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A Kinetic Study of the Osmium(VIII) Catalyzed Reduction of Octacyanomolybdate(V) and Octacyanotungstate(V) Ions by Selenium(IV) in an Alkaline Medium

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The kinetics of the osmium(VIII) catalyzed reduction of octacyanomolybdate(V) and octacyanotungstate(V) ions by Se(IV) have been studied in an alkaline medium. The reaction is first order with respect to $\mathrm{M(CN)}_8^{3-}$ *ions (M = Mo, W) and the osmium(VIII) catalyst. The second order reaction rate constants are* 4.30×10^4 M^{-1} min^{-1} *and* 2.60×10^3 M^{-1} sec^{-1} *at 293 K respectively. A reaction mechanism is proposed.*

Introduction

The kinetics of the osmium(VIII) catalyzed reduction of the hexacyanoferrate(III) ion by selenium(IV) [1] and tellurium(IV) [2] have been investigated. Osmium(VIII) is reported to be an efficient catalyst for such reductions in an alkaline medium [3, 4]. The oxidation of selenium(I) to selenium(VI) by the hexacyanoferrate(III) ion was found to be first order with respect to [Se(IV)], while that of tellurium(IV) to tellurium(V) was independent of [Te(IV)]. Both reactions were first order with respect to hydroxyl ion and catalyst concentrations. The kinetics of the osmium(VIII) catalyzed oxidation of selenium(IV) by octacyanomolybdate(V) and octacyanotungstate(V) ions in alkaline media have been investigated to compare the redox properties of the various complex cyanides.

Experimental

$\mathrm{K_4Mo(CN)_8 \cdot 2H_2O}$, $\mathrm{K_4W(CN)_8 \cdot 2H_2O}$, $\mathrm{Cs_3Mo(CN)_8 \cdot 2H_2O}$ and $\mathrm{Cs_3W(CN)_8 \cdot 2H_2O}$ were prepared as described by Leipoldt *et al.* [5–7]. The latter two compounds were obtained pure after recrystallization and used as primary standards. Analytical grade $\mathrm{Na_2SeO_3}$ was used as source of Se(IV). All other reagents were of analytical grade and redistilled water was used throughout. Reactions were carried out in a darkened laboratory as solutions of $\mathrm{Cs_3Mo(CN)_8}$ and $\mathrm{Cs_3W(CN)_8}$ are sensitive to light.

The kinetics of the oxidation of Se(IV) by $\mathrm{Mo(CN)}_8^{3-}$ ions were followed by measuring the decrease in $[\mathrm{Mo(CN)}_8^{3-}]$ at 390 nm using a Pye Unicam SP1700 spectrophotometer. The extinction coefficients of the $\mathrm{Mo(CN)}_8^{3-}$ and $\mathrm{Mo(CN)}_8^{4-}$ ions were taken as 1400 and 140 M^{-1} cm^{-1} respectively. The kinetics of the $\mathrm{W(CN)}_8^{3-}$ reaction were followed by measuring the decrease in $[\mathrm{W(CN)}_8^{3-}]$ at 357 nm using a Durrum-D110 stopped flow spectrophotometer. In both cases the temperature was controlled to within 0.1 K.

The desired buffer solutions at constant ionic strength, for varying pH, were prepared by mixing suitable volumes of $M/15$ $\mathrm{Na_2CO_3}$ and 0.2 M $\mathrm{NaHCO_3}$. An Orion pH-meter model 701, was used for pH measurements.

The stoichiometry of both reactions was determined volumetrically by oxidation of the product $\mathrm{Mo(CN)}_8^{4-}$ and $\mathrm{W(CN)}_8^{4-}$ ions with standard Ce(IV) solution using N-phenylantranilic acid as indicator.

Results

The pseudo first order plots of log $[\mathrm{M(CN)}_8^{3-}]$ (M = Mo, W) against time were linear for an excess of Se(IV). The observed second order rate constants for varying $[\mathrm{M(CN)}_8^{3-}]$, $[\mathrm{M(CN)}_8^{4-}]$, [Se(IV)], [Os(VIII)] and $[\mathrm{Na}^+]$ at constant $[\mathrm{OH}^-]$ and temperature are given in Tables I and II.

The results in Tables I and II show that both reactions are first order with respect to $[\mathrm{M(CN)}_8^{3-}]$ and [Os(VIII)]. In both cases the reaction is dependent on $[\mathrm{OH}^-]$ at low $[\mathrm{OH}^-]$ (below 0.015 M, Table III) and independent of $[\mathrm{OH}^-]$ at $[\mathrm{OH}^-]$ higher than 0.015 M. Varying $[\mathrm{Mo(CN)}_8^{4-}]$ has an insignificant effect upon the reaction rate, while increasing $[\mathrm{W(CN)}_8^{4-}]$ causes a decrease in reaction rate. Both reactions show an increase in rate with increasing ionic strength. According to these experimental results the rate equation is given by:

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TABLE I. Rate of Reduction of $Mo(CN)_8^{3-}$ by Se(IV). T = 293 K, $[OH^-]$ = 0.05 *M*.

[Mo(V)] × 10^4 *M*	[Se(IV)] × 10^3 *M*	[Os(VIII)] × 10^7 *M*	$[Na^+]$ *M*	k_{obs} × 10^{-4} M^{-1} min^{-1}
2.5	2.5	4.0	0.1	5.03
3.0	2.5	4.0	0.1	4.62
3.5	2.5	4.0	0.1	4.61
4.0	2.5	4.0	0.1	4.52
4.5	2.5	4.0	0.1	4.47
5.0	2.5	4.0	0.1	4.23
5.0	2.0	4.0	0.1	4.50
5.0	3.0	4.0	0.1	4.41
5.0	4.0	4.0	0.1	4.12
5.0	6.0	4.0	0.1	4.41
5.0	8.0	4.0	0.1	4.35
5.0	10.0	4.0	0.1	4.30
5.0	2.5	2.5	0.1	4.60
5.0	2.5	3.0	0.1	4.55
5.0	2.5	3.5	0.1	4.58
5.0	2.5	4.0	0.1	4.45
5.0	2.5	4.5	0.1	4.43
5.0	2.5	5.0	0.1	4.38
5.0	2.5	4.0	0.1	4.28
5.0	2.5	4.0	0.2	4.77
5.0	2.5	4.0	0.3	5.84
5.0	2.5	4.0	0.4	6.66
5.0	2.5	4.0	0.5	7.08
5.0	2.5	4.0	0.6	8.90
5.0	2.5	4.0	0.1	4.64[a]
5.0	2.5	4.0	0.1	4.44[b]
5.0	2.5	4.0	0.1	4.40[c]
5.0	2.5	4.0	0.1	4.32[d]
5.0	2.5	4.0	0.1	4.40[e]
5.0	2.5	4.0	0.1	4.67[f]
5.0	2.5	4.0	0.1	4.47[g]

a, b, c, d, e, f and g are at 0.00000, 0.000025, 0.000050, 0.000075, 0.00010, 0.00015 and 0.00020 *M* $M(CN)_8^{4-}$.

TABLE II. Rate of Reduction of $W(CN)_8^{3-}$ by Se(IV) T = 293 K, $[OH^-]$ = 0.1 *M*.

[W(V)] × 10^4 *M*	[Se(IV)] × 10^2 *M*	[Os(VIII)] × 10^5 *M*	$[Na^+]$ *M*	k_{obs} × 10^{-3} M^{-1} sek^{-1}
2.5	2.0	5.0	0.1	3.34
3.0	2.0	5.0	0.1	3.33
3.5	2.0	5.0	0.1	3.16
4.0	2.0	5.0	0.1	2.98
4.5	2.0	5.0	0.1	2.67
5.0	2.0	5.0	0.1	2.54
5.0	1.2	5.0	0.1	2.79
5.0	1.4	5.0	0.1	2.45
5.0	1.6	5.0	0.1	2.70
5.0	1.8	5.0	0.1	2.62
5.0	2.0	5.0	0.1	2.53
5.0	2.2	5.0	0.1	2.53
5.0	2.0	4.0	0.1	2.51
5.0	2.0	5.0	0.1	2.53
5.0	2.0	6.0	0.1	2.71
5.0	2.0	7.0	0.1	3.01

(continued on opposite page)

TABLE II. *(continued)*

[W(V)] × 10^4 *M*	[Se(IV)] × 10^2 *M*	[Os(VIII)] × 10^5 *M*	[Na$^+$] *M*	k_{obs} × 10^{-3} M^{-1} sek^{-1}
5.0	2.0	8.0	0.1	3.31
5.0	2.0	10.0	0.1	3.00
5.0	2.0	5.0	0.1	3.10
5.0	2.0	5.0	0.2	2.60
5.0	2.0	5.0	0.3	2.63
5.0	2.0	5.0	0.4	2.67
5.0	2.0	5.0	0.5	2.97
5.0	2.0	5.0	0.6	3.10
5.0	2.0	5.0	0.1	2.53[a]
5.0	2.0	5.0	0.1	2.03[b]
5.0	2.0	5.0	0.1	1.92[c]
5.0	2.0	5.0	0.1	1.70[d]
5.0	2.0	5.0	0.1	1.38[e]
5.0	2.0	5.0	0.1	1.08[f]
5.0	2.0	5.0	0.1	0.87[g]

a, b, c, d, e, f and g are at 0.00000, 0.000025, 0.000050, 0.000075, 0.00010, 0.00015 and 0.00020 *M* $M(CN)_8^{4-}$.

TABLE III. Rate of Reduction of $Mo(CN)_8^{3-}$ by Se(IV) Varying the pH.

$[Mo(CN)_8^{3-}] = 5 \times 10^{-4}$ *M*, $[Se(IV)] = 2.5 \times 10^{-3}$ *M*

$[Os(VIII)] = 2 \times 10^{-5}$ *M*, T = 293K $[Na^+] = 0.1$*M*

pH	$k_{obs} \times 10^{-4}$ M^{-1} min^{-1}
10.85	1.397
10.75	1.137
10.66	0.996
10.58	0.796
10.50	0.696

$$\text{Rate} = k[M(CN)_8^{3-}]\,[OH^-]\,[OS(VIII)] \qquad (1)$$

The stoichiometry determinations indicate that the overall reactions are given by:

$$2\,M(CN)_8^{3-} + Se(IV) \rightarrow 2\,M(CN)_8^{4-} + Se(VI)$$

Discussion

The OH$^-$ dependence indicates that the following equilibrium exists:

$$OsO_4 + OH^- \underset{}{\overset{K}{\rightleftharpoons}} HOsO_5^- \qquad (2)$$

The uncatalyzed oxidation of Se(IV) by $M(CN)_8^{3-}$ ions does not proceed at all. Thus we propose that the Os(VIII) catalyzed reactions proceed via the following complex formation:

$$HOsO_5^- + M(CN)_8^{3-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{complex} \qquad (3)$$

The formation of such a complex has been reported [8].

The subsequent course of the reactions can be represented as follows:

$$\text{Complex} + Se(IV) \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Se(V) + M(CN)_8^{4-} + HOsO_5^- \qquad (4)$$

$$Se(V) + M(CN)_8^{3-} \xrightarrow{k_4} Se(VI) + M(CN)_8^{4-} \qquad (5)$$

The formation of the complex in reaction (3) is slow and thus rate determining. The complex oxidizes the Se(IV) to Se(V) and regenerates Os(VIII). The existence of the Se(V) intermediate has been reported [9, 10]. The Se(V) is rapidly oxidized to Se(VI) by another $M(CN)_8^{3-}$ ion.

According to the proposed mechanism the following rate equation is obtained:

$$\text{Rate} = \frac{2k_2k_3k_4[M(CN)_8^{3-}]^2[Se(IV)][HOsO_5^-]}{k_{-2}k_{-3}[M(CN)_8^{4-}]\,[HOsO_5^-] + k_{-2}k_4 \times [M(CN)_8^{3-}] + k_3k_4[M(CN)_8^{3-}][Se(IV)]} \qquad (6)$$

Because reaction (3) is slow (rate determining step), k_{-2} and k_{-3} are much smaller than k_4 and $k_{-2}k_{-3}$ $[M(CN)_8^{4-}]$ $[HOsO_5^-]$ and k_{-2} $k_4[M(CN)_8^{3-}]$ are neglegible. Thus equation (6) simplifies to:

$$\text{Rate} = 2\,k_2[M(CN)_8^{3-}]\,[HOsO_5^-] \qquad (7)$$

Equation (7) suggests a reaction between two negatively charged species explaining the observed positive salt effect.

The following relation can be derived from equation (2):

$$[OsO_4] = \frac{[HOsO_5^-]}{K[OH^-]} \qquad (8)$$

If $[OsO_4] + [HOsO_5^-]$ is represented by $[Os(VIII)]_T$, substitution of the value of $[OsO_4]$ in equation (8) yields the following:

$$[Os(VIII)]_T = [HOsO_5^-]\,(1 + 1/K[OH^-])$$

Therefore

$$[HOsO_5^-] = \frac{K[OH^-]\,[Os(VIII)]_T}{1 + K[OH^-]} \qquad (9)$$

Substitution of this value of $[HOsO_5^-]$ in equation (7) yields the following rate equation:

$$\text{Rate} = \frac{2k_2K[M(CN)_8^{3-}]\,[Os(VIII)]_T[OH^-]}{1 + K[OH^-]} \qquad (10)$$

Equation (10) is in agreement with the experimental results. It also explains the first order dependence of $[OH^-]$ at low $[OH^-]$ (<0.01 *M*) and independence of $[OH^-]$ at high $[OH^-]$ (>0.015 *M*).

From equation (10) it follows that

$$k_{obs} = \frac{2k_2K[OH^-]}{1 + K[OH^-]}$$

Thus:

$$\frac{1}{k_{obs}} = \frac{1}{2k_2K[OH^-]} + \frac{1}{2k_2} \qquad (11)$$

According to equation (11) a plot of $1/k_{obs}$ against $1/[OH^-]$ should be linear with gradient $1/2k_2K$ and intercept $1/2k_2$. The quotient of the intercept and gradient yields the value of K and the inverse of the intercept the value of k_{obs} at high $[OH^-]$.

The effect of varying pH, over the range 10.50 to 10.85, on the reduction rate of $Mo(CN)_8^{3-}$ is given in Table III. A plot of $1/k_{obs}$ against $1/[OH^-]$ (values from Table 3) was found to be linear. By means of a least squares data fit the intercept and gradient were determined as 1.249×10^{-5} *M* min and 4.179×10^{-8} M^2 min respectively. The equilibrium constant, K, in reaction (2) was thus determined as 298.9 M^{-1}. This is in very good agreement with the value of 301.6 M^{-1} obtained for the reaction between $Mo(CN)_8^{3-}$ and Te(IV) [11]. The value of k_{obs} (8.008×10^4 M^{-1} min^{-1}) is in agreement with the values in Table I.

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References

1 V. K. Jindal, M. C. Agrawal, S. P. Mushran, *J. Chem. Soc. A*, 622 (1971).
2 V. K. Jindal, M. C. Agrawal, S. P. Mushran, *J. Inorg. Nucl. Chem.*, *33*, 2469 (1971).
3 F. Solymosi, *Magyar Kem. Folyiorat*, *63*, 294 (1975).
4 F. Solymosi, *Naturwissenschaften*, *44*, 374 (1957).
5 J. G. Leipoldt, L. D. C. Bok, P. J. Cilliers, *Z. Anorg. Allg. Chem.*, *407*, 350 (1974).
6 J. G. Leipoldt, L. D. C. Bok, P. J. Cilliers, *Z. Anorg. Allg. Chem.*, *409*, 343 (1974).
7 L. D. C. Bok, J. G. Leipoldt, S. S. Basson, *Z. Anorg. Allg. Chem.*, *415*, 81 (1975).
8 F. Solymosi, J. Csik, *Chemist–Analyst,*, *49*, 12 (1960).
9 M. C. Agrawal, R. K. Shinghal, S. P. Mushran, *Z. Phys. Chem.*, 112 (1968).
10 R. K. Singhal, M. C. Agrawal, S. P. Mushran, *J. Indian Chem. Soc.*, *46*, 1025 (1969).
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