

cury electrode polarogram of a freshly reduced solution of 12-molybdocerate in 1.0 M sulfuric acid showed no further reductions prior to -0.1 V, at which point a complex multi-electron process occurred, and (2) the absence of an intense $\text{Mo}^{\text{V}} \rightarrow \text{Mo}^{\text{VI}}$ intervalence transition (observed in all mixed-valence molybdates at 800–1000 nm¹⁶). Direct spectroscopic observation of Ce(III) is difficult owing to the weakness and position of the $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition (ca. 2250 cm⁻¹). A considerable, but unsuccessful, effort was made to detect this transition in the solids described above using Nujol mulls (at ambient and liquid nitrogen temperatures), KBr disks, and attenuated total reflectance of undiluted powdered material. In every case residual OH absorption obscured the region of interest. The observed transition at 450 nm in the spectrum of the freshly reduced solution can be assigned as a $\text{Ce}^{\text{III}} \rightarrow \text{Mo}^{\text{VI}}$ charge transfer, and its position and intensity are consistent with the arguments presented in the introduction.

There remains the discrepancy between our spectrum and that reported by Peacock and Weakley. Although these workers determined the reduction potential by stannous chloride titration, the spectral measurements were made on material that had been prepared by electrolysis of a neutral solution using a mercury cathode.¹⁷ The potential was unspecified and presumably uncontrolled. Since we have observed that molybdocerate(III) solutions are unstable and that the reduction of molybdocerate(IV) becomes less and less reversible as the pH is raised, it seems probable that the material examined by Peacock and Weakley did not contain the 12-molybdocerate(III) anion. We have not examined this further but have noted that if 1 equiv of SnCl_2 is added to 12-molybdocerate(IV), the resulting solution has the color and spectrum of 12-molybdocerate(III) as reported here. Addition of excess Sn(II) caused the color of the solution to darken, and such solutions showed no voltammogram characteristic of 12-molybdocerate.¹⁸

Experimental Section

Ammonium 12-molybdocerate was prepared by the method of Baker, *et al.*⁴. Anal. Calcd for $(\text{NH}_4)_6\text{H}_2\text{CeMo}_{12}\text{O}_{42} \cdot 9\text{H}_2\text{O}$: N, 3.76; Mo, 51.50; $\text{H}_2\text{O} + \text{NH}_3$, 14.23. Found: N, 3.26; Mo, 51.74; $\text{H}_2\text{O} + \text{NH}_3$, 14.70. Voltammetric measurements were made with wax-impregnated graphite and rotating platinum electrodes (wige and rpe) as described elsewhere.¹¹ Cary 14 and Perkin-Elmer 225 instruments were used for optical and vibrational spectroscopy. Electron spin resonance measurements were made on powdered samples of the reduced compound at 77°K using a JEOL MES-3X spectrometer. X-Ray powder diffraction was carried out as described elsewhere.¹⁹

Acknowledgments. We are grateful to Drs. T. J. R. Weakley and R. D. Peacock for supplying unpublished details of their work and for other helpful correspondence; to Dr. T. H. Siddall, III, for first drawing our attention to the paucity of direct spectral measurements of the Ce(III) f-f transition and thereby providing a further reason to reexamine the molybdocerate reduction; and to AFOSR for support of this work through Grant AF 70-1833.

Registry No. Ammonium 12-molybdocerate(IV), 12185-82-9; 12-molybdocerate(III) anion, 39465-42-4.

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Kinetics of the Permanganate Ion-Potassium Octacyanomolybdate(IV) Reaction

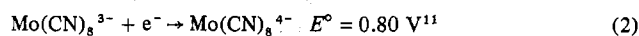
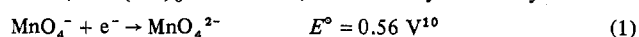
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Received May 8, 1973

The reactions of multiequivalent oxidizing reagents have stimulated the interest of chemical researchers for some time. Espenson has presented a review of the reaction of the chromate ion, CrO_4^{2-} , with a number of inorganic ions.¹ He showed the variety of reaction pathways and the mechanistic implications of the rate laws. The permanganate ion, MnO_4^- , like CrO_4^{2-} , is a multielectron-transfer reagent that has been extensively utilized in analytical chemistry for its oxidizing capacity with both organic and inorganic substances. The bulk of information concerning the mechanistic behavior of permanganate ion oxidations has been provided by organic systems.² Inorganic ions have found only limited examination. One such attempt by Rosenheim,³ the oxidation of potassium octacyanomolybdate(IV), $\text{K}_4\text{Mo}(\text{CN})_8$, by potassium permanganate, KMnO_4 , was complicated by the photosensitivity of the oxidation product, potassium octacyanomolybdate(V), $\text{K}_3\text{Mo}(\text{CN})_8$. The reaction product is easily reduced in light back to $\text{Mo}(\text{CN})_8^{4-}$.^{4,5}

The permanganate ion, unlike Ce(IV), is capable of reacting *via* one- or two-electron pathways and the reaction of MnO_4^- with $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{phen})_3^{2+}$ has been studied in an attempt to detect the existence of a two-electron step in the pathway. The study of the oxidation by Ce(IV) of a variety of iron(II)-phenanthroline complexes by Dulz and Sutin⁸ showed the existence of a common mode of reaction. It would be of interest to obtain information on a reaction system in which the free energy of reaction, ΔG° , varies over a wider range.

The $\text{Mo}(\text{CN})_8^{4-}$ ion was chosen since both it and MnO_4^- are kinetically inert complexes, allowing the application of Marcus' theory,⁹ and because the one-electron reduction pathway of the permanganate ion by $\text{Mo}(\text{CN})_8^{4-}$, unlike the MnO_4^- - $\text{Fe}(\text{CN})_6^{4-}$ reaction, is thermodynamically unfavor-



able. However, the 2-equiv reduction of the permanganate ion ($\text{MnO}_4^- + 2e^- \rightarrow \text{MnO}_4^{3-}$) is favorable, as it is in the MnO_4^- - $\text{Fe}(\text{phen})_3^{2+}$ system.

Experimental Section

$\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ was prepared by the method of Van der Poel

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(11) R. J. Campion, N. Purdie, and N. Sutin, *Inorg. Chem.*, **3**, 1091 (1964).

and Neumann.¹² The light yellow powder was prepared and handled under red light due to its photosensitivity and was analyzed spectrophotometrically (λ_{\max} 368 nm, ϵ 170 M^{-1} cm^{-1}).^{4,13} A stock solution of potassium permanganate was prepared by dissolving Baker Analyzed reagent grade KMnO_4 in distilled water, boiling the solution, and standardizing against As_2O_3 after a fine glass frit filtration to remove the MnO_2 . This solution was stored in a dark bottle away from light and restandardized periodically. No decomposition was observed over a 5-month period.

Perchloric acid solutions were prepared by the dilution of reagent grade concentrated HClO_4 with ion-exchanged permanganate-distilled water. The stock solutions were standardized against NaOH solutions. Stock solutions of sodium perchlorate were prepared by the addition of recrystallized reagent grade Na_2CO_3 to perchloric acid solutions of known concentration. The remaining hydrogen ion concentration was determined by titration against NaOH .

Kinetic Studies. The kinetics of the reaction were determined using an Aminco-Morrow stopped-flow apparatus attached to a Beckman DU monochromator. The progress of the reaction was monitored at 526 nm where MnO_4^- is the only absorbing species and was displayed on a Tektronix Model 564 storage-type oscilloscope. The stored trace was recorded with a Polaroid camera. Apparent first- and second-order rate constants were calculated from absorbance-time data using a linear least-squares program that minimizes the sum of the squared deviations between calculated and observed points.

The solutions of $\text{Mo}(\text{CN})_8^{4-}$ were prepared by weight; MnO_4^- solutions, by dilution from stock just prior to use. All solutions were checked spectrophotometrically after being diluted to volume with HClO_4 - NaClO_4 solutions such that $\mu = 1.00$. Red light conditions were used to prevent photolysis of $\text{Mo}(\text{CN})_8^{4-}$. For accurate temperature control ($\pm 0.02^\circ$), the reaction cell was attached to a thermostated stage.

Results and Discussion

The overall stoichiometry of the reaction between MnO_4^- and $\text{Mo}(\text{CN})_8^{4-}$ can be represented by



Spectro-titrimetric plots at different wavelengths of absorbance vs. $[\text{MnO}_4^-]$ for several different initial $\text{Mo}(\text{CN})_8^{4-}$ concentrations showed breaks corresponding to a $\text{Mo}(\text{CN})_8^{4-}$: MnO_4^- mole ratio of 5.01 ± 0.03 .

Spectral scans showed only the presence of $\text{Mo}(\text{CN})_8^{3-}$ as an absorbing reaction product based on the amount of MnO_4^- added, spectral change of $\text{Mo}(\text{CN})_8^{4-}$ envelope, and agreement with absorption maxima and extinction coefficients. Scans of solutions containing excess MnO_4^- were taken immediately after mixing to prevent interference from the MnO_4^- - $\text{Mn}(\text{II})$ reaction.

All of the kinetic data were obtained using excess $\text{Mo}(\text{CN})_8^{4-}$ to minimize possible further reaction of the $\text{Mn}(\text{II})$ produced with the excess MnO_4^- . The reaction was studied under both pseudo-first-order and second-order conditions.

All of the data could be represented by the second-order rate law

$$-d[\text{MnO}_4^-]/dt = k_{\text{obsd}} [\text{MnO}_4^-] [\text{Mo}(\text{CN})_8^{4-}]$$

The integrated form of the rate law was used where

$$k_{\text{obsd}} \gamma t = \ln [(5A - \epsilon' \gamma)/A] + I$$

and $\gamma = [\text{Mo}(\text{CN})_8^{4-}]_0 - 5[\text{MnO}_4^-]_0$, $A = A_t - A_\infty$ (A = absorbance values), $\epsilon' = \epsilon(\text{MnO}_4^-) + 5\epsilon(\text{Mo}(\text{IV}))$, and I = constant of integration. Individual runs under second-order conditions showed no apparent deviation from simple second-order behavior for more than 90% of the reaction.

The values for the observed rate constants at 22.5° for

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various initial concentrations of MnO_4^- and $\text{Mo}(\text{CN})_8^{4-}$ are shown in Table I.

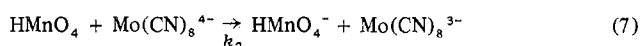
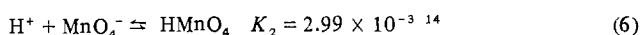
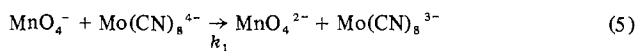
The concentration of products had no effect on the observed rate constant, as determined from the experiments containing added $\text{Mo}(\text{CN})_8^{3-}$ and from the adherence to simple second-order kinetics at long time when the buildup of the concentrations of both $\text{Mo}(\text{CN})_8^{3-}$ and $\text{Mn}(\text{II})$ is appreciable.

The hydrogen ion dependence of the reaction was investigated and k_{obsd} was found to be related linearly to $[\text{H}^+]$. A least-squares fit of the data in Table II yields an equation of the form

$$k_{\text{obsd}} = k_1 + k_2 [\text{H}^+] \quad (4)$$

The values of $k_{\text{obsd}} \times 10^{-3} M^{-1} \text{sec}^{-1}$ are 2.85, 3.16, 3.68, 3.76, 6.70, and 9.28 at 18.5, 19.5, 21.4, 22.5, 31.65, and 36.4° , respectively. From these values can be calculated $\Delta H_{\text{obsd}}^\ddagger = 10.8 \pm 0.5 \text{ kcal/mol}$ and $\Delta S_{\text{obsd}}^\ddagger = -5.6 \pm 1.4 \text{ eu}$.

The linear dependence of k_{obsd} on $[\text{H}^+]$ and the nonzero intercept suggest that two pathways are available for the reduction process. The reaction sequence can be represented by the equations



It is one in which the one-electron reduction of the permanganate ion (eq 5) is unfavored thermodynamically and the predominating pathway under the experimental conditions is viewed in terms of a reduction between the protonated permanganate ion, HMnO_4 ,¹⁵ and $\text{Mo}(\text{CN})_8^{4-}$. The observed expression, where rate = $(k_1 + k_2'K_2[\text{H}^+])[\text{MnO}_4^-][\text{Mo}(\text{CN})_8^{4-}]$ and k_1 and k_2' are $2.67 \times 10^2 M^{-1} \text{sec}^{-1}$ and $1.68 \times 10^7 M^{-1} \text{sec}^{-1}$ (22.5°), respectively, is typical of many outer-sphere reactions.

An estimate of the half-cell potential ($\text{HMnO}_4 + e^- \rightarrow \text{HMnO}_4^-$) of 1.3 V has been made in the MnO_4^- - $\text{Fe}(\text{phen})_3^{2+}$ reaction.⁷ While the reaction was studied in sulfate as opposed to perchloric media, the general trend to a higher formal potential for the protonated form should be applicable. It can be seen from the magnitude of the rate constants, k_1 and k_2' , for this reaction, and for the MnO_4^- - $\text{Fe}(\text{phen})_3^{2+}$ reaction ($k_1 = 6.1 \times 10^3 M^{-1} \text{sec}^{-1}$ and $k_1' = 2.4 \times 10^8 M^{-1} \text{sec}^{-1}$) that protonation of the MnO_4^- ion makes the one-electron step favorable both kinetically and thermodynamically.

The experimental value of k_2' ($1.87 \times 10^7 M^{-1} \text{sec}^{-1}$, 25.0°) may be compared with that obtained on the basis of Marcus' theory,⁹ $2.39 \times 10^7 M^{-1} \text{sec}^{-1}$. The theory correlates the rates of oxidation-reduction reactions occurring by outer-sphere type mechanisms with the rates of electron exchange for the component reactions and the resultant driving force for the reaction. The Marcus relation can be given by the expression

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2}$$

where

$$\ln f = (\ln K_{12})^2 / [4 \ln (k_{11}k_{22}/Z^2)]$$

k_{12} is the observed rate constant of the redox reaction, k_{11}

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Table I. Rate Constants for the MnO_4^- - $\text{Mo}(\text{CN})_8^{4-}$ Reaction (22.5°, $[\text{H}^+] = 0.065 M$, $\mu = 1.00$)

$10^5 [\text{MnO}_4^-]_0, M$	$10^5 [\text{Mo}(\text{CN})_8^{4-}]_0, M$	$10^6 [\text{Mo}(\text{CN})_8^{3-}]_0, M^a$	$k'_{\text{obsd}}, \text{sec}^{-1}$	$10^{-3} k_{\text{obsd}}, M^{-1} \text{sec}^{-1}$
22.6	453			3.70
13.3	453	7.00		3.68
3.38	313		12.2	3.90
2.83	313		11.8	3.79
26.6	246			3.62
4.44	246	5.00	9.18	3.73
13.30	107			3.78
6.66	107	5.00		3.78
4.44	107			3.67
6.66	91			3.77
4.44	91			3.93
				Av 3.76 (± 0.09)

$$^a [\text{Mn(II)}]_0 = [\text{Mo}(\text{CN})_8^{3-}]_0/5.$$

Table II. Dependence of the Rate Constant on Hydrogen Ion Concentration (22.5°, $\mu = 1.00$, $[\text{MnO}_4^-]_0 = 6.66 \times 10^{-5} M$, $[\text{Mo}(\text{CN})_8^{4-}]_0 = 3.56 \times 10^{-3} M$)

$[\text{H}^+], M$	$10^{-3} k_{\text{obsd}}, M^{-1} \text{sec}^{-1}$	$[\text{H}^+], M$	$10^{-3} k_{\text{obsd}}, M^{-1} \text{sec}^{-1}$
0.016	0.91	0.084	4.51
0.029	1.79	0.099	5.48
0.046	2.38	0.124	6.18
0.052	2.63	0.126	6.15
0.065	3.75	0.226	11.75
0.075	4.14		

$$^a k_{\text{obsd}} = [267 (\pm 12)] + [5.02 (\pm 0.08)] \times 10^4 [\text{H}^+].$$

(HMnO_4 - HMnO_4^- , $1.10 \times 10^3 M^{-1} \text{sec}^{-1}$) and k_{22} ($\text{Mo}(\text{CN})_8^{3-}$ - $\text{Mo}(\text{CN})_8^{4-}$, $3 \times 10^4 M^{-1} \text{sec}^{-1}$)¹¹ are the electron-exchange rate constants for the component couples, K_{12} is the equilibrium constant for the redox reaction, and Z is the collision frequency for the uncharged species ($10^{11} M^{-1} \text{sec}^{-1}$). The agreement is seen as additional evidence that the reaction is of an outer-sphere type.^{10,16,17}

A least-squares fit of $\ln(k_{\text{obsd}}/T)$ vs. $1/T$ was used to obtain the activation parameters. Since k_1 , the unprotonated pathway, makes only a small contribution to the observed rate constant, the values of $\Delta H^\ddagger = 10.8 \text{ kcal/mol}$ and $\Delta S^\ddagger = -5.6 \text{ eu}$ closely approximate the values of k_2 , the protonated pathway. Since $k_2 = k_2' K_2$, then $\Delta H_{\text{obsd}}^\ddagger = \Delta H^\ddagger(k_2') + \Delta H^\circ(K_2)$ and $\Delta S_{\text{obsd}}^\ddagger = \Delta S^\ddagger(k_2') + \Delta S^\circ(K_2)$. Using values approximated from the perchlorate ion¹⁸ for $\Delta H^\circ(K_2)$ and $\Delta S^\circ(K_2)$ and corrected for S° differences, $\Delta H^\ddagger(k_2')$ and $\Delta S^\ddagger(k_2')$ values become 8.3 kcal/mol and $+2.1 \text{ eu}$, respectively. These values when compared to those obtained for the MnO_4^- - $\text{Fe}(\text{CN})_6^{4-}$ reaction in the low-pH region show similar values of ΔH^\ddagger but significantly more positive values for ΔS^\ddagger . This may stem from the $\text{Fe}(\text{CN})_6^{4-}$ reaction having been studied in phosphate media and a smaller degree of ion pairing in perchlorate media or it may be a reflection of the rather low coulombic contribution to the entropy of activation, since the reaction is between a neutral species and a negatively charged anion.

It appears that while the two-electron pathway for the reduction of the permanganate ion is favorable thermodynamically for the reaction of MnO_4^- with both $\text{Fe}(\text{phen})^{2+}$ and $\text{Mo}(\text{IV})$ ions, the pathway is kinetically inaccessible. This may reflect the need, as presented by Gordon and Ondrus,¹⁹ for ligand exchange on the reductant to occur and the subsequent association of the oxidant into the

Table III. Dependence of Free Energy of Activation upon Free Energy of Reaction with Permanganate

Reductant	E° (reductant), V	ΔG° , kcal/Mol	ΔG^\ddagger , kcal/Mol	Ref
$\text{Fe}(\text{CN})_6^{4-}$, ³⁺	-0.36	-5.08	+10.2	6
$\text{Mo}(\text{CN})_8^{4-}$, ³⁻	-0.80	+5.35	+7.7	This work
$\text{Fe}(\text{phen})_3^{2+}$, ³⁺	-1.06	+11.08	+5.9	7

inner coordination sphere of the reductant for a "simultaneous" two-electron transfer to occur. The oxidations of I^- ,²⁰ CN^- ,²¹ Cl^- ,²² and $(\text{NH}_3)_5\text{CoO}_2\text{CH}^{2+}$,^{23,24} by MnO_4^- have been interpreted in terms of complex formation between the Mn(VII) species and reductant with the subsequent formation of a Mn(V) species. Many organic substrate-permanganate reactions have also been characterized as two-electron-transfer processes preceded by complex formation.²

A plot of ΔG^\ddagger vs. ΔG° for the one-electron reduction of the permanganate ion ($\text{Mn(VII)} \rightarrow \text{Mn(VI)}$) by three complex ions follows a linear free energy relationship (Table III).^{8,17,25}

Such agreement, while not in itself indicative of an outer-sphere mechanism, as is the probable situation with the $\text{S}_2\text{O}_8^{2-}$ reaction with a variety of $\text{Fe}(\text{phen})_3^{2+}$ complexes,²⁶ does point to a common mode of reaction. Such a mechanism, when viewed in light of the agreement of the experimental and calculated rate constants, approximates the "outer-sphere" type reaction.

Both the $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Mo}(\text{CN})_8^{4-}$ species are capable of ion-pair formation. The experimental results do not distinguish between a possible $\text{NaMo}(\text{CN})_8^{3-}$ ion pair and the free complex ion in that ionic strength variations show only a slight rate enhancement. The small cation may be incorporated into the $\text{Mo}(\text{CN})_8^{4-}$ envelope and lose its identity or may be no more effective than a proton in terms of a cation bridge.

Acknowledgments. The authors wish to acknowledge partial support of the research under a COSIP grant and an Eastern Michigan University Faculty Research grant. L. T.

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received support as a National Science Foundation Undergraduate Summer Research participant.

Registry No. $\text{Mo}(\text{CN})_6^{4-}$, 17923-49-8; $\text{Mo}(\text{CN})_6^{3-}$, 17845-99-7; MnO_4^- , 14333-13-2; Mn^{2+} , 16397-91-4.

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Interaction of Oxygen with the Cobalt(II)-Histidine Complex in Strongly Basic Solution

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Received June 4, 1973

Cobalt(II) ions can coordinate with two molecules of L-histidine to form an octahedral complex in which each ligand is tridentate both in solution¹ and in the solid state.² The complex reacts rapidly with oxygen in solution to form $\text{Co}_2(\text{his})_4\text{O}_2$ (his = histidine), almost certainly a binuclear complex containing an $-\text{O}-\text{O}-$ bridge.³ The kinetics of the reversible interaction of O_2 with the cobalt(II) complex in aqueous solution have been investigated.⁴ These are consistent with a two-step mechanism *via* the formation of a 1:1 Co- O_2 species, which is present, however, only in undetectable concentrations. The 2:1 oxygen adduct picks up more O_2 only very slowly to give a mixture of cobalt(III) mononuclear products.⁵

The addition of base to $\text{Co}(\text{L-his})_2$ produces a blue solution as soon as the pH reaches around 11.5. This was apparently first noted by McDonald and Phillips,¹ who examined the pmr of the blue solution. They concluded that there had been ionization of the proton at the 3-nitrogen position of the imidazole rings with the concomitant formation of a tetrahedral 2:1 histidine-cobalt(II) complex, with the four nitrogen binding and detachment of the carboxylate groups. Subsequent examination of cobalt(II)-histidine solutions from pH ~ 10 to 1 M OH^- indicated that the spectra cannot be interpreted simply in terms of an equilibrium between one octahedral and one tetrahedral species.^{6,7} However, one species with a violet color is fully developed in solutions 1 M in NaOH ^{6,7} and although it is not possible to establish the equivalents of protons lost per cobalt(II), the spectrum strongly suggests that it is a tetrahedral complex with four nitrogen donor atoms,⁷ and we shall refer to it as such. The tetrahedral, like the octahedral form, picks up O_2 also and turns brown.^{1,6,7,8} The stoichiometry of the oxygenation is $\text{Co}:\text{O}_2 = 2:1$, but the product has markedly different

spectral characteristics from that obtained from the octahedral form.⁸ It has only a single strong absorption maximum at 366 nm, whereas the oxygenated octahedral cobalt(II) complex (pH ~ 10) shows bands at 385 and 329 nm.⁸ This difference is attributed to the formation of a double O_2 -OH-bridged product from the tetrahedral and a single O_2 -bridged product from the octahedral starting material.⁷ In this note we report on the kinetics of O_2 uptake by the tetrahedral species in 1 M hydroxide solution, as well as brief examination of some other amino acid and peptide complexes.

Experimental Section

Materials. All chemicals were reagent grade. The L-histidine was supplied by Nutritional Biochemicals. Cobalt(II) solutions were standardized by titration with EDTA using murexide indicator.

Kinetic Experiments. The formation of the oxygenated histidine complex was followed spectrophotometrically using a Lucite stopped-flow apparatus. The optical density increases at 360–380 nm gave rate constants for the fast reaction which were identical with those obtained from the smaller optical density increase at ~ 475 nm. The slower second step in the reaction was followed by observing the subsequent slow decrease in optical density at 475 nm. The reactions were initiated in most cases by mixing a deoxygenated solution of cobalt(II), L-histidine, and either NaOH or KOH with a solution containing oxygen. Reactions were run both with 1 M OH^- in each syringe and with 2 M OH^- in the aqueous oxygen solution. At the low cobalt(II) concentrations necessary for observing the reaction using stopped-flow techniques a large excess of histidine was essential in order to prevent formation of cobalt-hydroxy species before the reaction with oxygen could be completed. Runs with low histidine:Co(II) ratios were achieved by allowing a low-pH solution of histidine and cobalt(II) to react with a solution containing oxygen and the desired concentration of OH^- . Solutions with NaOH and KOH as base gave identical results. Most kinetic runs were at a total $[\text{OH}^-]$ of 1.0 M but some runs at $[\text{OH}^-]$ up to 2.0 M indicated only a small rate dependence upon the OH^- concentration. No attempt was made to control ionic strength in these $\geq 1.0\text{ M}$ solutions. In the kinetic runs the concentration of Co(II) complexes was ≥ 10 times that of O_2 and pseudo-first-order rates were obtained. The kinetics of O_2 uptake by other cobalt(II) complexes were followed spectrally at appropriate wave lengths.

Results and Discussion

Our first experiments were carried out using a twofold ratio of histidine: Co^{2+} in 1 M OH^- concentration. It was usually difficult to maintain a homogeneous solution long enough to study the reaction with oxygen, when using the low cobalt(II) concentrations necessary to obtain reaction times within the stop-flow range. By mixing the cobalt(II)-histidine solution at low pH with O_2 - 2 M KOH or NaOH , the reaction, however, could be studied, the octahedral-tetrahedral conversion having been checked to be complete within mixing. In the ranges of $[\text{Co(II)}] = 1\text{--}44\text{ mM}$, $[\text{histidine}] = 2\text{--}88\text{ mM}$, and $[\text{KOH}] = 1.0\text{ M}$ the oxygenation was strictly second order at 25° , $k = 1.8 \pm 0.2 \times 10^3\text{ M}^{-1}\text{ sec}^{-1}$ (Table I). Only one reaction step was observed although a subsequent slower reaction (see below) may have been masked by precipitation.

When we used histidine: Co^{2+} ratios $>2:1$, it was easier to maintain dilute solutions of reactants, but then we found the surprising result that there was a marked dependence of the second-order rate constant associated with a fast step on the concentration of free histidine (Figure 1). The full rate law is shown in (1), where $^*\text{Co}(\text{his})_2$ represents the tetrahedral

$$\text{rate} = k_{\text{obsd}}[\text{O}_2] = k_1[^*\text{Co}(\text{his})_2][\text{O}_2] + k_2[^*\text{Co}(\text{his})_2][\text{his}][\text{O}_2] \quad (1)$$

species which is considered completely formed in 1 M OH^- . At 25° and $I = 1.0\text{ M}$, $k_1 = 1.8 \times 10^3\text{ M}^{-1}\text{ sec}^{-1}$ and $k_2 = 2.2 \times 10^6\text{ M}^{-2}\text{ sec}^{-1}$ (see Table I). In the experiments where excess histidine was used, it was easy to see, even visually, an

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