fe(C_5H_5)_2^+$ by O_2^- required the use of a modified technique because the ferrocenium ion is decomposed fairly rapidly in basic solution and because the electron-transfer rate is high. Reaction was initiated immediately after addition of $Fe(C_5H_5)_2^+$ by the in situ flash-photolytic generation[7,22] of O_2^- with a Xenon Corp. Model 710 unit. The reaction was monitored by noting the increase in transmittance at an absorption maximum of $Fe(C_5H_5)_2^+$, λ 617 nm (ε 450 M^{-1} cm^{-1}). The kinetic data were treated by the standard pseudo-first-order kinetic analysis detailed above. Values of k_{obsd} ranged from 264 to 879 s^{-1} ($t_{1/2}$ ~ 0.79–2.62 ms). Appropriate blank experiments were conducted to demonstrate the lack of effect on ferrocenium ion of the photochemical processes used to generate O_2^- in its presence. It was also shown that the technique whereby an acidic solution of $Fe(C_5H_5)_2^+$ was mixed with the "superoxide generating solution" so as to provide pH ~11 did not lead to appreciable decomposition (<2%) during these experiments. This consideration arises because $Fe(C_5H_5)_2^+$ undergoes a complicated decomposition to several products in the presence of OH^-.[23] A further blank was performed by repeating the flash-photolytic experiment in an identical fashion, save for use of argon-saturated rather than oxygen-saturated solutions. The reduction of $Fe(C_5H_5)_2^+$ occurs much more rapidly in the blank, which we attribute to its known reaction[24] with the aliphatic radicals [$Fe(C_5H_5)_2^+ + \cdot C(CH_3)_2OH \rightarrow Fe(C_5H_5)_2 + (CH_3)_2CO + H^+$]. The slower reduction of ferrocenium ion occurs only when O_2 is present, clearly implicating a reaction that involves a transient derived from O_2. Since O_2 destroys the aliphatic radical in a diffusion-controlled reaction, the absence of a fast reaction is in agreement with the formulation given; since the reaction of O_2 with $\cdot C(CH_3)_2OH$ in alkaline solution leads to O_2^-, it is reasonable to attribute the "slower" reduction of $Fe(C_5H_5)_2^+$ to its reaction with O_2^-, eq 2.

Additional evidence bearing on the correct formulation being that given in eq 2 comes from experiments in which $Fe(C_5H_5)_2^+$ was injected into preprepared solutions of O_2^-. Reduction of $Fe(C_5H_5)_2^+$ was complete upon mixing, yielding $Fe(C_5H_5)_2$. A spectrophotometric titration was carried out to determine the stoichiometry of the reaction between $Fe(C_5H_5)_2^+$ and O_2^-. The titration consists of a series of small, rapid injections of $Fe(C_5H_5)_2^+$ at pH 2.3 into 68 μM O_2^- at pH 11.7 contained in a 2-cm quartz cell. After each addition the absorbance was recorded at 300 nm, where the respective molar absorptivities of $Fe(C_5H_5)_2^+$, $Fe(C_5H_5)_2$, and O_2^- are ~5 × 10^3, 29, and ~0 M^{-1} cm^{-1}.

Table I. Summary of Rate Constants for the Oxidation of O_2^- by Cobalt(III) Complexes and Ferrocenium Ions[a]

		k/M^{-1} s^{-1}	
complex	temp/°C	oxygen	nitrogen
$Co(NH_3)_6^{3+}$[b]	34.4	61.5 ± 4.9	
	25.0	31.3 ± 0.5	63.9 ± 1.7
	10.9	11.7	
	9.8	12.1	
	2.1	6.2	
$Co(ND_3)_6^{3+}$[c]	25.0	28.4 ± 2.0	
$Co(en)_3^{3+}$[b]	25.0	23.8 ± 0.4	47.5 ± 1.1
	16.8	14.8	
	5.40	6.5 ± 0.6	
$Co(chxn)_3^{3+}$[d]	25.0	16.4 ± 0.3	31.2 ± 0.4
	15.2	8.84	
	9.0	5.66	
	6.2	4.78	
$Co(sep)^{3+}$[e]	25.0	0.87[e]	
$Co(phen)_3^{3+}$[f]	25.0	>10^4	
$Co(CN)_6^{3-}$[g]	25.0	<3	
$Fe(C_5H_5)_2^+$	25.0	8.6 × 10^6	

[a] In aqueous 1 M 2-propanol at pH 11.3–11.9; the rate constant k is the least-squares slope of k_{obsd} vs. $[Co(III)]_{av}$, and its uncertainty represents 1 standard deviation in 2–16 determinations. [b] Includes experiments with both chloride and perchlorate complexes. [c] In >90% D_2O. [d] Chloride complex only. [e] Calculated from the $E°$'s and k for the reverse reaction (ref 21 and 22; see text). [f] Reaction complete within mixing time. [g] No reaction in the lifetime of O_2^- toward disproportionation.

Results and Interpretation

Kinetics—Co(III) Reactions. The pseudo-first-order rate contants vary directly with [Co(III)], as shown in Figure 1. The rate equations thus all take the form shown in eq 3. As

$$-d[O_2^-]/dt = k[O_2^-][Co(III)] \qquad (3)$$

also depicted, the kinetic data for the cobalt complexes depend on whether or not O_2 was removed prior to reaction. The data, summarized in Table I, clearly show the character of the oxygen dependence. Consider the second-order rate constants k of eq 3, which represent the least-squares values of the slopes of the indicated plots. Within experimental error, the ratio $k(N_2)/K(O_2)$ in all three cases is precisely 2.0 (actually, 2.04 ± 0.09, 2.00 ± 0.08, and 1.90 ± 0.06 at 25.0 °C for $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, and $Co(chxn)_3^{3+}$, respectively).

Deuterium isotope effects are negligible. The rate constant for $Co(NH_3)_6^{3+}$ in H_2O as compared to $Co(ND_3)_6^{3+}$ in D_2O is 1.10 ± 0.09. The effects of temperature variation follow the Eyring equation of activated-complex theory. The activation parameters are

complex	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J mol^{-1} K^{-1}
$Co(NH_3)_6^{3+}$	47.2 ± 1.5	−57.8 ± 5.1
$Co(en)_3^{3+}$	44.1 ± 3.0	−70.7 ± 10.5
$Co(chxn)_3^{3+}$	43.4 ± 0.8	−76.2 ± 2.7

The kinetic studies were necessarily restricted to basic solution, because superoxide disproportionates too rapidly in acidic solution. Although the variation of [H^+] was small, only a factor of ca. 4 (pH 11.3–11.9), the rate constant was invariant within the range. This shows that the rate law of eq 3 is correctly formulated and that a conjugate-base pathway is not important.

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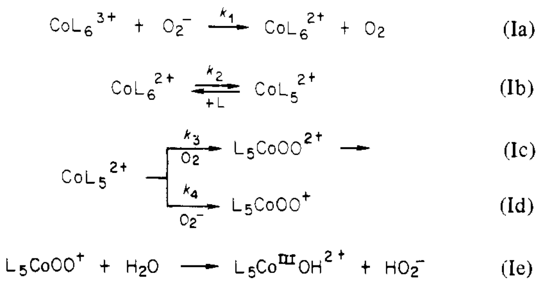
(22) Bakač, A.; Espenson, J. H.; Creaser, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 7624.

(23) (a) Pendin, A. A.; Leont'evskaya, P. K. *Kinet. Katal.* **1976**, *17*, 341. (b) Holecek, J.; Handlir, K.; Klikorka, J.; Dinh Bang, N. *Coll. Czech. Chem. Commun.* **1979**, *44*, 1379.

(24) (a) Teitelbaum, Z.; Meyerstein, D. *Proc. Int. Conf. Coord. Chem. 16th*, **1974**, R56. (b) McDowell, M. S. Ph.D. Thesis, Iowa State University, 1983.

Scheme I



The experimental design required fairly concentrated (>0.1 M) stock solutions of the Co(III) complexes for runs at the higher concentrations. This necessitated the use of chloride salts, since the perchlorate salts are insufficiently soluble. Free chloride ions have no effect on the rate constants as shown by alternative use of both salts in runs with $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$. The background absorbance in the UV is higher when Cl^- is present owing to the formation of highly absorbing but weakly bound ion pairs,[25] although no other effect of substituting Cl^- for ClO_4^- was noted.

Mechanism. The reactions shown in Scheme I are proposed to occur during the reactions of the cobalt(III) complexes with superoxide. The individual reactions, the reasons for including them, and precedents for each follow.

The first reaction, the rate-limiting step under all the conditions examined, is believed to occur by outer-sphere electron transfer. The six-coordinate, 18-electron Co(III) complexes employed are quite inert toward ligand substitution, are not prone to react via seven-coordinate intermediates, and yield products that would not benefit from a close interaction between CoL_6^{2+} and molecular oxygen. The rate constants k_1 are characterized by activation parameters quite typical of those for electron-transfer reactions, with moderate enthaplies of activation ($\Delta H^\ddagger = 43\text{–}47$ kJ mol^{-1}) and substantial negative values of the activation entropies ($\Delta S^\ddagger = -58$ to -76 J mol^{-1} K^{-1}). The electron-transfer rate constants are pH independent (pH 11.3–11.9) and are in addition relatively insensitive to which of the three cobalt–hexaammine complexes was used ($k_1 = 16\text{–}31$ M^{-1} s^{-1} at 25 °C). This can be attributed, in terms of the Marcus equation, to offsetting values of the CoL_6^{3+}/CoL_6^{2+} self-exchange rate constants[26] and reduction potentials.[27-29]

The second step consists of dissociation of a ligand from $Co^{II}L_6^{2+}$ prior to further reactions. In fact, two or even more ligands may dissociate, although for convenience these are not explicity noted in eq Ib. The amine ligands are not completely lost in alkaline solution, however, because of stability constant considerations as well as the known failure of cobalt(II) complexes containing only H_2O/OH^- ligands to react with either O_2 or O_2^-. The evidence for the involvement of one or more such dissociation steps comes from the kinetic effect of O_2, although in a general sense ample precedent for such fast ($>10^6$ s^{-1}) dissociation reactions exists.[30-33]

The twofold lower rate constant obtained in the presence of oxygen, as compared to the value determined under anaerobic conditions, is easily explained by the pair of reactions shown in Scheme I. The Co(II) complex CoL_5^{2+} (or CoL_{6-n}^{2+}) reacts competitively with O_2 or O_2^- (eq Ic and Id). The precisely twofold increase in the rate of superoxide disappearance upon removal of molecular oxygen prior to the reaction is reconciled by this mechanism. The reaction rate when O_2 remains is $-d[O_2^-]/dt = k_1[CoL_6^{3+}][O_2^-]$, whereas it is *twice* that when O_2 has been removed owing to the second O_2^- being consumed in reaction Id.

The only direct reason to involve the pair of reactions (Ic) and (Id) is to explain the change in the kinetic results, with and without O_2. On the other hand, there is ample precedent for both (Ic) and (Id) for closely related Co(II) complexes. The reactions of O_2 with Co(II), which lead to superoxo-, μ-peroxo-, and aquocobalt(III) complexes, have been widely studied.[32a,34,35] The reaction shown in (Ic) is the first step in all cases except those involving encapsulated complexes,[16,22] which is not the case here. The reaction of O_2^- with Co(II) complexes has been directly examined.[36] In cases resembling these, i.e., $[Co^{II}(N_4\text{-mac})(H_2O)_{1\text{ or }2}]^{2+}$, reactions analogous to (Id) are noted.[37] The chemistry of the subsequent reactions of the metastable product of eq Id was not fully resolved, but a logical fate is suggested by eq Ie.

The present work allows a rough inference, from the concentration ranges over which the rate law changes from one form to the other, that the rate constants for steps Ic and Id are of a similar magnitude. Most likely $k_4 = (1\text{–}10)k_3$.

$Fe(C_5H_5)_2^+$. Certain experimental aspects of the ferrocenium ion reduction deserve further comment. The efficient generation of O_2^- requires basic conditions, not simply because it is desirable to prolong the lifetime of O_2^- toward disproportionation[5,6] but also because the generation of O_2^- from its precursor, $HOC(CH_3)_2OO\cdot$, is base catalyzed.[38] The latter factor is not a major consideration with Co(III), where the O_2^- was independently generated.

The result of the spectrophotometric titration of separately prepared O_2^- with $Fe(C_5H_5)_2^+$ is shown in Figure 2. The breakpoint in the titration curve occurs at a ratio of 1.0 ± 0.1. This confirms the 1:1 stoichiometry written in eq 2.

The kinetics experiments were limited to $\lesssim 10^{-4}$ M $Fe(C_5H_5)_2^+$ by such considerations as (a) the necessity to avoid the reaction[24] of $Fe(C_5H_5)_2^+$ with the aliphatic radical $\cdot C(CH_3)_2OH$, whose reaction with O_2 occurs prior to O_2^- formation,[7] and (b) the reaction being monitored at 617 nm, the absorption maximum of $Fe(C_5H_5)_2^+$ reactant,[39] since there is no absorption maximum of $Fe(C_5H_5)_2$ that is suitable for this purpose. Over the concentration ranges 28–104 μM $Fe(C_5H_5)_2^+$ and 4–6 μM initial O_2^-, the pseudo-first-order rate constant is directly proportional to $[Fe(C_5H_5)_2^+]_{av}$. The rate law is thus

$$-d[O_2^-]/dt = k[O_2^-][Fe(C_5H_5)_2^+] \qquad (4)$$

A least-squares analysis of the results gives $k = (8.6 \pm 0.3)$

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(25) King, E. L.; Espenson, J. H.; Visco, R. E. *J. Phys. Chem.* **1959**, *63*, 755.

(26) Geselowitz, D.; Taube, H. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 391.

(27) Bartelt, H.; Skilandat, H. *J. Electroanal. Chem. Interfacial Electrochem.* **1969**, *23*, 407.

(28) Laitinen, H. A.; Kivalo, P. *J. Am. Chem. Soc.* **1953**, *75*, 2198.

(29) Bartelt, H. *J. Electroanal. Chem. Interfacial Electrochem.* **1970**, *25*, 79.

(30) Simic, M.; Lilie, J. *J. Am. Chem. Soc.* **1974**, *96*, 291.

(31) Lilie, J.; Shinohara, N.; Simic, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 6516.

(32) (a) Lilie, J.; Simic, M. G.; Endicott, J. F. *Inorg. Chem.* **1975**, *14*, 2129. (b) Murray, B.; Lincoln, S. F.; Glaeser, H. H.; Dodgen, H. W.; Hunt, J. P. *Inorg. Chem.* **1969**, *8*, 554.

(33) The work referred to acidic solution, but the same should apply at pH 11–12. The low formation constant of $Co(NH_3)_6^{2+}$ should be noted.[26]

(34) Wilkins, R. G. *Adv. Chem. Ser.* **1971**, *No. 100*, 111–134.

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

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

(37) One must distinguish these Co(II) complexes—which are either five-coordinate species or, if six-coordinate, have an extremely labile axial position—from others, most notably $Co(sep)^{2+}$, which react with O_2^- by an entirely different mechanism.[22]

(38) (a) Bothe, E.; Behreus, G.; Schulte-Frohlinde, D. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1977**, *32B*, 886. (b) Ilan, Y.; Rabani, J.; Henglein, A. *J. Phys. Chem.* **1976**, *84*, 1558. (c) Rabani, J.; Klug-Roth, D.; Henglein, A. *J. Phys. Chem.* **1974**, *78*, 2089. (d) Bothe, E.; Schuchmann, M. N.; Schulte-Frohlinde, D.; von Sonntag, C. *Photochem. Photobiol.* **1978**, *28*, 639.

(39) Espenson, J. H.; Pladziewicz, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 56.

Table II. Calculated Values of k_{11} for the O_2/O_2^- Self-Exchange Reaction[a]

oxidant	k_{12}	k_{22}	a_2/Å	K_{eq}	k_{11}[b]	ref
$Fe(CN)_6^{3-}$	2.7×10^2	5×10^3	9.0	9.6×10^8	1.1×10^{-8}	11
$Mo(CN)_8^{3-}$	3.0×10^5	3.0×10^4	10	2.7×10^{15}	8.2×10^{-8}	12
$Fe(C_5H_5)_2^+$	8.6×10^6	5.7×10^6 [c]	4.5	1.1×10^{12}	6.9×10^{-5}	*d*
$Co(sep)^{3+}$	0.87[e]	5.1	9.0	2.0×10^{-2}	1.6×10^{-1}	16
$Ru(NH_3)_4(phen)^{3+}$	3.5×10^9	1.2×10^7	9.0	5.6×10^{11}	1.0	15
$Ru(NH_3)_5(isn)^{3+}$	2.2×10^8	4.7×10^5	9.0	1.9×10^9	5.1	13, 15
$Ru(NH_3)_6^{3+}$	2.0×10^5	4.0×10^3	6.7	3.8×10^3	3.3	15
$Fe^{III}(edta)H_2O^-$	2×10^6	3×10^4 [f]	9.0	5.4×10^4	7.2×10^3	42
$Co(en)_3^{3+}$	2.4×10	2.4×10^{-5} [g]	8.4	4.4×10^{-2}	4.6×10^5	*d, h*
quinones	10^6–10^9	10^7–10^8		10^{-2}–10^{+4}	10^6–10^7	8–10

[a] Rate constants at 25 °C in units of $M^{-1}\ s^{-1}$; standard electrode potentials vs. NHE in volts; K_{eq} calculated by using $E°[O_2(aq)/O_2^-] = -0.16$ V; phen = 1,10-phenanthroline; isn = isonicotinamide; sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane. [b] Calculated from eq 6–8, with appropriate work terms, taking $a(O_2^-) = 2.66$ Å and values or estimates for the metal complexes as shown. [c] References 21 and 39. [d] This work. [e] Calculated from the reverse rate constant and K_{eq}. [f] Reference 43. [g] Reference 41. [h] Values are not cited for $Co(NH_3)_6^{3+}$ owing to the great uncertainty in $E°$ and k_{22} values.[26,33]

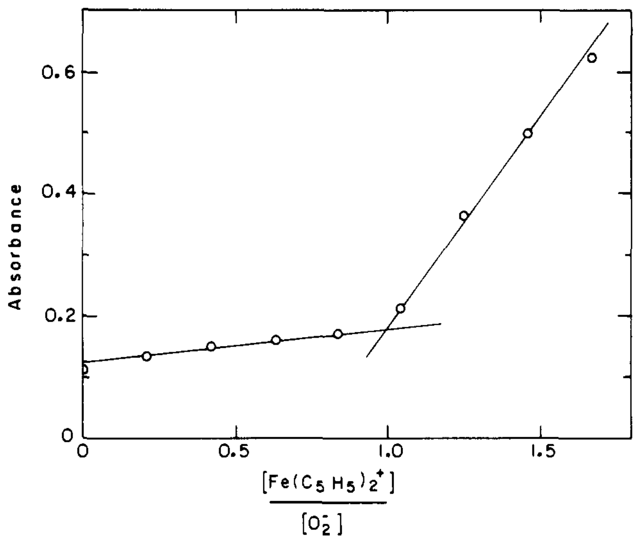

Figure 2. Absorbance changes accompanying the spectrophotometric titration of O_2^- with $Fe(C_5H_5)_2^+$ at 300 nm (2-cm cell).

× $10^6\ M^{-1}\ s^{-1}$ at 25.0 °C in 1.0 M 2-propanol.

The issue of a possible kinetic effect arising from O_2 removal could not be examined for the ferrocenium ion reaction owing to the techniques required and the time scale involved. On the other hand, none is anticipated since these products, oxygen and ferrocene, are stable toward decomposition or further reaction, unlike the cobalt system. Blank experiments also showed that no reaction occurred between O_2^- and ferrocene under these conditions.

No evidence suggests that O_2^- reacts with $Fe(C_5H_5)_2^+$ by any mechanism other than outer-sphere electron transfer. Although "direct" attack at the metal center or on the aromatic ring is conceivable, no data support that formulation, which also seems unlikely given the products formed and the lack of appreciable interaction between ferrocene and molecular oxygen.

O_2/O_2^- Self-Exchange. The Marcus cross-relation (eq 5) has previously been applied to the evaluation of k_{11} for this exchange.[13-15] The present results can be considered in the

$$k_{12} = (k_{11}k_{22}K_{eq}f)^{1/2} \qquad \log f = \frac{(\log K_{eq})^2}{4 \log (k_{11}k_{22}/Z^2)} \tag{5}$$

same fashion, which offers a particularly rewarding prospect since the earlier systems gave such a diversity of results. Because the reactions involve reactants of different charges it is necessary to introduce corrections for work terms; without that, the parameter k_{11} will contain sizable (and nonuniform) differences from case to case. The equations[40] used are

$$\Delta G_{12}^* = \tfrac{1}{2}(\Delta G_{11}^* + \Delta G_{22}^* + \Delta G_{12}^{\ominus} - w_{11} - w_{22} + w_{12} + w_{21}) + \frac{(\Delta G_{12}^{\ominus} + w_{21} - w_{12})^2}{8(\Delta G_{11}^* - w_{11} + \Delta G_{22}^* + w_{22})} \tag{6}$$

$$k = Z \exp(-\Delta G^*/RT) \tag{7}$$

$$w_{ij} = \frac{4.225 \times 10^{-8} Z_i Z_j}{a(1 + 3.285 \times 10^7 a\mu^{1/2})} \tag{8}$$

where a is the distance of closest approach and the other terms have their usual meaning.

The systems for which the necessary kinetic data[8-15,39,41-43] are known are summarized in Table II. The present results for $Co(en)_3^{3+}$ yield $k_{11} = 4.6 \times 10^5\ M^{-1}\ s^{-1}$, as compared to $Fe(C_5H_5)_2^+$, which provides $k_{11} = 6.9 \times 10^{-5}\ M^{-1}\ s^{-1}$. The situation as regards O_2/O_2^- self-exchange is thus no better resolved as a result of this calculation; indeed, the results found for the present systems widen even further the range of values.

The parameters labeled k_{11} clearly cannot represent the O_2/O_2^- self-exchange rate constant, since such inconsistent values are found. Perhaps several of the systems can be disregarded, because the mechanism may not be simple outer-sphere electron transfer. This is not very appealing, however, since in none of the studies was evidence noted for a more complex mechanism.

We thus suggest that other factors may invalidate the application of Marcus theory for the purposes of estimating an intrinsic rate of the O_2/O_2^- self-exchange rate. The superoxide anion is strongly hydrogen bonded in aqueous solution,[44] but the nonpolar oxygen molecule will experience only minimal specific solvation. The activation process accompanying electron-transfer reactions of O_2^- thus differs from those for corresponding reactions of a coordination complex. The reduced and oxidized forms of the latter are substantially similar entities. They interact with the solvent in a similar manner; the reorganization terms for both forms are those envisaged in the original formulation of the model. Thus we suggest that the variance in k_{11} may arise because O_2 and O_2^- differ so

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(40) Stanbury, D. M.; Gaswick, D.; Brown, G. M.; Taube, H. *Inorg. Chem.* **1983**, *22*, 1975.

(41) Dwyer, F. P.; Sargeson, A. M. *J. Phys. Chem.* **1961**, *65*, 1892.

(42) Bull, C.; McClune, G. J.; Fee, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5290.

(43) Wilkins, R. G.; Yelin, R. E. *Inorg. Chem.* **1968**, *7*, 2667.

(44) (a) Fee, J. A.; Valentine, J. S. In "Superoxide and Superoxide Dismutases"; Michelson, A. M.; McCord, J. M.; Fridovich, I., Eds.; Academic Press: New York, 1977; p 29. (b) Fee, J. A. In "Oxygen and Oxy Radicals in Chemistry and Biology"; Rodgers, M. A. J., Powers, E. L. Eds.; Academic Press: New York, 1981; p 206. (c) Hill, H. A. O. In "Oxygen Free Radicals and Tissue Damage"; Elsevier/North Holland: Amsterdam, 1979; p 54. The latter author summarizes matters succinctly "...there is no O_2^- in water, only solvated O_2^-".

greatly in their solvation characteristics. Depending on the local chemical environment of the redox partner, each reaction "prepares for" electron transfer in a different way, particularly as regards the extent of desolvation of $O_2(H_2O)_n^-$. Within a series of chemically similar oxidizing agents, however, consistency is obtained, but not when very diverse substances are considered. Thus the transition states may lie at quite different points along the reaction coordinate. To a first approximation an inverse correlation can be discerned between K_{eq} and the calculated value of k_{11}.

There are a number of other such pairs involving small molecules and their anions for which similar estimates of self-exchange rate constants have been made. These include ClO_2/ClO_2^- (4×10^2 M^{-1} s^{-1}),[45] NO_2/NO_2^- (10^{-2} M^{-1} s^{-1}),[46] and I_2/I_2^- ($\sim 10^2$ M^{-1} s^{-1}).[47,48] Each is derived from kinetic data from only one or two reactions. It is *not* our contention that more inclusive data sets will *necessarily* lead to discrepancies like those for O_2/O_2^-. *On the other hand, it is important to anticipate that such might possibly be the case.* The situation clearly calls for the study of many additional systems of some diversity and for continued caution as to whether such parameters are clearly assignable to the authentic self-exchange reactions.

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Registry No. O_2^-, 11062-77-4; O_2, 7782-44-7; $Fe(C_5H_5)_2^+$, 12125-80-3; $Co(NH_3)_6^{3+}$, 14695-95-5; $Co(en)_3^{3+}$, 14878-41-2; $Co(chxn)_3^{3+}$, 41970-05-2.

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(45) Lednicky, L. A.; Stanbury, D. M. *J. Am. Chem. Soc.* **1983**, *105*, 3098.

(46) Wilmarth, W. K.; Stanbury, D. M.; Byrd, J. E.; Po, H. N.; Chua, C.-P. *Coord. Chem. Rev.* **1983**, *51*, 155–179.

(47) Our estimate is based on published kinetic and equilibrium data for the reaction of $Os(bpy)_3^{3+}$ with I_2^- (Nord, G.; Pederson, B.; Farver, O. *Inorg. Chem.* **1978**, *17*, 2233) and uses a self-exchange rate constant for the osmium complexes which is itself a Marcus-equation estimate made by the same group (Nord, G.; Pedersen, B.; Yan-Lovborg, E.; Pagsberg, P. *Ibid.* **1982**, *21*, 2327). Another estimate for I_2/I_2^- has not been included. It was based on reactions of $Fe^{II}(edta)^{2-}$ (Woodruff, W. H.; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2578), a reaction that is demonstrably inner sphere. Since $IFe^{III}(edta)^{2-}$ and I^- are formed, or at best I_2^- within the coordination shell of the metal, and not free I_2^-, it seems to us unlikely that properties of the latter are calculable from these data.

(48) Values for Br_2/Br_2^- or Cl_2/Cl_2^- self-exchange are also discounted. That from $Fe^{II}(edta)$ is not included for the reason stated above.[47] A second value was based on $Fe(phen)_3^{2+}$ (Ige, J.; Ojo, J. F.; Oloboyide, O. *Can. J. Chem.* **1979**, *57*, 2065), a reaction claimed to proceed by initial outer-sphere electron transfer: $Fe(phen)_3^{2+} + X_2 = Fe(phen)_3^{3+} + X_2^-$. The small equilibrium constant ($\sim 10^{-11}$ for X = Br) requires a very large reverse rate constant ($\sim 10^{11}$ M^{-1} s^{-1}), which not only may exceed the diffusion-controlled limit but also is likely to cause the subsequent reaction steps to influence the kinetic measurements, a point that was not included in analysis of the published kinetic data.

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Solid-State Kinetic Parameters for the Deaquation–Anation of the Tetracyanonickelate(II), Tetracyanopalladate(II), and Tetracyanoplatinate(II) of Aquopentaamminecobalt(III). Influence of the Metal–Metal Interactions on the Platinum Complex

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Three new dinuclear complexes of (μ-cyano)(tricyanometal(II))pentaamminecobalt(III), metal(II) being nickel, palladium, and platinum, have been obtained by solid-state reaction of the tetracyanometalate(II) of aquopentaamminecobalt(III). This solid-state deaquation–anation has been studied by thermogravimetric measurements under both nonisothermal and isothermal conditions. The activation energies so obtained are 117.4 ± 6 kJ/mol for the Ni compound, 131.0 ± 5 kJ/mol for the Pd compound, and 66.7 ± 1 kJ/mol for the Pt compound. These values are found on the basis of the agreement between nonisothermal and isothermal methods, by applying the expressions for the solid-state models (growth, nucleation, nucleation–growth, and diffusion). The marked difference in the kinetic parameters between the Ni and Pd compounds and the Pt compound may be explained in terms of Pt–Pt association in the crystal lattice, which causes distortions and allows water molecules to escape easily from the crystal structure. For this reason and because of the low values of activation energy, an S_N1 dissociative mechanism is proposed with an activated complex of square-based-pyramidal geometry. The Pt–Pt interactions are shown in the electronic spectrum by the appearance of a very strong band at about 355 nm in the solid state, which does not belong to the parent compounds. The Pt–Pt interaction is also found in solution by the appearance of new bands at about 300 and 330 nm, which do not follow Beer's law. We attribute these new bands to the oligomeric association of the dinuclear cations. The conductivity measurements in the solid state for the Pt compound also indicate its special behavior, which may be explained in terms of Pt–Pt interactions that remove the Pt–Pt symmetrical packing typical of many cyano compounds of platinum(II).

Introduction

In the literature there are a great number of papers on the kinetic parameters of aquoamine complexes of cobalt(III).[1] Focusing our interest only on the kinetics of the deaquation–anation of the reaction

$$[Co(H_2O)(NH_3)_5]X_3(s) \rightarrow [Co(X)(NH_3)_5]X_2(s) + H_2O(g)$$

we find that there is a poor agreement in kinetic parameters reported in the literature, as has been indicated by LeMay.[2]

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(1) (a) Wendlandt, W. W.; Bear, J. L. *J. Phys. Chem.* **1961**, *65*, 1516. (b) Mori, R.; Tsuchiya, R.; Okano, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 1029. (c) Tsuchiya, R.; Omote, M.:; Uehara, A.; Kyuno, E. *Ibid.* **1976**, *49*, 1027. (d) Smith, J. P.; Wendlandt, W. W. *Nature (London)* **1964**, *201*, 291. (e) Wendlandt, W. W.; D'Ascenzo, G. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3404.

(2) LeMay, H. E.; Babich, M. W. *Thermochim. Acta* **1981**, *48*, 147.

0020-1669/84/1323-2236$01.50/0