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An Investigation of the Vanadium(V)–Octacyanomolybdate(IV) Reaction

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The rapid oxidation of $Mo(CN)_8^{4-}$ *by* VO_2^+ *was studied in acidic perchlorate media by the use of stopped-flow spectrophotometric techniques.*

Using a large excess of VO_2^+*, the formation of* $Mo(CN)_8^{3-}$ *was described by the expression* $(A_\infty - A_t) = B_0e^{-k_ft} + P_0e^{-k_st}$ *and the two reaction pathways at constant* $[H^+]$ *showed a simple first order dependence upon both reactants. Variation of the* $[H^+]$ *demonstrated the direct involvement of one proton in each pathway.*

The experimental data suggest the reaction of sodium ion pairs of $Mo(CN)_8^{4-}$ *with* VO_2^+*. Relative rate studied indicate that the faster reaction is of an outer-sphere type.*

Introduction

We have attempted a study of the reaction of various oxidants (MnO_4^-, XeO_3, VO_2^+) with several substitution inert cyanometalate compounds in an effort to demonstrate the presence of a two electron transfer pathway and/or detect the formation of a binuclear intermediate [1]. Gordon and co-workers have presented evidence to indicate that for the operation of a two electron exchange pathway, ligand exchange on the reductant must occur with the subsequent association of the oxidant into the inner coordination sphere of the reductant [2]. The oxidation of VO^{2+} by MnO_4^- is one such reaction in which the conditions for the two electron transfer pathway (Mn(VII) → Mn(V) and 2 VO^{2+}) were not observed [3].

The reaction of the permanganate ion, MnO_4^-, with hexacyanoferrate(II), $Fe(CN)_6^{4-}$ [4], and with octacyanomolybdate(IV), $Mo(CN)_8^{4-}$ [1], has been shown to proceed via consecutive one electron transfer steps. They were characterized as proceeding via an outer-sphere type mechanism as both oxidant and reductant are substitution inert ions. This outer-sphere mechanistic behavior is in contrast to that observed by Birk in the reaction of similar cyanometallate compounds with vanadium(V) and chromium(VI), where the presence of binuclear intermediate was observed with $Fe(CN)_6^{4-}$ and substituted Fe(II) cyano-bipyridyl compounds [5–7].

Since vanadium(V), a d^0 metal ion, is isoelectronic with chromium(VI) and MnO_4^- and is a stronger oxidant ($\epsilon^0 = 1.00$ v [8]) than both Cr(VI–V) ($\epsilon^0 = 0.60$ v [8]) and Mn(VII–VI) ($\epsilon^0 = 0.56$ v [8]), the oxidation of $Mo(CN)_8^{4-}$ by VO_2^+ was studied to determine if kinetic patterns similar to those found in the reaction of $Mo(CN)_8^{4-}$ with Cr(VI) (inner sphere) [9] or with MnO_4^- (outer sphere) [1] were observable.

Experimental

$K_4Mo(CN)_8 \cdot 2H_2O$ was prepared by the method of van der Poel and Neumann [1, 10] and was handled under red light conditions due to its photosensitivity. The light yellow powder was analyzed spectrophotometrically ($\lambda_{max} = 368$ nm, $\epsilon = 170$ M^{-1} cm^{-1}) [11].

Stock VO_2^+ was prepared by dissolving reagent grade vanadium pentoxide in 1.0 *M* $HClO_4$. Undissolved V_2O_5 was removed by fine glass frit filtration. Stock solutions of vanadium(IV) perchlorate were prepared by the addition of a stoichiometric amount of $Ba(ClO_4)_2$ to a solution of $VOSO_4$ dissolved in 0.1 *M* $HClO_4$. $BaSO_4$ was removed by centrifugation. Total vanadium content for both solutions was determined spectrophotometrically as the V(V)–H_2O_2 complex [12]. [V(V)] was determined via titration with Fe(II) in sulfuric acid. The [V(V)] and total vanadium content agreed within ±0.5%. [V(IV)] was analyzed spectrophotometrically at its maximum absorbance ($\lambda_{max} = 760$ nm, $\epsilon = 17.1$ M^{-1} cm^{-1}) [13]. Hydrogen ion content of the vanadium stock solutions was determined by ion exchange. Ionic strength was maintained at 1.0 with $NaClO_4$. Spectral scans of solutions were recorded with a Beckman DK-2A Spectrophotometer and the oxidation of $Mo(CN)_8^{4-}$ by VO_2^+ was followed at the absorbance maximum of Mo(V), $\lambda_{max} = 388$ nm, with an Aminco-Morrow stopped-flow apparatus previously

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described [1]. The molar absorptivities of Mo(CN)$_8^{4-}$, VO$_2^+$, and Mo(CN)$_8^{3-}$ at λ = 388 nm are 126, 16.9, and 1364 M^{-1} cm^{-1} respectively.

Results

Stoichiometry

The reaction of octacyanomolybdate(IV) and VO$_2^+$ is rapid and quantitative. Potentiometric titrations and spectrophotometric titrations in which the absorbance due to Mo(CN)$_8^{3-}$ was followed, upon the addition of various amounts of VO$_2^+$, showed breaks corresponding to a 1:1 stoichiometry. Batch mixing experiments gave identical results (Table I) and the overall reaction can be represented by the equation

$$\mathrm{Mo(CN)_8^{4-} + VO_2^+ + 2H^+ \rightarrow Mo(CN)_8^{3-} + VO^{2+} + H_2O}$$

TABLE I. Stoichiometry of the Mo(CN)$_8^{4-}$–VO$_2^+$ Reaction. [H$^+$] = 0.10 M, μ = 1.00.

[Mo(CN)$_8^{4-}$]$_0$ $M \times 10^4$	[VO$_2^+$]$_0$ $M \times 10^4$	[Mo(CN)$_8^{3-}$]$_\infty$ / [VO$_2^+$]$_0$
5.80	2.26	1.0
4.16	3.76	1.1
1.54	0.61	1.0

Spectral scans of reaction solutions were taken between 750 and 325 nm. These scans showed no evidence of the presence of a stable binuclear intermediate as the observed absorbance values at the various wavelengths could be calculated using the molar absorption coefficients and the concentrations of the reactants and expected products.

Kinetics

The decrease in the percent transmittance at 388 nm, the absorbance maximum of Mo(CN)$_8^{3-}$, was too rapid to be followed by conventional rapid mixing techniques and necessitated the use of stopped-flow instrumentation. A large excess of VO$_2^+$ was maintained in all of the reactions and the kinetic traces were treated as those of a pseudo-first order reaction. The percent transmittance at 388 nm undergoes a decrease for the overall reaction.

Plots of ln(A_∞ – A_t) *vs.* time we found to curve significantly at early times but became linear at longer times. The data indicated behavior of the sort (A_∞ – A_t) = $B_0e^{-k_ft} + P_0e^{-k_st}$. Here k_f and k_s are the first order rate constants for the fast and slow reaction, while B_0 and P_0 represent the absorbance change for the fast and slow reacting species, respectively. The rate constants, presented in Table II, were obtained by drawing a straight line through the long time linear portion (k_s) of the first-order plot and extrapolating the line back to zero time (P_0). The rate constant, k_f, for the more rapid reaction was obtained from plots of the form $\ln[(A_\infty - A_t) - (A_\infty - A_t')]$ *vs.* time. The quantity ($A_\infty - A_t$) represents the experimental point and (A_∞ – A_t') represents the extrapolated point at time t [14] (Fig. 1).

The results at constant at [H$^+$] indicate that each process can be described by a simple second order rate law, d[Mo(v)]/dt = k_j[VO$_2^+$][Mo(IV)]. Here k_j represents either k_1 and k_2, obtained by dividing the appropriate first order rate constant (k_f or k_s) by [VO$_2^+$].

A stopped-flow spectral scan (330–400 nm) showed no indication of an absorbing intermediate. Repeated recrystallizations of K$_4$Mo(CN)$_8$ and the

TABLE II. Rate Constants for the VO$_2^+$–Mo(IV) Reaction. [H$^+$] = 0.105 M, μ = 1.0, Temp. = 22.4 °C.

10^4[VO$_2^+$], M	10^4[Mo(CN)$_8^{4-}$], M	10^4[Mo(CN)$_8^{3-}$], M	k_s, sec^{-1}	$10^{-3}k_2$, M^{-1} sec^{-1}	k_f, sec^{-1}	$10^{-3}k_1$, M^{-1} sec^{-1}
47.0	0.852		13.23	2.77		
	1.28		13.08	2.78		
	2.13		12.29	2.61		
	4.26		13.79	2.83		
28.2	0.624		8.75	3.10		
	0.936		8.06	2.86		
	1.56		8.40	2.98	32.9	11.7
	2.50		8.17	2.90	41.2	14.6
	4.68		8.43	2.99		
25.3	0.363		7.33	2.90	49.58	17.6
		0.49	7.36	2.91	49.81	17.6
		0.77	7.34	2.90	59.28	21.0
		13.4	8.11	3.21	49.25	17.5
14.1	0.60		4.13	2.98		
9.40	0.248		3.07	3.27	12.1	12.9
7.00	0.60		2.01	2.86	8.55	12.2
				Avg. 2.93 ± 0.16		Avg. 15.7 ± 3

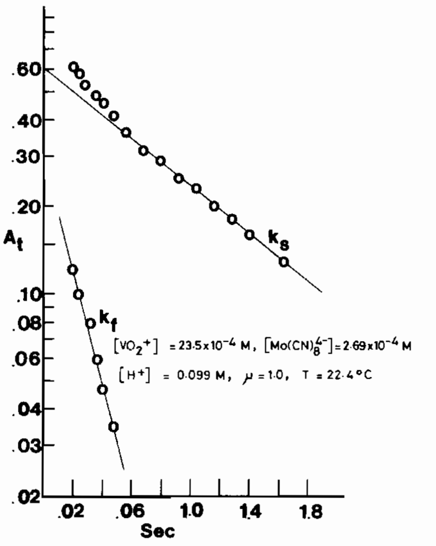

Fig. 1. Semi-Log plot of A_t *vs.* time. λ = 388 nm.

TABLE III. Hydrogen Ion Dependence of the Rate Constant. μ = 1.0, T = 22.4 °C.

$[H^+]$, *M*	$10^{-3}k_1$ M^{-1} sec^{-1}	$10^{-3}k_2$ M^{-1} sec^{-1}
0.095	21.0	2.57
0.099	22.6	2.60
0.105	17.7	2.93
0.159	40.1	4.14
0.218	53.2	6.68
0.299	58.2	8.34
0.339	61.2	9.78
0.418		11.38
$[VO_2^+]$ = 23.5 x 10^{-4} *M*	$[Mo(CN)_8^{4-}]_0$ = 2.69 x 10^{-4} *M*	

utilization of another VO_2^+ source gave spectra and molar absorption coefficients of the $Mo(CN)_8^{4-}$ and $Mo(CN)_8^{3-}$ identical to that previously obtained. These changes produced no alteration in kinetic behavior of the reaction or in the values of the rate constants.

Table III presents the effect of $[H^+]$ on the reaction rate constants. A least squared fit of both k_1 and k_2 *vs.* $[H^+]$ were linear and had, within experimental error, a zero intercept. Although the values of k_1 at high $[H^+]$ show more deviation, this is not thought to be indicative of additional hydrogen ion dependency since both processes are rapid and these rate constants were difficult to obtain with a high degree of accuracy. The dependence of the observed rate constants on $[H^+]$ can be represented by the expressions

$$d[Mo(v)]/dt = k_1'[Mo(IV)][VO_2^+][H^+]; \quad k_1' = 24.6 \pm 8.1 \times 10^5\ M^{-2}\ sec^{-1}$$

$$\text{and } d[Mo(v)]/dt = k_2'[Mo(IV)][VO_2^+][H^+]; \quad k_2' = 2.81 \pm 0.08 \times 10^4\ M^{-2}\ sec^{-1}$$

Since the kinetic behavior of the reaction system suggested a possible existence of another Mo(IV) species in solution, an acid solution ($[H^+]$ = 0.095 *M*) of $Mo(CN)_8^{4-}$ (4.02 X 10^{-4} *M*) was immersed in an ice bath and photolyzed with a U.V. lamp for one minute intervals to convert $Mo(CN)_8^{4-}$ to $Mo(CN)_7H_2O^{3-}$. Nitrogen gas was bubbled through the solution to remove the HCN formed by the photolytic reaction and to prevent the reformation of the octacyano complex [15]. Repetitive scans with the DK-2A were used to monitor the extent of the photolysis reaction. Heptacyanoaquomolybdate(IV) has a characteristic absorption maximum absorbance bands at 368 nm (ϵ = 170 M^{-1} cm^{-1}) and 512 nm (ϵ = 90 M^{-1} cm^{-1}) [16]. The solutions were equilibrated at 22.4 °C and then reacted with VO_2^+ in the stopped-flow apparatus. Although the second order rate constants showed a slight decrease with the increased photolysis time and an increased production of $Mo(CN)_7(H_2O)^{3-}$, the overall kinetic behavior of the reaction remained the same (Table IV). This slight decrease in the values of the rate constants can be attributed to a decrease in $[H^+]$ as HCN is removed from the Mo(IV) solution.

The temperature dependence of the observed rate constants is presented in Table V.

TABLE IV. VO_2^+ Reaction of Photolyzed $Mo(CN)_8^{4-}$ Solutions. $[Mo(CN)_8^{4-}]_0$ = 4.02 x 10^{-4} *M*, $[VO_2^+]_0$ = 5.02 x 10^{-3} *M*, $[H^+]$ = 0.095 *M*, μ = 1.00 *M*, temp. = 22.4 °C.

$10^4[Mo(CN)_7H_2O^{3-}]$, *M*	$10^{-3}k_1$, M^{-1} sec^{-1}	$10^{-3}k_2$, M^{-1} sec^{-1}
0	21.0	2.55
2.02	19.1	2.57
2.64	22.5	2.44
3.74	21.5	2.34

TABLE V. Temperature Dependence of the Rate Constants. $[Mo(CN)_8^{4-}]_0$ = 2.69 x 10^{-4} *M*, $[VO_2^+]_0$ = 3.77 x 10^{-3} *M*, $[H^+]$ = 0.105 *M*, μ = 1.00.

Temp.	$10^{-3}k_1$, M^{-1} sec^{-1}	$10^{-3}k_2$, M^{-1} sec^{-1}
14.0	8.13	1.45
17.2	7.71	2.00
22.4	19.6	2.84
23.2	23.2	2.93
29.0		4.46
$\Delta H^{\ddagger}$, Kcal/mol	14.3 ± 3.2	12.0 ± 0.7
$\Delta S^{\ddagger}$, e.u.	+8.9 ± 3.1	−2.1 ± 0.5

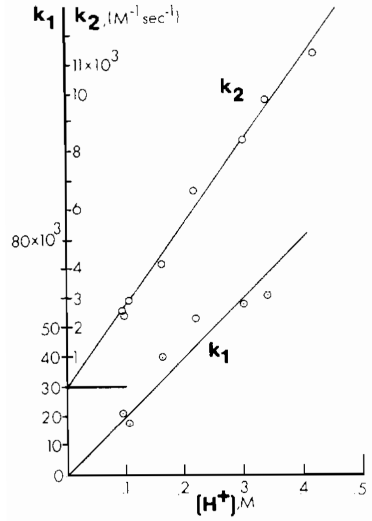

Fig. 2. Plots of k_1 (outer scale) and k_2 (inner scale) *vs.* $[H^+]$. $T = 22.4$ °C, $\mu = 1.0\,M$ ($NaClO_4$).

Discussion

The production of $Mo(CN)_8^{3-}$ from the reaction of $Mo(CN)_8^{4-}$ with an excess of VO_2^+ gives biphasic results that can be interpreted in terms of 2 parallel reactions, *i.e.*, $\begin{array}{l} A \xrightarrow[k_f]{} C \\ B \xrightarrow[k_s]{} C \end{array}$ or two consecutive first order reactions, i.e. $A \xrightarrow[k_f]{} B \xrightarrow[k_s]{} C$. While the second mechanism cannot be conclusively eliminated, the experimental results seem best interpreted in favor of the first mechanism.

The rapid, one electron transfer reaction between VO_2^+ and $Mo(CN)_8^{4-}$ can be understood in terms of a system consisting of both an inner and outer sphere reaction between V(V) and Mo(IV) occurring simultaneously at different rates. The idea that rapid complexation of VO_2^+ and $Mo(CN)_8^{4-}$ can occur is not without merit as VO_2^+ has been shown to form transient intermediate species (inner sphere complexes) in oxidation reactions involving both inorganic and organic compounds [19].

The reaction of VO_2^+ with $Fe(CN)_6^{4-}$ [7], Fe(bipy)-$(CN)_4^{2-}$ and $Fe(bipy)_2(CN)_2$ [6] were shown by Birk to proceed via a two step mechanism involving the rapid production and decomposition of a binuclear intermediate. The studies of the reaction of Cr(VI) with the aforementioned Fe(II) complexes and with $Mo(CN)_8^{4-}$ [9] have also demonstrated the presence of an inner-sphere reaction pathway for these cyanometalate compounds. The binuclear intermediate formed in the oxidation reduction reaction of VO_2^+ with the Fe(II) complexes and of Cr(VI) with $Mo(CN)_8^{4-}$ was of sufficient stability to permit spectral characterization and/or isolation. These observations, however, are in contrast to the present study where no short or long term stable intermediate was observed via a stopped-flow spectral scan batch mixing techniques, or a precipitate formed. The lack of detection of a separate spectral envelope for the absorbing species may however be an indication that its absorption spectra do not differ significantly from the combined spectral envelopes of the products and was not taken as conclusive proof of its absence. Such was the case in the VO_2^+–$Fe(CN)_6^{4-}$ reaction [7] and has been observed in other redox reactions which involved binuclear complex formation [17, 18].

The formation of a precipitate and the formation of the intermediate in the VO^{2+}–$Fe(CN)_6^{4-}$ reaction system may also reflect the greater ability of $Fe(CN)_6^{4-}$ to associate with cations than $Mo(CN)_8^{4-}$. $HMo(CN)_8^{3-}$ is reported to have a pk_a of 0.7 [9] compared to 4.17 for $Fe(CN)_6^{4-}$ [20]. The presence of a complex between VO_2^+ and $Mo_2O_4^{2+}$ has also been observed, indicating that the charge of the reductant is not a dominant factor [28].

The presence of only one proton in the rate expression is also in contrast to the observation in the VO_2^+–$Fe(CN)_6^{4-}$ reaction and that of the Cr(VI)–$Mo(CN)_8^{4-}$ reaction. Birk reported the absence of any influence due to hydrogen ion over a 10 fold $[H^+]$ range for the VO_2^+–$Fe(CN)_6^{4-}$ reaction while McKnight and Haight demonstrated that the hydrogen ion concentration of the Cr(VI)–Mo(IV) reaction carries a second order dependence, Rate = $k[HCrO_4^-][Mo(CN)_8^{4-}][H^+]^2$. Such dependence is characteristic of one-electron reductions of $HCrO_4$. The lack of a hydrogen independent pathway for the Mo(IV)/VO_2^+ reaction system suggests that the presence of a proton is essential for reaction and that the unprotonated forms of Mo(IV) or VO_2^+ play no direct part in the electron transfer process. The presence of protons in the rate determining step is a common feature in reactions where the net structural change converts an oxo ligand to an aquo ligand, $VO_2^+ \rightarrow VO(H_2O)^{2+}$. It is presumed that the coordination of a proton to VO_2^+ in the activated complex assists in the production of a water molecule [21, 22] and that the addition of the second proton is rapid and occurs after the electron transfer step. The lack of variation in the rate constant obtained from the reaction of VO_2^+ with the photolyzed solutions containing a mixture of Mo(IV) ions suggests that the octacyano- and the heptacyanoaquo- Mo(IV) complexes react with VO_2^+ at nearly the same rate. The replacement of one CN^- group by a water molecule would not be expected to greatly affect the kinetic behavior of the Mo(IV) ion. Using infrared studies of the adduct formed between $Mo(CN)_8^{4-}$ and UO_2^{2+}, Allen and Lippard [23] concluded that there was direct interaction between the CN group and uranium atom. Thus an inner-sphere complex formed between

TABLE VI. Rate Comparisons for the Oxidation of Several Complex Ions.[a]

Complex	M^{-1} sec^{-1}([H$^+$] = 0.105 M, T = 25 °C)						k_{ce}/k_{cr}	k_{ce}/k_v
	$10^{-5}k_v$		$10^{-4}k_{cr}$		$10^{-6}k_{ce}$ [26, 5]			
$Fe(CN)_6^{4-}$	12.0	(IS) [7]	2.20	(IS) [5]	1.90	(OS)	86	1.6
$Fe(bipy)(CN)_4^{2-}$	24.0	(IS) [6]	9.40	(IS) [5]	12.5	(OS)	133	5.2
$Mo(CN)_8^{4-}$	0.049	This work	8.3	(IS) [9]	14.0	(OS)	169	2.9×10^3
$Fe(phen)_3^{2+}$	1.6×10^{-6}	(OS) [7]	~0.0014	(OS) [27]	0.142	(OS)	~10^4	8.9×10^4
$Fe(bipy)_3^{2+}$	0.29×10^{-6}	(OS) [7]			0.196	(OS)	–	6.8×10^6

[a] (IS) = inner sphere, (OS) = outer sphere.

$Mo(CN)_8^{4-}$ and VO_2^+ would be consistent with Mo– –C≡N···VO_2^+ binding. In addition, the slow rate of ligand exchange by $Mo(CN)_8^{4-}$ does not present the opportunity for the formation of $Mo(CN)_7(H_2O)^{3-}$ via a thermal route during the course of the reaction. Thus the observed kinetic behavior is not thought to be due to a mixture containing $Mo(CN)_7(H_2O)^{3-}$ ions.

The presence of other species of V(V) are discounted as only $VO_2(H_2O)_4^+$ has been shown to exist under the [H$^+$] conditions used. Examination of the ratio, $B_0/(B_0 + P_0)$, the fraction of the initial absorbance change for the faster reaction to the total absorbance change for both steps was found to be independent of reactant and product concentration and of the different preparations of Mo(IV). The value of 0.31 ± 0.02 was obtained from more than fifty reaction plots and showed no apparent trend with [H$^+$] or [Mo(IV)]. Extrapolation of reaction plots back to $t = 0$ gave agreement with values calculated on the basis of the molar absorption coefficients of the reactions at $\lambda = 388$ nm. These observations indicate that the Mo(V) species is being formed by two distinct pathways and that some 30% of the Mo(V) product occurs via the more rapid pathway.

The slope from plots of ln k_j *vs.* $\sqrt{u}$ from ionic strength dependence studies indicate that the net charge of the activative species (Z_aZ_b) responsible for k_f and k_s differ by one unit (–0.9 for k_1 and –1.8 for k_2). Since $Mo(CN)_8^{4-}$, like $Fe(CN)_6^{4-}$ is capable of ion pair formation, it would be reasonable to expect a reaction between VO_2^+ and ion pairs of the Mo(IV) complex ($HNa_2Mo(CN)_8^-$ and $HNaMo(CN)_8^{2-}$). The ratio $B_0/(B_0 + P_0)$ increased slightly as the ionic strength was increased. This change is seen as an indication that the proportion of the disodium species that is responsible for the pathway described by k_1 is increasing over that of the monosodium species. No spectral changes were observed.

An alternative reaction scheme involving the protonation of VO_2^+ ($H^+ + VO_2^+ \rightleftharpoons VO(OH)^{2+}$) was discounted on the basis of the magnitude of K_{eq} ($(1.0–4.4) \times 10^{-6}$ M^{-1}) [24] and that the values of Z_aZ_b would be too large.

The reactions of $Fe(phen)_3^{2+}$ and $Fe(bipy)_3^{2+}$ with $HCrO_4^-$, VO_2^+ and Ce(IV) have been characterized as outer-sphere, while the reactions of $Fe(CN)_6^{4-}$ with both CrO_4^{2-} and VO^{2+} and the reaction of $Mo(CN)_8^{4-}$ with CrO_4^{2-} have been termed inner-sphere. Thus it is quite possible that $Mo(CN)_8^{4-}$ is capable of showing the presence of both pathways. It is also of interest to compare the relative rates of the Ce(IV)–reductant ion reaction with those of the VO_2^+–reductant ion systems. Relative rate studies have been used to differentiate between inner- and outer-sphere reactions [25] with various degrees of success. The Ce(IV) ion has often been used as a comparison ion since it is thought to react via an outer-sphere pathway.

Table VI list the rate constants and the relative rates for the oxidation of several complex ions by V(V), Cr(VI) and Ce(IV). The relative rate ratios for the Ce(IV)–Cr(VI) and Ce(IV)–V(V) systems show a small ratio in each case where the reaction has been shown to be inner-sphere while the relative rates for the reaction of the outer-sphere reductants, $Fe(phen)_3^{2+}$ and $Fe(bipy)_3^{2+}$, are large. The value of the k_{Ce}/k_V ratio for $Mo(CN)_8^{4-}$ appears more in line with those of the known outer-sphere reductant ions.

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