interelectronic repulsions and pairing energy requirements that result upon one-electron reduction of I and partial occupation of this orbital. Further reduction to the $[Mo_4O_{10}(C_6H_2O_4)_2]^{4-}$ state fully occupies this level, and no transitions are observed. Similar features in the 590-720-nm region of III also disappear upon two-electron reduction and may be ascribed to transitions involving the electroactive ligand orbital.

Conclusions. The exploitation of polyoxoanions soluble in organic solents allows the isolation of novel oxomolybdate complexes. The chemistry of oxomolybdates with polyhydroxybenzene and polyhydroxyquinone ligands reflects solvent, counterion, and stoichiometry influences.

The complexes I, III, and IV are structurally similar, with two or three $[Mo_2O_5]^{2+}$ units serving to hold the two semiquinone planes in a parallel staggered orientation with short interplanar distances. A major consequence of the overlap of ligand orbitals is significant charge delocalization, facilitating redox chemistry and resulting in a number of readily accessible redox states.

Acknowledgment. This research was supported by NSF Grant CHE8514634.

Supplementary Material Available: Tables S1, S6, S10, and S15, listing bond lengths for I-IV, Tables S2, S7, S11, and S16, listing bond angles for I-IV, Tables S3, S8, S12, and S17, listing anisotropic temperature factors for I-IV, Tables S4, S13, and S18, listing calculated H atom positions, and Table S20, summarizing the crystal data and data collection methods (13 pages); Tables S5, S9, S14, and S19, listing calculated and observed structure factors (52 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Brandeis University, Waltham, Massachusetts 02254

Kinetics and Mechanism of the Oxidation of Hexacyanoferrate(II) by Bromate[1]

Gyula Rábai[2] and Irving R. Epstein*

Received July 12, 1988

The kinetics of the reaction between $Fe(CN)_6^{4-}$ and BrO_3^- have been studied spectrophotometrically in the pH range 3.6-5.8. A mechanism is proposed in which the active species is $Fe(CN)_5H_2O^{3-}$. The mechanism accounts for the observed complex kinetics, including the dependence on reactant concentrations and the effects of light. Numerical simulations with this mechanism give excellent agreement with the experimental results.

Introduction

A recent paper in this series on the systematic design of chemical oscillators reported the occurrence of high-amplitude (pH = 3 to pH = 7) oscillations in the unbuffered reaction of bromate, sulfite, and hexacyanoferrate(II) in a flow reactor (CSTR).[3] This oscillatory system consists of two overall component reactions. First, in a relatively slow, Landolt type, autocatalytic reaction, sulfite is oxidized by bromate, and hydrogen ions are liberated:

$$3HSO_3^- + BrO_3^- \rightarrow 3SO_4^{2-} + Br^- + 3H^+ \tag{1}$$

The second reaction is the bromate oxidation of ferrocyanide, which consumes hydrogen ions:

$$BrO_3^- + 6Fe(CN)_6^{4-} + 6H^+ \rightarrow Br^- + 6Fe(CN)_6^{3-} + 3H_2O \tag{2}$$

The kinetics of the latter reaction have been studied by Birk and Kozub,[4] and the reaction was found to be partially autocatalytic. Their investigations were carried out at a relatively high acidity ($[H^+]$ = 0.05-0.5 M), and the autocatalytic behavior was attributed to the bromine formed in the reaction

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \tag{3}$$

The bromate-bromide reaction is relatively rapid because of the high acid concentration, and its rate increases with accumulation of bromide ion from step 2. The bromine-hexacyanoferrate(II) reaction has also been shown to be very fast.[4]

If we extrapolate Birk and Kozub's results to the higher pHs of interest in the oscillatory system, the rate of the bromate-hexacyanoferrate(II) reaction becomes independent of pH when pH > 3, and its value is too high to allow oscillation in the BrO_3^--SO_3^{2-}-$Fe(CN)_6^{4-}$ system.[3] Our preliminary experiments showed that the rate depends on the pH, and its value is not as high as expected from Birk and Kozub's results when pH > 3. Consequently, extrapolation of their rate law to lower acidities is not possible.

No other investigations of this reaction appear in the literature. In order to obtain relevant kinetic data for modeling the oscillatory reaction, it is therefore necessary to study the kinetics of the bromate oxidation of hexacyanoferrate(II) under the conditions in which the oscillations occur. In this paper we report such a kinetic study.

The reducing agent hexacyanoferrate(II) plays a role in many mechanistic investigations but in only a few with other oxyhalogen ions, notably with iodate[5,6] and chlorite.[7] A kinetics study of the oxidation of $Fe(CN)_6^{4-}$ by chlorite has been carried out in buffered aqueous solutions at pH 5-7, with $Fe(CN)_6^{4-}$ in excess. This pH range is very close to the one we used, but we have studied the oxidation of hexacyanoferrate(II) in an excess of oxidant.

Experimental Section

Materials. Chemicals used were, where possible, commercial products. All were used without further purification. Aqueous solutions of hexacyanoferrate(II) ion are stable if kept in the dark or in weak diffuse light under argon. There is only a slow aquation reaction, which leads to an equilibrium between the hexacyanoferrate(II) and pentacyanoaquoferrate(II) complexes. Kinetic runs performed with freshly prepared stock solutions of hexacyanoferrate(II) showed some irreproducibilities. It was therefore necessary to leave these solutions overnight at room temperature, under argon, in the dark before use.

Sodium pentacyanoaquoferrate(II) was prepared from pentacyanonitrosylferrate(II) using Hofmann's method[8] as modified by Asperger et al.[9] The stock solution of pentacyanoaquoferrate(II) was prepared with deoxygenated water and was used within 30 min of preparation. Its concentration was determined by spectrophotometry, after oxidation with bromate. $Fe(CN)_5H_2O^{2-}$ has an absorption maximum[10] at 394 nm with an extinction coefficient of ϵ = 743 M^{-1} cm^{-1}.

Kinetics Experiments. It has long been known that reactions of hexacyanoferrate(II) are affected by light and air-oxygen. For this reason, most of the kinetics runs were done in the absence of air and with min-

---

(1) Systematic Design of Chemical Oscillators. 47. Part 46: Luo, Y.; Epstein, I. R. *J. Phys. Chem.*, in press.

(2) Permanent address: Institute of Physical Chemistry, Kossuth Lajos University, H-4010 Debrecen, Hungary.

(3) Part 45: Edblom, E. C.; Luo, Y.; Orbán, M.; Kustin, K.; Epstein, I. R. *J. Phys. Chem.*, in press.

(4) Birk, J. P.; Kozub, S. G. *Inorg. Chem.* **1973**, *12*, 2460.

(5) Sulfab, Y.; Elfaki, H. A. *Can. J. Chem.* **1974**, *52*, 2001.

(6) Abdel-Khalek, A. A. *Transition Met. Chem.* (*Weinheim, Ger.*) **1987**, *11*, 67.

(7) Khan, H. A.; Higginson, W. C. E. *J. Chem. Soc., Dalton Trans.* **1981**, 2537.

(8) Hofmann, K. A. *Justus Liebigs Ann. Chem.* **1900**, *312*, 1.

(9) Asperger, S.; Murati, I.; Pavlovic, D. *J. Chem. Soc. A* **1969**, 2044.

(10) Deford, D. D.; Davidson, A. W. *J. Am. Chem. Soc.* **1951**, *73*, 1469.

0020-1669/89/1328-0732$01.50/0

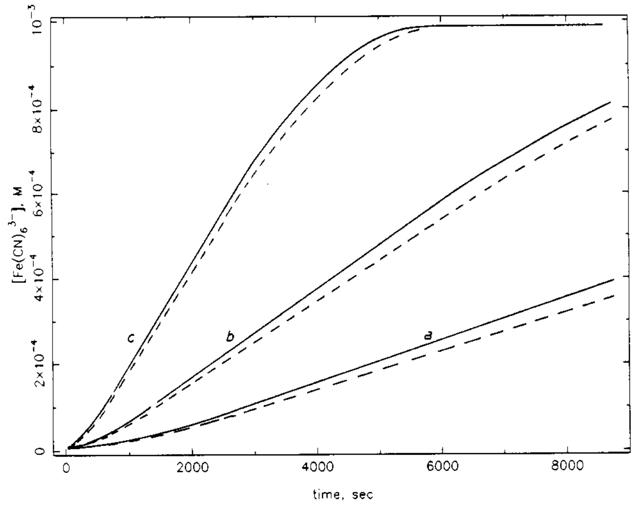

Figure 1. Measured (solid) and calculated (dashed) kinetic curves in the bromate–hexacyanoferrate(II) reaction (T = 25 °C, pH = 4.2, $[Fe(CN)_6^{4-}]_0 = 1.0 \times 10^{-3}$ M): (a) $[BrO_3^-]_0 = 0.002$ M; (b) $[BrO_3^-]_0 = 0.01$ M; (c) $[BrO_3^-]_0 = 0.06$ M.

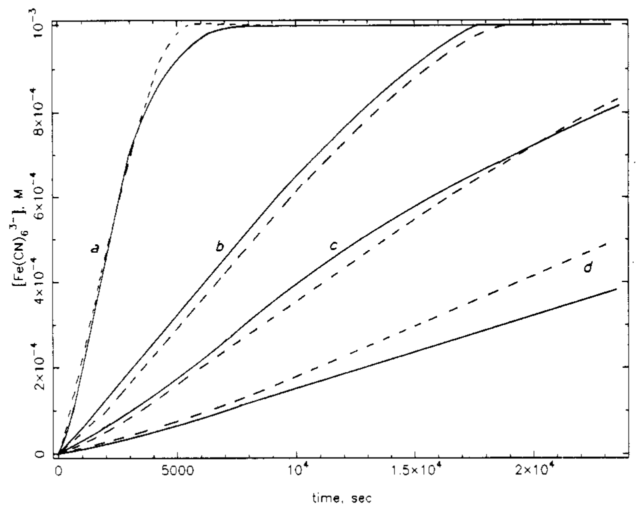

Figure 2. Effect of pH on measured (solid) and calculated (dashed) kinetic curves (T = 25 °C, $[BrO_3^-]_0 = 0.02$ M, $[Fe(CN)_6^{4-}]_0 = 0.001$ M): (a) pH = 3.6; (b) pH = 4.86; (c) pH = 5.32; (d) pH = 5.85.

imum exposure of the reaction mixture to daylight. The reactions were followed by continuous measurement of the absorbance of $Fe(CN)_6^{3-}$ at its maximum (420 nm, $\epsilon = 1040$ M^{-1} cm^{-1}). The absorbance of other species at this wavelength is negligible.[11] The light beam of the spectrophotometer does not significantly affect the rate. The pH and the ionic strength were maintained with acetate buffer. The concentration of hexacyanoferrate(II) was usually 0.001 M, while the sum of the acetic acid and sodium acetate concentrations was maintained at 0.2 M. Under these conditions the pH of the reaction mixture could be kept constant during a single run. Changing the buffer concentration in the range 0.1–1.0 M does not affect the reaction rate. It has been reported[7] that the surface material of the optical cell in which the reaction takes place affects the rate of the hexacyanoferrate(II)–chlorite reaction. We found no such surface effect on the rate of the present reaction when it takes place in a silica or in a plastic spectrophotometer cell. The buffer solutions were mixed with bromate stock solutions, and the reaction mixtures were deoxygenated with argon and thermostated. The reactions were started by adding a small volume of deoxygenated hexacyanoferrate(II) stock solution to the mixture. Several experiments were performed in unbuffered solutions, and the pH change was determined simultaneously with the measurement of light absorption.

The rate of reaction between pentacyanoaquoferrate(II) and bromate was measured at 394 nm. At this wavelength both the ferrate(II) and ferrate(III) complexes absorb light, but the latter has a higher molar absorbance,[10] and the absorbance increases with time because of the appearance of pentacyanoaquoferrate(III).

Results

Stoichiometry. Although the stoichiometry of the bromate–hexacyanoferrate reaction is expected to be simple, some stoichiometric studies were carried out in acetate buffer in the pH range 3.6–5.8, with $[Fe(CN)_6^{4-}]$ between 10^{-4} and 10^{-3} M and $[BrO_3^-]$ between 10^{-4} and 10^{-2} M. No formation of elementary bromine was observed even with bromate in high excess. Spectrophotometric determination of the hexacyanoferrate(III) formed confirmed the overall stoichiometry given in eq 4. The stoichiometry is independent of the ratio of initial reactant concentrations.

$$BrO_3^- + 6Fe(CN)_6^{4-} + 6H^+ = Br^- + 6Fe(CN)_6^{3-} + 3H_2O \qquad (4)$$

Kinetics and Mechanism. Absorbance versus time traces for the reaction of bromate with hexacyanoferrate(II) showed a brief induction period and an increasing slope during the early phase of the reaction. Figure 1 gives examples of these curves at three initial bromate concentrations and pH = 4.2. The reaction rate remains almost constant after the initial increasing phase for about 70–90% of the duration of the reaction, suggesting that the rate does not depend upon the concentration of $Fe(CN)_6^{4-}$ and that the concentration of the reaction intermediate from which the product is formed is nearly constant during this period.

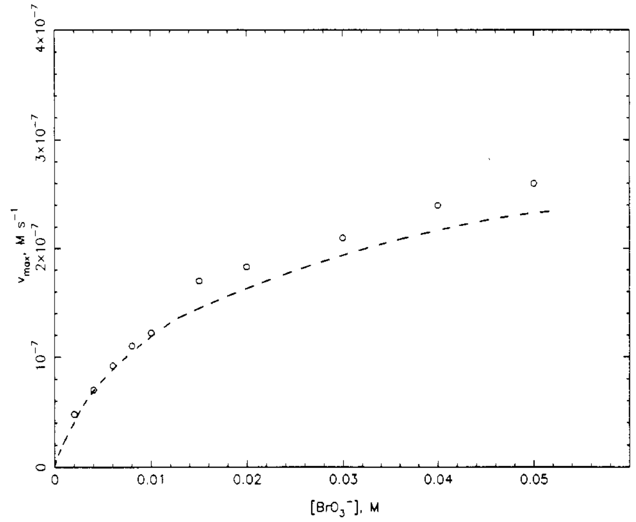

Figure 3. Dependence of maximum rate on initial bromate concentration (pH = 4.2, $[Fe(CN)_6^{4-}]_0 = 0.001$ M, T = 25 °C). Circles indicate measured values; the dashed line shows calculated values.

Figure 2 shows several kinetic curves at different pH values. The reaction rate increases with decreasing pH, a key point in modeling the pH oscillation in the bromate–sulfite–hexacyanoferrate(II) system.[3] The rate of hydrogen ion consumption increases as the pH drops. We have determined the highest slope (the maximum rate) of these kinetic curves. As Figure 3 shows, this maximum reaction rate shows a saturation dependence on the initial bromate concentration. Figure 4 gives the dependence of the maximum rate on $[H^+]_0$.

It is impractical to construct a single rate law for this complicated reaction. It appears more useful to propose a multistep mechanism to describe the experimental kinetic curves.

A similar pH dependence was found in the chlorite[7] oxidation of hexacyanoferrate(II), but no autocatalysis was reported. In the iodate–hexacyanoferrate(II) reaction, autocatalytic behavior was noted in iodate excess at about pH 2, but the reaction has not been studied in detail under these conditions.[5] It is likely that the Dushman (iodate–iodide) reaction[12] accelerates the overall reaction. The rate of the Dushman reaction is high enough, and it increases with $[I^-]$. Iodine formed in the Dushman reaction reacts with hexacyanoferrate(II) very rapidly.[13] The experimental

---

(11) Espenson, J. H.; Wolunek, S. *Inorg. Chem.* **1972**, *11*, 2034.

(12) Dushman, S. *J. Phys. Chem.* **1904**, *8*, 453.

(13) Reynolds, W. L. *J. Am. Chem. Soc.* **1958**, *80*, 1830.

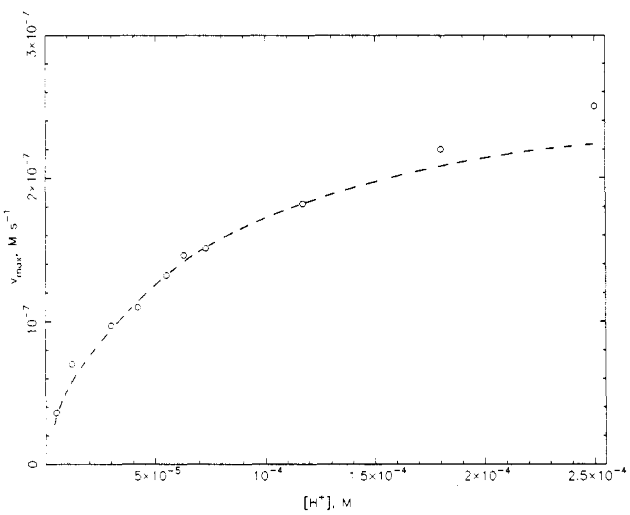

Figure 4. Measured (circles) and calculated (dashed line) maximum rates as a function of hydrogen ion concentration ($[BrO_3^-]_0 = 0.02$ M, $[Fe(CN)_6^{4-}]_0 = 0.001$ M, $T = 25$ °C).

observation of partially autocatalytic behavior in the bromate–hexacyanoferrate(II) reaction at $[H^+] = 0.05$–0.5 M was explained on a similar basis.[4] However, Birk and Kozub's rationale cannot explain the autocatalysis we find at pH > 3.6. The rate of the bromate–bromide reaction is practically zero at pH > 3.6, because of its quadratic dependence on $[H^+]$ and the low concentration of Br^- formed in the reaction.[14] We also find that the addition of 0.01 M bromide ion to the initial reaction mixture does not accelerate the reaction at pH > 3.6. Thus, the autocatalysis cannot be due to the bromate–bromide reaction in this pH range.

No induction period was observed in the kinetic curves when the solution of hexacyanoferrate(II) was mixed with the acidic buffer solution and stored in darkness for at least 1 h before the reaction was initiated by addition of the bromate. This observation suggests that the active species forms from hexacyanoferrate(II) in acidic solution in darkness. We have arrived at the conclusion that this active species is $Fe(CN)_5H_2O^{3-}$, formation of which is favored in acidic solution. $Fe(CN)_5H_2O^{3-}$ forms in neutral solution also, but its concentration in dark equilibrium is very low. Reversible formation of pentacyanoaquoferrate(II) can be induced by light.[18] If the oxygen-free, neutral stock solution of 0.01 M hexacyanoferrate(II) was exposed to direct daylight in a glass flask for 60 min or more and the reaction was started by immediate addition of the irradiated solution to the reaction mixture, the induction period was eliminated and the reaction proceeded at a more rapid rate than with the stock solution that had been kept in darkness (Figure 5).

The oxidation of $Fe(CN)_6^{4-}$ by molecular oxygen was studied by Asperger[15] and co-workers at pH 4.5. They do not mention any autocatalytic behavior, but from the similarity of solvent effects on the replacement of X in $Fe^{II}(CN)_5X^{3-}$ and the oxidation of $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$, they suggest that the oxidation involves dissociation of a cyanide group and that this dissociation is the rate-determining step. That the addition of $Fe(CN)_5H_2O^{3-}$ accelerates the oxidation of $Fe(CN)_6^{4-}$ supports this claim.

There is a similar situation in the case of the oxidation of hexacyanoferrate(II) by hydrogen peroxide. The replacement of a cyanide ligand by a water molecule, either by photolysis or thermolysis, is a necessary first step:[16,17]

$$Fe(CN)_6^{4-} + H_2O \rightleftarrows Fe(CN)_5H_2O^{3-} + CN^- \qquad (5)$$

Reaction 5 is a very slow substitution reaction that is catalyzed by light. Gâspâr and Beck[18] studied the kinetics of this photocatalytic aquation in alkaline, neutral, and acidic media. They obtained quantitative values for the quantum yield and the rate constants of the thermal forward and reverse reactions in alkaline medium: $k_5 = 3 \times 10^{-8}$ s^{-1}, $k_{-5} = 1.5$ M^{-1} s^{-1}.

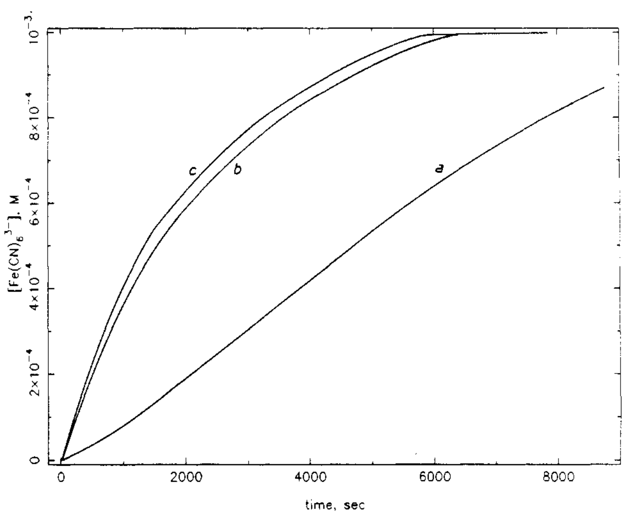

Figure 5. Kinetic curves for the bromate–hexacyanoferrate(II) reaction ($[BrO_3^-]_0 = 0.02$ M, $[Fe(CN)_6^{4-}]_0 = 0.001$ M, pH = 4.2). The stock solution of $Fe(CN)_6^{4-}$ was (a) stored in the dark, (b) placed in sunlight for 2 h, or (c) incubated in acetate buffer (pH = 4.2) for 2 h in the dark before the reaction was started.

Our investigations were carried out in acidic solution at pH 3.6–5.8. According to Jordan and Ewing,[19] the protonation of hexacyanoferrate(II) takes place in this pH range:

$$Fe(CN)_6^{4-} + H^+ \rightleftarrows HFe(CN)_6^{3-} \qquad (6)$$

The equilibrium constant for reaction 6 is $K_6 = 1470$ M^{-1}. No further protonation steps need be taken into account at pH > 3.6. It seems likely that the protonated hexacyanoferrate(II) exchanges its cyanide ligand for a water molecule faster than the unprotonated species does:

$$HFe(CN)_6^{3-} + H_2O \rightleftarrows Fe(CN)_5H_2O^{3-} + HCN \qquad (7)$$

Reaction 7 is the first and slowest step in our mechanism for the oxidation of hexacyanoferrate(II) in acidic medium. The rate of the reverse reaction 7 has been given by Gâspâr and Beck[16] as $k_{-7} = 3.3 \times 10^{-2}$ M^{-1} s^{-1}, but we had to use slightly higher values to describe the effect of HCN on the reaction rate. The rate constant for the forward reaction is not known.

The next step is the relatively fast oxidation of pentacyanoaquoferrate(II) to pentacyanoaquoferrate(III):

$$Fe(CN)_5H_2O^{3-} + BrO_3^- \xrightarrow{2H^+} Fe(CN)_5H_2O^{2-} + BrO_2^{\bullet} + H_2O \qquad (8)$$

The similar oxidation of pentacyanoaquoferrate(II) by H_2O_2 was found to be a rather fast reaction[17] with a second-order rate constant of 214 M^{-1} s^{-1} independent of pH in acidic medium.

We measured the rate of reaction 8 separately. The reaction is first order with respect to both ferrate complex and bromate ion, and its rate does not depend on $[H^+]$ in the pH range 3.6–5.8. The second-order rate constant is $k_8 = 6.8$ M^{-1} s^{-1} at 25 °C.

On the basis of our experiments we can propose further mechanistic features of reaction 8. The initial absorbance at 394 nm depends on the initial concentration of bromate, which implies that the reaction consists of two parts: a very fast, reversible interaction between bromate and pentacyanoaquoferrate(II) is followed by an irreversible redox reaction, which is slow compared with the first step but is nevertheless fairly rapid:

$$(CN)_5FeO^{*}H_2^{3-} + BrO_3^- \rightleftarrows (CN)_5FeO^{*}BrO_2^{4-} + H_2O \qquad (8a)$$

---

[14] Râbai, Gy.; Bazsa, Gy.; Beck, M. T. *Int. J. Chem. Kinet.* **1981**, *13*, 1277.

[15] Asperger, S.; Murati, I.; Pavlovic, D.; Sustra, A. *J. Chem. Soc., Chem. Commun.* **1986**, 814.

[16] Baxendale, J. H. *Adv. Catal.* **1952**, *4*, 67.

[17] Davis, G.; Garafalo, A. R. *Inorg. Chem.* **1976**, *15*, 1101.

[18] Gâspâr, V.; Beck, M. T. *Polyhedron* **1983**, *2*, 38.

[19] Jordan, J.; Ewing, J. G. *Inorg. Chem.* **1962**, *1*, 587.

Table I. Reaction Scheme and Rate Constants for the Calculations

reacn	k_i, $M^{-1}\ s^{-1}$	k_{-i}, $M^{-1}\ s^{-1}$
$Fe(CN)_6^{4-} + H^+ \rightleftarrows HFe(CN)_6^{3-}$	1×10^{10}	$7 \times 10^{6\,a}$
$HFe(CN)_6^{3-} + H_2O \rightleftarrows Fe(CN)_5H_2O^{3-} + HCN$	$4 \times 10^{-6\,a}$	0.15
$Fe(CN)_5H_2O^{3-} + BrO_3^- \xrightarrow{2H^+} Fe(CN)_5H_2O^{2-} + BrO_2^\bullet + H_2O$	6.8	
$Fe(CN)_5H_2O^{2-} + Fe(CN)_6^{4-} \rightarrow Fe(CN)_5H_2O^{3-} + Fe(CN)_6^{3-}$	1×10^3	
$5Fe(CN)_6^{4-} + BrO_2^\bullet \xrightarrow{4H^+} 5Fe(CN)_6^{3-} + Br^- + 2H_2O$	1×10^5	
$Fe(CN)_6^{3-} + Fe(CN)_5H_2O^{3-} \rightleftarrows Fe_2(CN)_{11}^{6-} + H_2O$	1×10^4	1^a

[a] First-order rate constants have units of s^{-1}.

As indicated by the asterisk, the substitution reaction 8a can take place by rapid oxygen exchange between the coordinated water molecule and the bromate ion, and it does not require breaking the inert metal–ligand bond.

$$(CN)_5FeO^*BrO_2^{4-} \xrightarrow{\text{slow}} (CN)_5FeO^{*4-} + BrO_2^\bullet \quad (8b)$$

The experimental results show the rate of oxidation of pentacyanoaquoferrate(II) to be independent of $[H^+]$, so the rate-determining process 8b does not involve any hydrogen ion. Reaction 8b is followed by a rapid protonation (eq 8b′) and further fast

$$(CN)_5FeO^{4-} + 2H^+ \rightarrow (CN)_5FeOH_2^{2-} \quad (8b')$$

steps involving the ferrate(II) complex and bromine-containing species of various oxidation states. The pentacyanoaquoferrate(III) complex formed in reaction 8 reacts with hexacyanoferrate(II)

$$Fe(CN)_5H_2O^{2-} + Fe(CN)_6^{4-} \rightarrow Fe(CN)_5H_2O^{3-} + Fe(CN)_6^{3-} \quad (9)$$

with rate constant $k_9 = 1 \times 10^3\ M^{-1}\ s^{-1}$.[20] Strong experimental evidence for the significant role of pentacyanoaquoferrate(II) (and/or pentacyanoaquoferrate(III)) in the oxidation of hexacyanoferrate(II) is shown in Figure 6. Addition of a catalytic amount of the $Fe(CN)_5H_2O^{3-}$ complex eliminates the induction period and markedly accelerates the reaction. The oxidized complex (pentacyanoaquoferrate(III)) has the same effect as the same concentration of the reduced form (Figure 6), as it should. Further, addition of HCN to the reaction mixture decreases the rate of oxidation, as expected from the reversibility of reaction 7.

Several additional fast steps lead to formation of bromide:

$$Fe(CN)_6^{4-} + BrO_2^\bullet \rightarrow Fe(CN)_6^{3-} + BrO_2^- \quad (10)$$

Reaction 10 was found to be very fast; $k_{10} = 1.9 \times 10^9\ M^{-1}\ s^{-1}$.[21] The following reactions are also expected to be quite rapid:

$$Fe(CN)_6^{4-} + BrO_2^- \xrightarrow{2H^+} Fe(CN)_6^{3-} + BrO^\bullet + H_2O \quad (11)$$

$$Fe(CN)_6^{4-} + BrO^\bullet \rightarrow Fe(CN)_6^{3-} + BrO^- \quad (12)$$

$$Fe(CN)_6^{4-} + BrO^- \xrightarrow{2H^+} Fe(CN)_6^{3-} + Br^\bullet + H_2O \quad (13)$$

$$Fe(CN)_6^{4-} + Br^\bullet \rightarrow Fe(CN)_6^{3-} + Br^- \quad (14)$$

An additional interaction between pentacyanoaquoferrate(II) and hexacyanoferrate(III) is included to take into account the decrease in the concentration of catalyst in the final stage of reaction:

$$Fe(CN)_6^{3-} + Fe(CN)_5H_2O^{3-} \rightleftarrows Fe_2(CN)_{11}^{6-} + H_2O \quad (15)$$

Such a reaction has been suggested previously.[20] It presumably involves the formation of cyanide-bridged dimers (or polymers) rather than any redox process. No precise value for the rate constant of reaction 15 is available, but the half-time of this reaction was found to be 70 ms.[20] We chose $k_{15} = 1 \times 10^4\ M^{-1}\ s^{-1}$, which corresponds to the reported half-time. The rate constant for the reverse reaction is $k_{-15} = 1\ s^{-1}$.

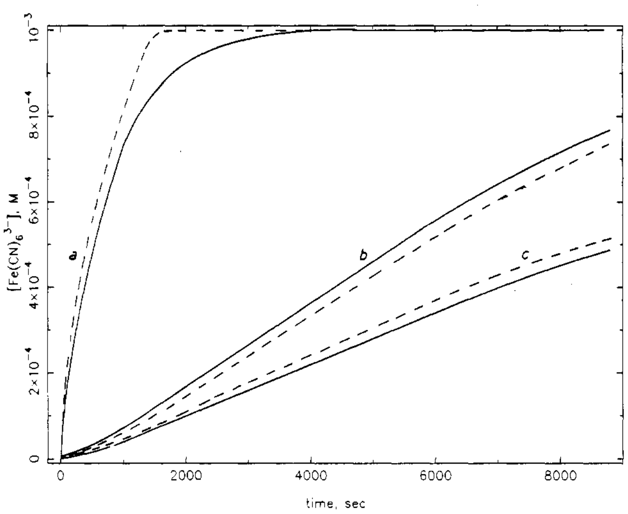

Figure 6. Effect of pentacyanoaquoferrate(II) and of HCN on the measured (solid) and calculated (dashed) kinetic curves ($[BrO_3^-]_0 = 0.01$ M, $[Fe(CN)_6^{4-}]_0 = 0.001$ M, pH = 4.2, T = 25 °C): (a) $[Fe(CN)_5H_2O^{3-}]_0 = 1 \times 10^{-5}$ M; (b) no other species added; (c) $[HCN]_0 = 0.01$ M.

Calculations. The mechanism developed above, eq 4–15, served as the basis for numerical simulations by the GEAR method.[22] In the simulations, we combined steps 10–14 into a single overall process:

$$5Fe(CN)_6^{4-} + BrO_2^\bullet \xrightarrow{4H^+} 5Fe(CN)_6^{3-} + Br^- + 2H_2O \quad (14')$$

A second-order rate equation was used for reaction 14′ with rate constant $k_{14'} = 1 \times 10^5\ M^{-1}\ s^{-1}$. All the other rate constants are known except k_7, which was fitted to the experimental kinetic curves. The reactions and rate constants used are summarized in Table I.

When the initial concentration of pentacyanoaquoferrate(II) was calculated by using the dark stability constant of the sixth cyanoferrate(II) complex ($5.2 \times 10^7\ M^{-1}$), which follows from Gâspâr and Beck's kinetic data,[18] the calculated rates were much faster than the experimental values, and no induction period appeared in the simulations. It seems likely that the concentration of kinetically active pentacyanoaquoferrate(II) is less than at thermodynamic equilibrium ($[Fe(CN)_5H_2O^{3-}]_0 = 4 \times 10^{-6}$ M when the concentration of hexacyanoferrate(II) is 1×10^{-3} M). The kinetically active initial concentration of pentacyanoaquoferrate(II) was taken to be 2×10^{-8} M.

The dashed lines on the figures show the kinetic curves calculated with this modification. We note that the reproducibility of the kinetics experiments is only ±10% because of the sensitivity of the reaction rate to light, air, and the length and manner of storage of the hexacyanoferrate(II) stock solutions. The calculated and experimental curves agree in almost every case to within this 10% tolerance, suggesting that the mechanism accounts adequately for the observed data.

Conclusion

By taking into account the role of pentacyanoaquoferrate(II), we have constructed a mechanism for the $Fe(CN)_6^{4-}$ reaction that accounts not only for the observed kinetics but also for the de-

---

[20] Stasiv, R.; Wilkins, R. G. *Inorg. Chem.* **1969**, *8*, 156.

[21] Field, R. J.; Raghavan, N. V.; Brummer, J. G. *J. Phys. Chem.* **1982**, *86*, 2443.

[22] Hindmarsh, A. C. "GEAR: Ordinary Differential Equation Solver" Technical Report No. UCM-30001, Rev. 2; Lawrence Livermore Laboratory: Livermore, CA, 1972.

pendence on the concentrations of reactants, added aquo complexes, and HCN as well as for the sensitivity of the system to light. With only a handful of adjustable parameters, the numerical simulations give results in excellent agreement with experiment.

The elements of this mechanism appear applicable to other oxidations of ferrocyanide, and their extension to such systems is currently under investigation. We also hope in the near future to include the results obtained here in a detailed mechanistic study of the oscillatory $Fe(CN)_6^{4-}$–BrO_3^-–SO_3^{2-} reaction.

Acknowledgment. We thank Kenneth Kustin and Mihaly T. Beck for helpful discussions. This work was supported by the National Science Foundation (Grant No. CHE-8800169) and by a U.S.-Hungarian Cooperative Grant from the NSF (Grant No. INT-8613532) and the Hungarian Academy of Sciences.

Registry No. $Fe(CN)_6^{4-}$, 13408-63-4; BrO_3^-, 15541-45-4.

Contribution from Anorganische Chemie III, Eduard-Zintl-Institut der Technischen Hochschule Darmstadt, D-6100 Darmstadt, Federal Republic of Germany

Kinetics of the Acid Dissociation of Oligopeptide Complexes of Copper(II) and Nickel(II): General-Acid Catalysis with "Noncoordinating" 2,6-Lutidine Type Buffers

Maria Hauröder, Monika Schütz, Klaus J. Wannowius,* and Horst Elias*

Received May 6, 1988

Stopped-flow spectrophotometry was used to study the general-acid catalytic activity of 2,6-lutidine type buffers in the protonation and acid dissociation of the deprotonated triglycine and tetraglycine copper(II) and nickel(II) complexes $Cu(H_{-2}G_3)^-$, $Cu(H_{-1}G_3)$, $Cu(H_{-2}G_4)^-$, $Cu(H_{-1}G_4)$, and $Ni(H_{-2}G_3)^-$ at 298 K and μ = 0.3 M ($NaClO_4$). The buffers applied possess a very limited coordination power only since they are based on H(LS) (=2,6-lutidine-3-sulfonic acid; pK_a = 4.8), AC (=3-acetyl-2,4,6-collidine; pK_a = 5.9), and a series of other sterically hindered substituted 2,6-lutidines to cover the pH range 7.4–3.1. It was found that, at a given pH, the increase of the experimental rate constant with increasing total buffer concentration, which corresponds to rate constant k_{HB} as a measure for general-acid catalysis of an acid HB, is very small. For H(LS) the rate constant k_{HB} ranges from <0.3 $M^{-1}\ s^{-1}$ (reaction with $Ni(H_{-2}G_3)^-$) to 5.5 $M^{-1}\ s^{-1}$ (reaction with $Cu(H_{-1}G_3)$), whereas for protonated AC the range is k_{HB} < 0.3 $M^{-1}\ s^{-1}$ (reaction with $Cu(H_{-2}G_4)^-$) and k_{HB} = 54.7 $M^{-1}\ s^{-1}$ (reaction with $Cu(H_{-2}G_3)^-$). Comparing the general-acid catalytic activity of acetic acid with that of H(LS), one finds that H(LS) is less active than acetic acid by a factor of >2000 (reaction with $Ni(H_{-2}G_3)^-$) and approximately 260 (reaction with $Cu(H_{-1}G_3)$ and $Cu(H_{-1}G_4)$). It follows from the results that 2,6-lutidine type buffers are well suited to suppress general-acid catalysis in kinetic studies and that especially the H(LS) buffer with its very reduced activity in general-acid catalysis is an attractive substitute for the standard acetate buffer.

Introduction

The kinetics of the acid-catalyzed protonation and dissociation of deprotonated oligopeptide complexes of copper(II) and nickel(II) have been the subject of numerous studies[1-7] by Margerum and co-workers. It was found that the dissociation according to eq 1 (M = Cu(II), Ni(II); $HL^\pm$ = triglycine, tetraglycine; $H_{-x}L$

$$M(H_{-x}L)^{(x-1)-} + (x+1)H^+ \rightarrow M^{2+} + HL^\pm \qquad (1)$$

= x-fold deprotonated peptide) is the overall result of a series of protonation steps, each of which follows rate law 2. The observed

$$\text{rate} = k_{obsd}[M(H_{-x}L)^{(x-1)-}] \qquad (2)$$

first-order rate constant proves the existence of several pathways in the sense that, according to (3), water molecules, protons, and

$$k_{obsd} = k_{H_2O} + k_H[H^+] + k_{HB}[HB] \qquad (3)$$

the applied acid HB itself can induce the reaction.[2,4,6] As a matter of fact, the situation can even be more complicated as indicated by eq 4 and eq 5.[7] The contribution of the terms $k_H[H^+]$ and

$$k_H = k'_H + k_{H,H}[H^+] \qquad (4)$$

$$k_{HB} = k'_{HB} + k_{H,HB}[H^+] \qquad (5)$$

$k_{HB}[HB]$ in eq 3 is referred to as being specific-acid catalysis and general-acid catalysis, respectively.[2,7] It is well-known that the extent of general-acid catalysis caused by an acid HB in reaction 1 depends strongly on the nature of HB. With sterically hindered acids such as HB = $H(MES)^\pm$, $H(PIPES)^\pm$ there is practically no general-acid catalysis,[7] whereas acetic acid gives rise to a substantial contribution of the term $k_{HB}[HB]$ in eq 3.

We reported earlier[8] that buffers based on sterically hindered derivatives of 2,6-lutidine can be used as practically "noncoordinating" buffers. The present kinetic investigation was undertaken to test the behavior of these buffers as acids HB in the acid-catalyzed dissociation of several triglycine (=$HG_3^\pm$) and tetraglycine (=$HG_4^\pm$) complexes of copper(II) ($Cu(H_{-2}G_3)^-$, $Cu(H_{-1}G_3)$, $Cu(H_{-2}G_4)^-$, $Cu(H_{-1}G_4)$) and nickel(II) ($Ni(H_{-2}G_3)^-$) according to (1). More specifically, the determination of the catalytic activity of these buffers in general-acid catalysis was the main goal, the comparison of acetic acid (pK_a = 4.64) and sterically hindered 2,6-lutidine-3-sulfonic acid (pK_a = 4.80[8]) being of special interest.

Experimental Section

Complexes. The aqueous solutions of the complexes (ionic strength μ = 0.3 M ($NaClO_4$)) were prepared from $Cu(ClO_4)_2\cdot 6H_2O$ and $Ni(ClO_4)_2\cdot 6H_2O$ (Alfa) and a 10% excess of the ligands triglycine and tetraglycine (Sigma), respectively. The pH of the solutions was adjusted with NaOH. Only freshly prepared solutions were used for the kinetic runs.

Buffers. The following abbreviations are assigned to the various buffers: H(LS) = 2,6-lutidine-3-sulfonic acid; AC = 3-acetyl-2,4,6-collidine; H(PS) = pyridine-3-sulfonic acid; py = pyridine; ML = 4-methoxy-2,6-lutidine; lu = 2,6-lutidine; NL = 3-nitro-2,6-lutidine; NC = 3-nitro-2,4,6-collidine; CL = 4-cyano-2,6-lutidine; H(MES) = 2-morpholinoethanesulfonic acid, HOAc = acetic acid.

H(LS) (Merck) and H(MES) (Sigma) were commercially available. The $H(AC)^+$ salts of the acids HBF_4, HNO_3, benzenesulfonic acid, and p-toluenesulfonic acid were supplied by Merck, Darmstadt, FRG. The other lutidine type buffers were prepared as described earlier.[8] Their purity was checked by ^1H NMR and microanalysis (C, H, N). The

---

(1) Pagenkopf, G. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1968**, *90*, 6963.
(2) Billo, E. J.; Margerum, D. W. *J. Am. Chem. Soc.* **1970**, *92*, 6811.
(3) Bannister, C. E.; Margerum, D. W.; Raycheba, J. M. T.; Wong, L. F. *Faraday Symp. Chem. Soc.* **1975**, *No. 10*, 78.
(4) Youngblood, M. P.; Margerum, D. W. *Inorg. Chem.* **1980**, *19*, 3072.
(5) Raycheba, J. M. T.; Margerum, D. W. *Inorg. Chem.* **1980**, *19*, 837.
(6) Youngblood, M. P.; Chelappa, K. L.; Bannister, C. E.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 1742.
(7) Bannister, C. E.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 3149.
(8) Bips, H.; Elias, H.; Hauröder, M.; Kleinhans, G.; Pfeifer, S.; Wannowius, K. J. *Inorg. Chem.* **1983**, *22*, 3862.

0020-1669/89/1328-0736$01.50/0