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

J. G. LEIPOLDT*, C. R. DENNIS, A. J. van WYK and L. D. C. BOK
Department of Chemistry, University of the Orange Free State, Bloemfontein, Republic of South Africa

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The kinetics of the osmium(VIII) catalyzed oxidation of Te(IV) by octacyanomolybdate(V) and octacyanotungstate(V) ions have been investigated in an alkaline medium. The reactions are first order with respect to $M(CN)_8^{3-}$ ion (M = Mo, W) and catalyst concentrations. The second order reaction rate constants are 2.756×10^3 M^{-1} sec^{-1} and 5.221×10^2 M^{-1} sec^{-1} at 298 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] as well as the osmium(VIII) catalyzed reduction of the octacyanomolybdate(V) and octacyanotungstate(V) ions by selenium(IV) [3] have been investigated. Osmium(VIII) is reported to be an efficient catalyst for such reductions in an alkaline medium [4, 5]. The oxidation of selenium(IV) 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(VI) was independent of [Te(IV)]. The oxidation of selenium(IV) to selenium(VI) by both octacyanomolybdate(V) and octacyanotungstate(V) ions was independent of [Se(IV)]. All the investigated reactions were first order with respect to hydroxyl ion and catalyst concentrations.

Experimental

$K_4Mo(CN)_8 \cdot 2H_2O$, $K_4W(CN)_8 \cdot 2H_2O$, $Cs_3Mo(CN)_8 \cdot 2H_2O$ and $Cs_3W(CN)_8 \cdot 2H_2O$ were prepared as described by Leipoldt *et al.* [6–8]. The latter two compounds were obtained pure after recrystallization and used as primary standards. Analytical grade Na_2TeO_3 was used as source of Te(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 $Cs_3Mo(CN)_8$ and $Cs_3W(CN)_8$ are sensitive to light.

The kinetics of the oxidation of Te(IV) by $Mo(CN)_8^{3-}$ and $W(CN)_8^{3-}$ ions was followed by measuring the decrease in $[Mo(CN)_8^{3-}]$ and $[W(CN)_8^{3-}]$ at 390 nm and 357 nm respectively using a Durrum-D110 stopped flow spectrophotometer. 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 0.067 *M* Na_2CO_3 and 0.2 *M* $NaHCO_3$. An Orion pH-meter model 701 was used for pH measurements.

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

Results

The pseudo first order plots of $\log[M(CN)_8^{3-}]$ (M = Mo, W) against time were linear for an excess of Te(IV). The observed second order rate constants for varying $[M(CN)_8^{3-}]$, $[M(CN)_8^{4-}]$, [Te(IV)], [Os(VIII)] and $[Na^+]$ at constant $[OH^-]$ 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 $[M(CN)_8^{3-}]$ and [Os(VIII)]. In both cases the reaction is dependent on $[OH^-]$ at low $[OH^-]$ (below 0.015 *M*, Table III) and independent of $[OH^-]$ at concentrations higher than 0.015 *M*. In both reactions an increase in $[M(CN)_8^{4-}]$ causes a decrease in reaction rate, while an increase in ionic strength shows an increase in reaction rate. According to these experimental results the rate equation is given by:

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

The stoichiometry determinations indicate that the overall reactions are:

$$2M(CN)_8^{3-} + Te(IV) \longrightarrow 2M(CN)_8^{4-} + Te(VI)$$

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*Author to whom correspondence should be addressed.

TABLE I. Rate of Reduction of the $Mo(CN)_8^{3-}$ Ion by Te(IV). $[OH^-] = 0.050\ M$, T = 298 K.

$[Mo(CN)_8^{3-}]$ × 10^4 *M*	[Te(IV)] × 10^3 *M*	[Os(VIII)] × 10^5 *M*	$[Na^+]$ × 10 *M*	$k_{obs} \times 10^{-3}$ M^{-1} sec^{-1}
2.5	5.0	7.0	1.0	3.153
3.0	5.0	7.0	1.0	2.809
3.5	5.0	7.0	1.0	2.719
4.0	5.0	7.0	1.0	2.773
4.5	5.0	7.0	1.0	2.478
5.0	5.0	7.0	1.0	2.751
5.0	3.0	7.0	1.0	3.261
5.0	4.0	7.0	1.0	2.641
5.0	5.0	7.0	1.0	2.742
5.0	6.0	7.0	1.0	3.153
5.0	7.0	7.0	1.0	2.599
5.0	8.0	7.0	1.0	2.741
5.0	5.0	5.0	1.0	2.617
5.0	5.0	6.0	1.0	2.695
5.0	5.0	7.0	1.0	2.720
5.0	5.0	8.0	1.0	2.628
5.0	5.0	9.0	1.0	2.759
5.0	5.0	10.0	1.0	2.784
5.0	5.0	7.0	1.0	2.734
5.0	5.0	7.0	2.0	2.745
5.0	5.0	7.0	3.0	2.767
5.0	5.0	7.0	4.0	2.782
5.0	5.0	7.0	5.0	2.901
5.0	5.0	7.0	6.0	3.214
5.0	5.0	7.0	1.0	2.716[a]*
5.0	5.0	7.0	1.0	2.047[b]
5.0	5.0	7.0	1.0	1.389[c]
5.0	5.0	7.0	1.0	1.017[d]
5.0	5.0	7.0	1.0	0.660[e]
5.0	5.0	7.0	1.0	0.454[f]

*a, b, c, d, e and f are at 0.00000, 0.000025, 0.000050, 0.000075, 0.000100 and 0.000125 *M* $Mo(CN)_8^{4-}$ respectively.

TABLE II. Rate of Reduction of the $W(CN)_8^{3-}$ Ion by Te(IV). $[OH^-] = 0.050\ M$, T = 298 K.

$[W(CN)_8^{3-}]$ × 10^4 *M*	[Te(IV)] × 10^5 *M*	[Os(VIII)] × 10^5 *M*	$[Na^+]$ × 10 *M*	$k_{obs} \times 10^{-2}$ M^{-1} sec^{-1}
2.5	5.0	10.0	1.0	6.906
3.0	5.0	10.0	1.0	6.606
3.5	5.0	10.0	1.0	5.538
4.0	5.0	10.0	1.0	5.508
4.5	5.0	10.0	1.0	5.429
5.0	5.0	10.0	1.0	5.354
5.0	3.0	10.0	1.0	5.182
5.0	4.0	10.0	1.0	5.152
5.0	5.0	10.0	1.0	5.078
5.0	6.0	10.0	1.0	5.130
5.0	7.0	10.0	1.0	4.652
5.0	8.0	10.0	1.0	4.512
5.0	5.0	4.0	1.0	5.000
5.0	5.0	6.0	1.0	4.865
5.0	5.0	7.0	1.0	4.627
5.0	5.0	8.0	1.0	4.883

(continued on facing page)

TABLE II. *(continued)*

$[W(CN)_8^{3-}]$ $\times 10^4$ *M*	[Te(IV)] $\times 10^5$ *M*	[Os(VIII)] $\times 10^5$ *M*	$[Na^+]$ $\times 10$ *M*	$k_{obs} \times 10^{-2}$ M^{-1} sec^{-1}
5.0	5.0	9.0	1.0	4.992
5.0	5.0	10.0	1.0	5.033
5.0	5.0	10.0	1.0	5.002
5.0	5.0	10.0	2.0	5.007
5.0	5.0	10.0	3.0	5.050
5.0	5.0	10.0	4.0	5.091
5.0	5.0	10.0	5.0	5.107
5.0	5.0	10.0	6.0	5.150
5.0	5.0	10.0	1.0	5.181[a*]
5.0	5.0	10.0	1.0	2.785[b]
5.0	5.0	10.0	1.0	1.883[c]
5.0	5.0	10.0	1.0	1.643[d]
5.0	5.0	10.0	1.0	1.059[e]
5.0	5.0	10.0	1.0	0.691[f]

*a, b, c, d, e and f are at 0.00000, 0.000025, 0.000050, 0.000075, 0.000100 and 0.000125 *M* $W(CN)_8^{4-}$ respectively.

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

$[Mo(CN)_8^{3-}] = 5 \times 10^{-4}$ *M*;
$[Te(IV)] = 5 \times 10^{-3}$ *M*;
$[Na^+] = 0.1$ *M*;
$[Os(VIII)] = 6 \times 10^{-5}$ *M*;
T = 298 K

pH	$k_{obs} \times 10^{-2}$ M^{-1} sec^{-1}
10.92	3.333
10.85	2.873
10.75	2.563
10.66	2.058
10.58	1.737
10.48	1.425
10.28	0.926

Discussion

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

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

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

$$HOsO_5^- + M(CN)_8^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Complex} \quad (3)$$

The formation of such a complex has been reported [9].

The subsequent course of the reactions is the following:

$$\text{Complex} + Te(IV) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Te(V) + M(CN)_8^{4-} + HOsO_5^- \quad (4)$$

$$Te(V) + M(CN)_8^{3-} \xrightarrow{k_3} Te(VI) + M(CN)_8^{4-} \quad (5)$$

The formation of the complex in reaction (3) is slow and thus rate determining. The complex oxidizes the Te(IV) to Te(V) and regenerates Os(VIII). The existence of the Te(V) intermediate has been reported [10, 11]. The Te(V) is rapidly oxidized to Te(VI) by another $M(CN)_8^{3-}$ ion.

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

$$\text{Rate} = \frac{2k_1k_2k_3[M(CN)_8^{3-}]^2[Te(IV)][HOsO_5^-]}{k_{-1}k_{-2}[M(CN)_8^{4-}][HOsO_5^-] + k_{-1}k_3[M(CN)_8^{3-}] + k_2k_3[M(CN)_8^{3-}][Te(IV)]}$$

Because reaction (3) is slow (rate determining step), k_{-1} and k_{-2} are much smaller than k_3 and $k_{-1}k_{-2}[M(CN)_8^{4-}][HOsO_5^-]$ and $k_{-1}k_3[M(CN)_8^{3-}]$ are negligible. Thus equation (6) simplifies to:

$$\text{Rate} = 2k_1[M(CN)_8^{3-}][HOsO_5^-] \quad (7)$$

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

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:

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

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:

$$\text{Rate} = \frac{2k_1K[M(CN)_8^{3-}]\,[Os(VIII)]_T[OH^-]}{1 + K[OH^-]} \qquad (10)$$

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

From equation (10) it follows that

$$k_{obs} = \frac{2k_1K[OH^-]}{1 + K[OH^-]}$$

Thus

$$\frac{1}{k_{obs}} = \frac{1}{2k_1K[OH^-]} + \frac{1}{2k_1} \qquad (11)$$

According to equation (11) a plot of $1/k_{obs}$ against $1/[OH^-]$ should be linear with gradient $1/2k_1K$ and intercept $1/2k_1$. 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 the pH over the range 10.28 to 10.92 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 III) was found to be linear. By means of a least squares data fit the intercept and gradient was determined as 5.866×10^{-4} *M* sec and 1.945×10^{-6} M^2 sec respectively.

The equilibrium constant, K, in reaction (2) was thus determined as 301.6 M^{-1}. This is in very good agreement with the value of 298.9 M^{-1} obtained for the reaction between $Mo(CN)_8^{3-}$ and Se(IV) [3]. The value of k_{obs} (1.705×10^3 M^{-1} min^{-1}) is in agreement with the values in Table I.

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