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The Reaction of $Os(CN)_6^{4-}$ and its Iron Family Analogues with MnO_4^- in Acidic Media

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In the recent study of the reaction of MnO_4^- with $Ru(CN)_6^{4-}$ [1] it was observed that the various forms of the Ru(II) ions ($Ru(CN)_6^{4-}$, $HRu(CN)_6^{3-}$, and $H_2Ru(CN)_6^{2-}$) present in acidic perchlorate media were considerably less reactive with Mn(VII) than the corresponding Fe(II) complexes [2]. The study also showed that the monoprotonated form, $HRu(CN)_6^{3-}$, was considerably more reactive than both $Ru(CN)_6^{4-}$, and $H_2Ru(CN)_6^{2-}$.

We wish to report a study of the permanganate ion with the third member of the iron family of hexacyanometallates, hexacyanoosmiate(II).

Experimental

The samples of $K_4Os(CN)_6 \cdot H_2O$ used was obtained as a gift from Dr. William Waltz, Univ. of Saskatchewan and purchased from Pfaltz and Bauer Chemicals. Both samples gave identical kinetic results, although the sampel from Waltz was of higher purity. Weighed samples were dissolved in solutions of the desired acidity and ionic strength (maintained by $NaClO_4$ and/or $LiClO_4$). Solutions in which the pH > 1.5 were prepared using buffers consisting of $LiClO_4/H_3PO_4$ or $LiClO_4/H_2PO_4^-$ solutions ($\mu = 1.0$).

Solutions were analyzed for $Os(CN)_6^{4-}$ by oxidation to $Os(CN)_6^{4-}$ with $XeO_3(aq)$ or MnO_4^- standardized solutions. Reactions with Ce(IV) gave low and unreliable results. Spectrophotometric analysis gave molar absorption coefficients values for $Os(CN)_6^{3-}$ of $\epsilon = 1625 \pm 43$ M^{-1} cm^{-1} ($\lambda = 328$ nm) and $\epsilon = 1450 \pm 52$ $M^{-1} \cdot cm^{-1}$ ($\lambda = 400$ nm) in good agreement with literature [3–5].

Although $Os(CN)_6^{4-}$ is not reported to be photochemically active [6], all solutions were used immediately upon dissolving and were handled in subdued or red-light conditions. Solutions of $Os(CN)_6^{4-}$ were found to be stable to oxidation upon standing in the dark in 0.1 M $HClO_4$ for several days.

The pH was measured with a Leed and Northrup pH meter and calibrated against standard buffer solutions in the appropriate pH region.

Results and Discussion

The progress of the reaction was followed using stopped-flow techniques at 400 nm where the change in absorbance is due to the production of Os(III). Neither MnO_4^- or Os(II) absorb appreciable at this wavelength. The ratio, $[Os(III)]_\infty/[MnO_4^-]_o = 4.94 \pm 0.12$, was found to hold in accordance with eqn.1

$$Mn(VII) + 5\ Os(II) \xrightarrow{H^+} Mn^{2+} + 5\ Os(III) \qquad (1)$$

The production of Os(III) under pseudo-first order conditions ($[Os(II)]_o \geqslant 25\ [MnO_4^-]_o$) was well

TABLE I. Rate Constants for the MnO_4^- Os(II) Reaction.[a]

$[Os(CN)_6^{4-}]_o$, 10^3 M	$[MnO_4^-]_o$ 10^5 M	$[H^+]$, M		10^{-3}, k_{obsd} M^{-1} sec^{-1}
1.69	4.32	Na^+	0.21	3.40 ± 0.25
	2.16		0.21	3.48 ± 0.18
1.57	5.40	Li^+/Na^+	0.26	3.00 ± 0.11
	4.32			3.00 ± 0.13
	3.24			3.14 ± 0.08
	2.16			3.00 ± 0.13
	1.08			3.32 ± 0.28
0.54	2.16	Li^+	0.21	3.78 ± 0.28
	1.08		0.15	4.30 ± 0.34

[a] T = 25.0 °C, $\mu = 1.0$.

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TABLE II. k_{obsd} as a Function of Hydrogen Ion Concentration.[a]

$[H^+]$, *M*	$-\log [H^+]$	10^{-3}, k_{obsd} M^{-1} sec^{-1}	$[H^+]$, *M*	$-\log [H^+]$	10^{-3}, k_{obsd} M^{-1} sec^{-1}
	5.35[b]	17.5	0.26	0.59	3.00[d]
	3.80[b]	17.2	0.26	0.59	3.00
	2.50[b]	16.0	0.27	0.57	3.38[c]
0.026	1.59	10.2	0.30	0.52	2.54[d]
0.046	1.34	9.41	0.42	0.38	2.11
0.066	1.18	7.80[d]	0.46	0.34	1.90
0.105	0.98	5.18[d]	0.51	0.29	1.80
0.107	0.97	4.98	0.58	0.24	1.62
0.144	0.84	5.10[d]	0.58	0.24	1.75
0.15	0.82	4.00[c]	0.66	0.18	1.88[c]
0.18	0.74	4.08[d]	0.70	0.15	1.83[c]
0.20	0.70	3.96	0.72	0.14	1.80[c]
0.21	0.68	3.74[c]	0.80	0.097	1.57[c]
0.21	0.68	3.40[c]	0.82	0.086	1.56[c]
0.24	0.62	3.48			
0.24	0.62	3.24[d]			

[a] T = 25.0 °C, μ = 1.0, H^+/Li^+ perchlorate mixture. [b] pH maintained with appropriate phosphate/$HClO_4$ mixture. [c] Na^+. [d] Li^+/Na^+ perchlorate mixture.

behaved and showed no deviation from the expression $d[Os(III)]/dt = 5k'[MnO_4^-]$. The second order rate constant, k_{obsd}, was obtained from $k'/[Os(II)]_0$. The results of the concentration dependence are presented in Table I.

Variation of the reaction hydrogen ion concentration showed k_{obsd} to be constant in the high acid region ($[H^+]$ = 0.9 *M* to 0.5 *M*), to rise rapidly between pH ~ 0.2 to 2 and again become invariant with further decreasing $[H^+]$. The behaviour is due to coupled pH-dependent reactions [7]. A set of equilibria,

$$H_2Os(CN)_6^{2-} \rightleftharpoons H^+ + HOs(CN)_6^{3-} \qquad K_3$$

$$HOs(CN)_6^{3-} \rightleftharpoons H^+ + Os(CN)_6^{4-} \qquad K_4$$

similar to those of $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$ is expected for the osmium analogue [8, 1].

The rate law

$$d[Os(CN)_6^{3-}]/dt = (k_0 + k_1K_4[H^+] + k_2K_3K_4[H^+]^2)\text{-}[Os(CN)_6^{4-}][MnO_4^-]$$

can be written where

$$MnO_4^- + Os(CN)_6^{4-} \xrightarrow{k_0} \text{products}$$

$$MnO_4^- + HOs(CN)_6^{3-} \xrightarrow{k_1} \text{products}$$

$$MnO_4^- + H_2Os(CN)_6^{2-} \xrightarrow{k_2} \text{products}$$

In this experiments, like the $Ru(CN)_6^{4-}$ study, the equilibrium constants for the protonation of $Os(CN)_6^{4-}$ have not been reported. However using a pattern similar to the decrease in the equilibrium constants for the appropriate ions from Fe(II) to Ru(II) to Os(II) as an initial estimation, the solution of the equation

$$k_{obsd} = \frac{k_2[H^+]^2 + k_1K_3[H^+] + k_0K_4K_3}{[H^+] + K_3[H^+] + K_4K_3}$$

yielded values for the equilibrium constants of $K_4(HOs(CN)_6^{3-}) \cong 0.002_2$ *M* and $K_3(H_2Os(CN)_6^{2-}) \cong 0.003_1$ *M*. The rate constants were $k_0 = 33 \times 10^3$ M^{-1} sec^{-1}, $k_1 = 18 \times 10^3$ M^{-1} sec^{-1} and $k_2 = 7.0 \times 10^3$ M^{-1} sec^{-1}.

Ionic strength studies at pH = 3.8 and $[H^+]$ = 0.58 *M*, showed an increase in k_{obsd} with increasing μ, supporting the idea that reaction is between MnO_4^- and various ions of $Os(CN)_6^{4-}$. The reaction between MnO_4^- and $Mo(CN)_8^{4-}$ or $W(CN)_8^{4-}$ did not exhibit an ionic strength dependence. The major reaction pathway in these reactions was interpreted to be between $HMnO_4$ and the reductant ion.

The kinetic behaviour of the hexacyanometallates of the iron family with MnO_4^- show a greater similarity in the rate constants between the corresponding Fe(II) [2] and Os(II) ions than with the Ru(II) species. It was observed that the ions of the Ru(II) react much more slowly with MnO_4^- than the iron or osmium analog (Fig. 1). This study also indicates a relative preference of MnO_4^- for the various $M(CN)_6^{4-}$ forms. The most reactive species of Fe(II) is $H_2Fe(CN)_6^{2-}$, while MnO_4^- prefers $HRu(CN)_6^{3-}$ and $Os(CN)_6^{4-}$, or its Na^+ ion pair as its reaction partner.

TABLE III. Experimental and Calculated Rate Constants for $M(CN)_6^{4-}$–MnO_4^- Reaction.

Metal Species	k_{11}, M^{-1} sec^{-1}	k_{22} M^{-1} sec^{-1} [b]	E°, (c) V	k_{12} (calc) M^{-1} sec^{-1}	k_{12} (obs) M^{-1} sec^{-1}
Fe(II)	7.4×10^2	3×10^3	+0.36 (8)	6.1×10^4	2.4×10^4 (2)
Ru(II)	2×10^2	3×10^3	+0.86 (4, 10)	1.42	0.93 (1)
Os(II)	1×10^7 [a]	3×10^3	+0.63 (5)	3.9×10^4	3.3×10^4

[a] k_{11} of $Os(dipy)_3^{2+}$ [12]. [b] Self exchange for MnO_4^-–$MNo_4^=$ (13). [c] E° ($MnO_4^-/MnO_4^=$) = +0.56 V.

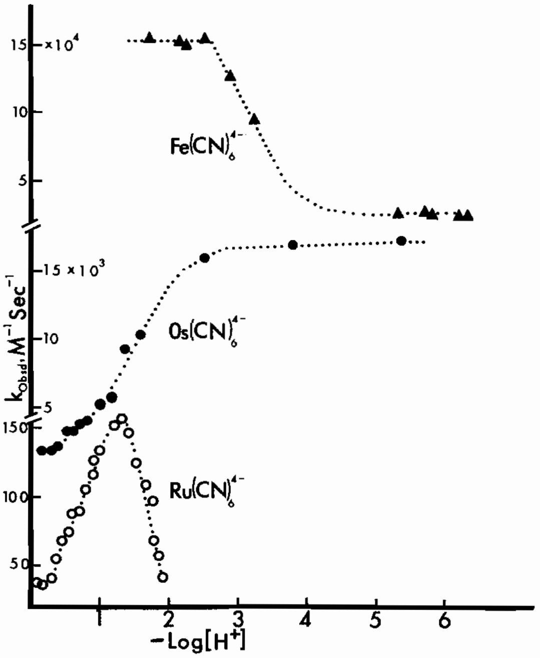

Fig. 1. k_{obsd} *vs.* $\log[H^+]^{-1}$ for Fe(II), Ru(II) and Os(II)-hexacyanometallates.

The lithium ion pair has reactivity similar to the $NaOs(CN)_6^{3-}$ ion pair. This trend in reactivity may be controlled in part by the magnitude of the repulsive coulombic charge between MnO_4^- and the hexacyanometalate species. Perhaps the large $Os(CN)_6^{4-}$ presents an electron cloud to MnO_4^- similar to those of $HRu(CN)_6^{3-}$ and $H_2Fe(CN)_6^{2-}$.

Since the $M(CN)_6^{4-}$–MnO_4^- systems are outer sphere reactants, the Marcus Cross reaction equation can be applied to predict a rate constant for that system [11]. Using the appropriate values in the Cross reaction equation $k_{12} = (k_{11}k_{22}K_{12}f)^{1/2}$ where $\log f = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2)$; k_{12} is the rate constant for the Cross reaction, k_{11} and k_{22} are the exchange rate constants of $M(CN)_6^{4-}$ and MnO_4^- respectively, K_{12} is the equilibrium constant for the Cross reaction and $Z = 10^{11}$ M^{-1} sec^{-1}, it is seen that the low reactivity observed (Table III) for the Ru(II)–MnO_4^- system is due in part to $Ru(CN)_6^{4-}$ being more difficult to oxidize to $Ru(CN)_6^{3-}$ (E° = +0.86 V) [4, 8] than the analogous Fe(II) (E° = +0.36 V) [8] and Os(II) (E° = +0.63 V) [5] species. This coupled with a self exchange rate of the Ru(II)–Ru(III) couple that is less than the self exchange rate for the iron analog and several orders of magnitude slower than the osmium system serves to severely limit the rate constant for the Ru(II)–MnO_4^- reaction.

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