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Reactions of Octacyanomolybdate(IV). I. Kinetics of Oxidation by Chromium(VI)

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The reaction $3Mo(CN)_8{}^{4-} + Cr(VI) \rightarrow Cr(III) + 3Mo(CN)_8{}^{3-}$ follows the rate law $d[Cr(VI)]/dt = k[HCrO_4{}^-][Mo(CN)_8{}^{4-}]\cdot[H^+]^2$, where $k = (8.3 \pm 2.0) \times 10^{-4}\ M^{-3}\ sec^{-1}$. Anionic chromium(III) products are formed, but could not be identified precisely. Results are discussed in terms of thermodynamically weak coordination of $Mo(CN)_8{}^{4-}$ to positive centers, the inertia to substitution of Cr(III), $Mo(CN)_8{}^{4-}$, and $Mo(CN)_8{}^{3-}$, and the Espenson–King mechanism for 1-equiv reductions of chromium(VI).

Introduction

Octacyanomolybdate(IV) is a substitution-inert complex capable of outer-sphere electron-transfer reactions as evidenced by the rapid exchange of electrons with octacyanomolybdate(V)[1]

$$Mo(CN)_8{}^{4-} \rightleftharpoons Mo(CN)_8{}^{3-} + e^- \qquad (1)$$

However, the possibility exists for inner-sphere electron transfer to positive centers through bridging cyanide ligands.

Such reducing agents as $Fe(o\text{-phen})_3{}^{2+}$ and $Fe(CN)_6{}^{4-}$ have been observed[2-3] to give reactions with $HCrO_4{}^-$, which are first order in reducing agents, as opposed to similar reactions which are second order for Fe^{2+} and VO^{2+} in aqueous perchloric acid.[2] This study was undertaken in order to compare $Mo(CN)_8{}^{4-}$ with $Fe(CN)_6{}^{4-}$ and as part of a general examination of reactions of eight-coordinated $Mo(CN)_8{}^{4-}$.

Experimental Section

A. Materials. $K_4Mo(CN)_8\cdot 2H_2O$ was prepared by the method of Furman and Miller[4] previously described. Solutions of $K_4Mo(CN)_8\cdot 2H_2O$ were prepared by weight and used immediately or else stored in the dark for no more than 1 day. Concentrations were checked by titration with standard Ce^{4+} solution. Stock solutions of $HCrO_4{}^-$ were prepared from reagent grade $Na_2Cr_2O_7\cdot 2H_2O$ and standardized spectrophotometrically at 375 nm (molar absorptivity equal to 4810) after being made basic with KOH. Perchloric acid solutions were prepared by dilution of reagent grade concentrated $HClO_4$ (11.4 *M*). For the ion-exchange studies Dowex 50W-8X resin in the H^+ form and Dowex 1-X8 resin in the Cl^- form were used.

B. Instrumentation. All spectra were recorded on a Beckman Acta V recording spectrophotometer using 1-cm quartz cells. Potentiometric titrations were performed using a Radiometer-Copenhagen pH meter, automatic titrator II, and titrigraph. The titrations were run using the calomel electrode (Radiometer K401) containing saturated sodium chloride solution as the standard electrode and the platinum electrode (Radiometer P101) as the indicator electrode. Kinetic measurements were made at 388 nm using a Beckman DU-2 spectrophotometer equipped with a constant-temperature cell compartment. At this wavelength the molar absorbances for $Mo(CN)_8{}^{3-}$, $Mo(CN)_8{}^{4-}$, and $HCrO_4{}^-$ are 1431, 126, and 900, respectively. $A_\infty - A_0$ never exceeded 0.1 absorbance unit. Good straight-line plots for $\log (A_\infty - A)$ were generally obtained for 3 half-lives, but the scatter in slopes for replicate runs is understandably large, usually from 10 to 20%. For all the kinetic runs the ionic strength was maintained constant at 0.1 *M* with $KClO_4$, and except in the H^+ dependence study the $[H^+]$ was held constant at 0.01 *M* with $HClO_4$.

C. Product Analysis. Chromium(III) content of product solutions of the $HCrO_4{}^-$–$Mo(CN)_8{}^{4-}$ reaction before and after passage through the anion- and cation-exchange columns was determined in the following manner. The Cr(III) was oxidized to Cr(VI) with H_2O_2. This solution then was boiled to drive off excess H_2O_2, allowed to cool, and made basic with KOH. The absorbance was then measured at 375 nm where Cr(VI) has a molar absorptivity of 4810. $Mo(CN)_8{}^{3-}$ content was determined by reducing $Mo(CN)_8{}^{3-}$ to $Mo(CN)_8{}^{4-}$ with I^-, producing I_2 which was then titrated with standard thiosulfate solution using a starch indicator.

Results

A. Stoichiometry. The stoichiometry of the reaction between $HCrO_4{}^-$ and $Mo(CN)_8{}^{4-}$ in 10^{-2} *M* $HClO_4$ was determined by means of potentiometric titrations of 1.06×10^{-2} *M* $HCrO_4{}^-$ solution into 1-ml samples of 3.26×10^{-2} *M* $Mo(CN)_8{}^{4-}$ solution. The $Mo(CN)_8{}^{4-}$ samples were protected from light to prevent decomposition. The slowness of the reaction ($t_{1/2}$ being *ca.* 10 min) necessitated very slow addition of the $HCrO_4{}^-$ solution to ensure complete reaction. Results of several potentiometric titrations established the mole ratio of $Mo(CN)_8{}^{4-}$ to $HCrO_4{}^-$ as 2.9 ± 0.2. This result is consistent with the description of the reduction of $HCrO_4{}^-$ given in

$$3Mo(CN)_8{}^{4-} + Cr(VI) \rightarrow Cr(III) + 3Mo(CN)_8{}^{3-} \qquad (2)$$

This stoichiometry was further checked by means of spectrophotometric titrations of $Mo(CN)_8{}^{4-}$ with $HCrO_4{}^-$. These were done in 10^{-2} *M* $HClO_4$ by adding varying amounts of $HCrO_4{}^-$ to a constant amount of $Mo(CN)_8{}^{4-}$ and diluting to a constant volume. The absorbances of the various solutions were measured at different wavelengths. Breaks in the plots of the absorbance *vs.* the $[HCrO_4{}^-]$ occurred when the mole ratio of $Mo(CN)_8{}^{4-}$ to $HCrO_4{}^-$ was 3.0 ± 0.2, confirming the stoichiometry described in eq 2.

Attempts to check the stoichiometry potentiometrically and spectrophotometrically by addition of $Mo(CN)_8{}^{4-}$ solution to a known amount of $HCrO_4{}^-$ solution were unsuccessful. In neither case could distinct and reproducible breaks be obtained. Inability to obtain reproducible breaks in potentiometric titrations, where $Mo(CN)_8{}^{4-}$ solution is the titrant, has been noted elsewhere.[5,6] The reason for this behavior is not known.

B. Product Formation. Chromium(III) products are often substitution inert and may be separated and identified using ion-exchange columns. Different results were obtained when reaction mixtures were passed successively through cation columns followed by anion columns and when the order was reversed.

When solutions were passed first through the cation column, no chromium or molybdenum adhered to the column. ($Mo(CN)_8{}^{3-}$ product was quantitatively found to be present by iodometric titration (eq 3) of the eluent from the cation

$$2Mo(CN)_8{}^{3-} + 3I^- \rightarrow 2Mo(CN)_8{}^{4-} + I_3{}^- \qquad (3)$$

column.) If the cation eluent was then passed through an anion column, all the chromium and molybdenum was re-

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Table I. Rate Constants for the Reaction of $Mo(CN)_8^{4-}$ with $HCrO_4^-$ in 1.04×10^{-2} M H^+

$[HCrO_4^-]_0, M$	$[Mo(CN)_8^{4-}]_0, M$	$[Mo(CN)_8^{3-}]_0, M$	10^3k_{obsd},[a] sec^{-1}	k'', M^{-1} sec^{-1}
1.65×10^{-5}	4.94×10^{-4}		3.86 ± 0.26	7.82 ± 0.52
1.65×10^{-5}	9.89×10^{-4}		8.17 ± 0.66	8.24 ± 0.63
1.65×10^{-5}	1.48×10^{-3}		12.28 ± 0.39	8.28 ± 0.33
1.48×10^{-5}	3.15×10^{-4}	3.98×10^{-5}	3.34 ± 0.18	12.0 ± 0.61
1.48×10^{-5}	6.70×10^{-4}	3.98×10^{-5}	6.21 ± 0.64	9.8 ± 1.04
1.48×10^{-5}	1.04×10^{-3}	3.98×10^{-5}	10.38 ± 0.80	10.1 ± 0.71
3.52×10^{-4} (3.41)	8.90×10^{-5}		10.42 ± 0.48	9.87 ± 0.47
5.28×10^{-4} (5.06)	8.90×10^{-5}		15.36 ± 1.31	9.70 ± 0.61
7.04×10^{-4} (6.65)	8.90×10^{-5}		21.05 ± 2.28	9.96 ± 1.05
			Av	9.93 ± 1.34

[a] $k'' = k_{obsd}/[Mo(CN)_8^{4-}]$ when [Mo(IV)] > [Cr(VI)]; $k'' = k_{obsd}/3[HCrO_4^-]$ when [Cr(VI)] > [Fe(II)].

tained on the column. $Mo(CN)_8^{3-}$ and $Mo(CN)_8^{4-}$ could be removed with 3-5 M NaCl. Cr(III) required 10 M HCl for removal. The eluent with 10 M HCl exhibited the spectrum of $Mo(CN)_8^{4-}$.

When solutions are passed first through the anion column and then through the cation column, about 20% of the chromium(III) escapes in the anion effluent but is captured by the cation column. It is puzzling how chromium(III) can be labilized in one instance and not the other.

C. Kinetics. Reactions were studied by following the increase in absorbance at 388 nm due to formation of $Mo(CN)_8^{3-}$. Both $Mo(CN)_8^{4-}$ and $HCrO_4^-$ also absorb at this wavelength. Pseudo-first-order rate laws may be derived, *e.g.*, (1) with $Mo(CN)_8^{4-}$ in excess

$$\ln \frac{A_\infty - A_0}{A_\infty - A} = k''[Mo(CN)_8^{4-}]_0 t \tag{4a}$$

and (2) with $HCrO_4^-$ in excess

$$\ln \frac{A_\infty - A_0}{A_\infty - A} = 3k''[HCrO_4^-]_0 t \tag{4b}$$

Rate constants were evaluated from graphical plots of ln ($A_\infty - A$) *vs.* time. Rather large scatter in values of constants resulted from the fact that readings involved small differences in large numbers and uncertainty in the A_∞ point when $Mo(CN)_8^{4-}$ was in excess. Results are given in Tables I and II, for $[H^+] = 1.04 \times 10^{-2}$ M. Table III shows the dependence of k'' on $[H^+]^2$. These results are in accord with the rate law

$$\frac{d[HCrO_4^-]}{dt} + k[HCrO_4^-][Mo(CN)_8^{4-}][H^+]^2$$

where $k = (8.8 \pm 1.5) \times 10^{-4}$ M^{-3} sec^{-1}.

Discussion

Stoichiometry and Product Formation. In a similar study with $Fe(CN)_6^{4-}$ Birk[3] observed the following phenomena: (a) titrations with $Fe(CN)_6^{4-}$ showed a second break at a ~3.7:1.0 mole ratio of $Fe(CN)_6^{4-}$ to $HCrO_4^-$; (b) chromium(III) was not absorbed on either anion or cation columns suggesting a neutral $CrNCFe(CN)_5$ product; (c) only 2 mol of $Fe(CN)_6^{3-}$, of the 3 formed, liberated iodine on addition of I^-. In each instance the behavior of $Mo(CN)_8^{4-}$ is substantially different.

We found that titrations with sharp end points at a Cr:Mo mole ratio of 1:3 are obtained only on adding Cr(VI) to Mo(IV). The authors suspect that $Mo(CN)_8^{4-}$ reduces $Mo(CN)_8^{3-}$ bound to the Cr^{3+} product increasing the mole ratio. The end point is too ill defined to warrant firm conclusions in the matter.

In the present study isolation of the chromium(III) products was not achieved. Their strong adherence to an anion-exchange column suggests that $Cr[Mo(CN)_8]_n^{3-4n}$ or $Cr[Mo(CN)_8]^{3-3n}$ (anions of exceedingly high charge) complexes are formed. It seems unlikely that Cr(IV) precursors to Cr(III) could coordinate to more than one $Mo(CN)_8^{4-}$ before electron transfer takes place. This suggests that $Mo(CN)_8^{4-}$ reacts with Cr(V) by an inner-sphere process giving $CrNCMo(CN)_7^+$. If the high charges on Cr^{4+} and $Mo(CN)_8^{3-}$ hold this species together until Cr^{4+} is reduced, a second octacyanide could be oxidized giving a complex of Cr(III) with two $Mo(CN)_8^{3-}$ ligands as a product. Reduction of coordinated $Mo(CN)_8^{3-}$ by $Mo(CN)_8^{4-}$ would give a species of 5− charge, $Cr(Mo(CN)_8)_2^{5-}$. Such reasoning is speculative to a degree but seems the only immediate explanation of the experimental results.

Table II. Rate Constants for the Reaction of $HCrO_4^-$ with $Mo(CN)_8^{4-}$ in Presence of Mo(V) in 10^{-2} M H^+

[Mo(IV)], M	[Cr(VI)], M	[Mo(V)], M	10^3k_{obsd}, sec^{-1}	k'', M^{-1} sec^{-1}
9.59×10^{-3}	1.77×10^{-5}		6.48	7.07
7.55×10^{-4}	9.83×10^{-6}	4.42×10^{-5}	6.19	8.46
5.87×10^{-4}	9.83×10^{-6}	6.15×10^{-5}	5.25	9.31
4.65×10^{-4}	9.83×10^{-6}	7.59×10^{-5}	3.70	8.40
9.39×10^{-3}	1.77×10^{-5}		8.25	9.24
7.82×10^{-4}	9.83×10^{-6}	4.42×10^{-5}	7.70	10.13
6.27×10^{-4}	9.83×10^{-6}	6.15×10^{-5}	6.66	11.02
4.98×10^{-4}	9.83×10^{-6}	7.59×10^{-5}	4.59	9.65

Table III

k'', M^{-1} sec^{-1}	$[H^+]$, M	$10^4k''/[H^+]^2$, M^{-3} sec^{-1}
34 ± 1.7	2.07×10^{-2}	7.8 ± 0.3
9.5 ± 0.5	1.04×10^{-2}	8.6 ± 1.0
4.4 ± 0.1	7.26×10^{-3}	8.2 ± 0.2
0.44 ± 0.1	2.07×10^{-3}	10.5 ± 2.5

Kinetics. The kinetics of the reaction under study also clearly differ from those found for $Fe(CN)_6^{4-}$ in important respects. First the $Mo(CN)_8^{4-}$ reaction is much slower. Second, Birk[3] found a much more complicated hydrogen ion dependence for the oxidation of $Fe(CN)_6^{4-}$ due to the ability of $Fe(CN)_6^{4-}$ to associate with protons. Presumably the protonation of $Fe(CN)_6^{4-}$ will inhibit interaction between that species and $HCrO_4^-$ and reduce the order in H^+ below the usual value of 2 as is, in fact, observed. Despite this inhibition the rate of reduction of chromium(VI) is considerably faster for $Fe(CN)_6^{4-}$ than for $Mo(CN)_8^{4-}$, where such inhibition is absent. $HMo(CN)_8^{3-}$ has a pK_a of 0.7 compared to 4.17 for $HFe(CN)_6^{3-}$.[7,8]

A possible explanation for the much lower rate of reaction for $Mo(CN)_8^{4-}$ is to be found in its relative weakness as a Lewis base. Let us assume that the reactions proceed by way of a preequilibrium in which the cyano complex coordinates to chromium(VI) through a -CN- bridge bond, *i.e.*

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(7) J. Jordan and G. J. Ewing, *Inorg. Chem.*, 1, 587 (1962).

(8) Part II: G. F. McKnight and G. P. Haight, Jr., submitted for publication.

$$\mathrm{Cr(VI)} + \mathrm{Mo(CN)_8}^{4-} \overset{K_1}{\rightleftharpoons} \text{complex} \tag{5}$$

$$\text{complex} \xrightarrow{k_2} \mathrm{Cr(V)} + \mathrm{Mo(CN)_8}^{3-} \tag{5a}$$

$$\text{rate} = \frac{k_2K_1[\mathrm{Cr(VI)}][\mathrm{Mo(CN)_8}^{4-}]}{1 + K_1[\mathrm{Cr(VI)}] + K_1[\mathrm{Mo(CN)_8}^{4-}] + K_1^2[\mathrm{Mo(CN)_8}^{4-}][\mathrm{Cr(VI)}]} \tag{6}$$

When other denominator terms are $\ll 1$, the observed rate constant becomes k_2K_1. If k_2 for internal electron transfer is about the same for the two proposed complexes, then the difference in K_1 for $\mathrm{Mo(CN)_8}^{4-}$ and $\mathrm{Fe(CN)_6}^{4-}$ would be correlated with the difference in rates. The difference in rates is, in fact, comparable with the difference in protonation constants for these species.

As pointed out by Birk, the King-Espenson mechanism for the oxidation of 1-equiv reducing agents by $\mathrm{HCrO_4}^-$ usually involves three one-electron-transfer steps

$$\mathrm{Cr(VI)} + \mathrm{R} \underset{k_{56}}{\overset{k_{65}}{\rightleftharpoons}} \mathrm{Cr(V)} + \mathrm{R}^+ \tag{7}$$

$$\mathrm{Cr(V)} + \mathrm{R} \overset{k_{54}}{\rightleftharpoons} \mathrm{Cr(IV)} + \mathrm{R}^+ \tag{8}$$

$$\mathrm{Cr(IV)} + \mathrm{R} \overset{k_{43}}{\rightleftharpoons} \mathrm{Cr(III)} + \mathrm{R}^+ \tag{9}$$

with the second step rate determining. This leads to the generalized rate law

$$\text{rate} = \frac{k_{54}k_{65}[\mathrm{HCrO_4}^-][\mathrm{R}]^2}{k_{56}[\mathrm{R}^+] + k_{54}[\mathrm{R}]} \tag{10}$$

If k_{54} is large, the first step is rate determining and k_{65} becomes the observed rate constant. Espenson has shown that in a number of cases the first step is second order in hydrogen ion.[2] It appears that the reaction under study is a simple case of a one-electron reduction of chromium(VI) in which the kinetics of the first step determines the rate of the reaction. In accord with Espenson's results and interpretation of other systems, the first and rate-determining step for the present reaction can be formulated as

$$\mathrm{HCrO_4}^- + \mathrm{Mo(CN)_8}^{4-} + 2\mathrm{H}^+ \rightarrow \mathrm{H_3CrO_4} + \mathrm{Mo(CN)_8}^{3-} \tag{11}$$

This raises the question as to why reduction of $\mathrm{HCrO_4}^-$ is the slow step in this case and reduction of $\mathrm{H_3CrO_4}$ is the slow step when metal ions such as Fe^{2+}, VO^{2+}, $\mathrm{NpO_2}^+$, and others are the reducing agents.

It has been suggested that outer-sphere reducing agents will somehow require that k_{56} be much smaller than k_{54},[3] since $\mathrm{Fe(dipy)_3}^{2+}$ and $\mathrm{Fe(\mathit{o}\text{-}phen)_3}^{2+}$ also give first-order kinetics in R. However, the present study presents strong circumstantial evidence for inner-sphere electron transfer *in each* of the three steps in the reaction. One then asks why reductions of $\mathrm{H_3CrO_4}$ by $\mathrm{Fe(CN)_6}^{4-}$ and $\mathrm{Mo(CN)_8}^{4-}$ are respectively much faster than the oxidations by $\mathrm{Fe(CN)_6}^{3-}$ and $\mathrm{Mo(CN)_8}^{3-}$. Also since k_{65} represents the slow step in these cases k_{54} is probably much larger than k_{65} as well as k_{56}. In the case of the cyanometalates an alternative mechanism involving inner-sphere transfer may be written in which formation of Cr^{4+} is rate determining, *i.e.*

$$2\mathrm{H}^+ + \mathrm{HCrO_4}^- + \mathrm{Mo(CN)_8}^{4-} \rightleftharpoons \mathrm{H_3CrO_4\text{-}NC\text{-}Mo(CN)_7}^{5-} \tag{12}$$

$$\mathrm{H_3O_4CrNCMo(CN)_7}^{5-} + \mathrm{Mo(CN)_8}^{4-} \rightarrow \mathrm{Cr^{IV}(Mo(CN)_8)_2}^{2-} \tag{13}$$

$$\text{rate} = \frac{k_{13}k_{12}[\mathrm{HCrO_4}^-][\mathrm{Mo(CN)_8}^{4-}]^2[\mathrm{H}^+]^2}{k_{-12} + k_{13}[\mathrm{Mo(CN)_8}^{4-}]}$$

If $k_{-12} \ll k_{13}[\mathrm{Mo(CN)_8}^{4-}]$, then

$$\text{rate} = k_{12}[\mathrm{HCrO_4}^-][\mathrm{Mo(CN)_8}^{4-}][\mathrm{H}^+]^2 \tag{14}$$

in agreement with experiment. $\mathrm{Mo(CN)_8}^{3-}$ would not inhibit the reaction in this mechanism. In any case association of cyanometalates with Cr(VI) resulting in inner-sphere electron transfer appears to be plausible. The bis(octacyanomolybdato)chromate(IV) complex would be a logical precursor of the polycoordinated chromate(III) product observed.

One-equivalent reducing agents now appear divided into three categories: (a) metal cations which form O-bridged complexes to chromium(VI) and give the kinetics of eq 10, (b) cyanometalates which coordinate directly to Cr(VI) and Cr(V) through CN^- bridges and give the kinetics of eq 14, and (c) outer-sphere reagents such as $\mathrm{Fe(dipy)_3}^{2+}$, $\mathrm{Fe(\mathit{o}\text{-}phen)_3}^{2+}$, and $\mathrm{Fe(cp)_2}$ which conform to

$$\text{rate} = k_{15}[\mathrm{HCrO_4}^-][\mathrm{Fe(II)}] \tag{15}$$

Data on (c) systems are not at present able to distinguish the mechanisms of eq 7-9 from those of eq 12 and 13.

The form of the rate law for inner-sphere one-electron reductions of chromium(VI) thus appears to depend on two effects: (a) the reorganization energy needed to change four-coordinate chromium(V) and/or chromium(VI) to six-coordinate chromium(IV) and (b) the relative abilities of reducing agents to associate with chromium(VI) enroute to the activated state.

If effect (a) is dominant, the second step (eq 8) will be rate determining, giving a second-order term in reducing agent. If coordination of reducing agent to chromium(VI) is followed by fast reaction of the resulting complex with reducing agent, the first step may become the slow step in the reaction.

Registry No. $\mathrm{K_4Mo(CN)_8}$, 17456-18-7; $\mathrm{Mo(CN)_8}^{3-}$, 17845-99-7; $\mathrm{Mo(CN)_8}^{4-}$, 17923-49-8; $\mathrm{HCrO_4}^-$, 15596-54-0.

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