

Kinetics of the Oxidation of Octacyanomolybdate(IV) by Periodate in Aqueous Acid

Mohamed Ali Hussein and Yousif Sulfab*

Department of Chemistry, University of Kuwait, P.O. Box 5969, Kuwait

Summary

The kinetics of oxidation of $[\text{Mo}(\text{CN})_8]^{4-}$ by IO_4^- in aqueous acid is described by the equation: $d\{[\text{Mo}(\text{CN})_8]^{3-}\}/dt = 2k_3\{[\text{Mo}(\text{CN})_8]^{4-}\}[\text{IO}_4^-][\text{H}^+]$. Unlike IO_4^- oxidations of $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{W}(\text{CN})_8]^{4-}$, no $[\text{H}^+]$ independent term exists in the $[\text{Mo}(\text{CN})_8]^{4-}$ reaction, which indicates that, in neutral and alkaline solutions, oxidation of $[\text{Mo}(\text{CN})_8]^{4-}$ is thermodynamically unfavourable. An inner-sphere mechanism, consistent with the rate law, is proposed. This conclusion is based, in the absence of direct evidence, on the observed behaviour of IO_4^- as an inner-sphere oxidant.

Introduction

Metal complexes, which are relatively easily oxidized by IO_4^- in aqueous solutions, seem to fall into one of two classes: (i) labile complexes^(1–4) or, (ii) inert complexes that can offer a bridging ligand^(5–7). The mechanism of oxidation of the labile complexes is believed to be of the inner-sphere type, and in several cases direct evidence in support of this mechanism has been presented^(2–4). An inner sphere process is also believed to be operating in the oxidation of inert complexes. Thus in the oxidation of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ the hydroxo species, $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$, is the reactive Cr^{III} ion with the hydroxide acting as the bridging ligand⁽⁶⁾. In the oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ ⁽⁵⁾ and $[\text{W}(\text{CN})_8]^{4-}$ ⁽⁷⁾ the cyanide may bridge the reductant to IO_4^- . Substitution into the inner coordination sphere of the IO_4^- ion, which is labile, is likely⁽⁸⁾.

Periodate oxidations of other substrates may also be explained in terms of inner-sphere mechanism. The oxidation of I^- is believed to proceed *via* oxygen atom transfer and the formation of IOH , which rapidly reacts with another iodide ion, to give I_2 ⁽⁹⁾. In the oxidation of 1,2-diols, cyclic esters are formed with periodate and hence inner-sphere electron transfer seems to function⁽¹⁰⁾. In this study, the kinetics of oxidation of $[\text{Mo}(\text{CN})_8]^{4-}$ by IO_4^- is reported.

Experimental

NaIO_4 , HNO_3 , NaNO_3 and NaOAc (reagent grade) were used without further purification. A solution of the ligand CDTA (CDTA = *trans*-1,2-diaminocyclohexanetetraacetate) was prepared as the disodium salt by half neutralization of the acid form. The $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ complex was prepared by the method of van der Poel and Neumann⁽¹¹⁾. Its purity was checked spectrophotometrically: $\epsilon_{\text{max}}^{368} = 170 \text{ M}^{-1}\text{cm}^{-1}$ for $[\text{Mo}(\text{CN})_8]^{4-}$. The complex was also oxidized to $[\text{Mo}(\text{CN})_8]^{3-}$ and its absorption was found to be in excellent agreement with molar absorption of $1280 \text{ M}^{-1}\text{cm}^{-1}$ at $\epsilon_{\text{max}}^{388}$ ⁽¹²⁾. A stock solution of HNO_3 was prepared by dilution of the concentrated acid and standardized against NaOH solution. Solutions of the $[\text{Mo}(\text{CN})_8]^{4-}$ complex were prepared by weighing and were

kept away from light⁽¹⁴⁾. Buffer solutions were made up from HNO_3 and NaOAc .

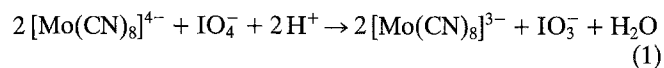
Kinetic procedure

The two reactants, in an indented flask, were thoroughly mixed after temperature equilibration, and the rate of reaction was followed on a Unicam SP 700 spectrophotometer equipped with thermostated cell-holders. The formation of the $[\text{Mo}(\text{CN})_8]^{3-}$ product was monitored at 388 nm. The results were irreproducible under these conditions, possibly owing to trace metal ion impurities. Several metal ions are known to catalyse oxidations by periodate^(15, 16). The kinetic experiments were therefore carried out in the presence of CDTA as a scavenger, and in these cases the kinetic results were reproducible. Over the pH range employed CDTA will be protonated, yet it suppressed catalysis by metal ion impurities.

All runs were carried out in presence of an excess of NaIO_4 in order to avoid any likely oxidation of $[\text{Mo}(\text{CN})_8]^{4-}$ by the IO_3^- product. Pseudo-first order conditions were maintained in all runs. The pH of the reaction mixture was measured on a radiometer digital pH-meter model PHM 62. In reactions where the pH was varied, the ionic strength was adjusted with NaNO_3 .

Results and Discussion

The stoichiometry of the reaction between $[\text{Mo}(\text{CN})_8]^{4-}$ and IO_4^- in aqueous acid may be represented by Equation (1), where IO_4^- represents the total periodate and not the reactive periodate species.



The reaction product was identified spectrophotometrically and was found to be the same, whether CDTA was added to the mixture or not. Addition of CDTA, under experimental conditions, to the $[\text{Mo}(\text{CN})_8]^{4-}$ complex did not produce any change in its absorption spectrum during several hours.

Plots of $-\ln(A_\infty - A_t)$ vs. time were linear up to $\geq 90\%$ of reaction and the pseudo first-order rate constant, k_{obs} , was obtained from the slopes of these plots. At a fixed periodate concentration, pH, ionic strength and temperature, the value of k_{obs} is independent of $[\text{Mo}(\text{CN})_8]^{4-}$ as shown in Table 1. The reaction is therefore first-order with respect to this reactant.

The dependence of k_{obs} on periodate concentration was investigated over the 0.010–0.050 M range. The results in Table 1 show that k_{obs} varies linearly with $[\text{IO}_4^-]$. The second-order rate constant, k_2 , was obtained from $k_{\text{obs}}/2[\text{IO}_4^-]$; the factor 2 was included because $d\{[\text{Mo}(\text{CN})_8]^{3-}\}/dt = -2d[\text{IO}_4^-]/dt$.

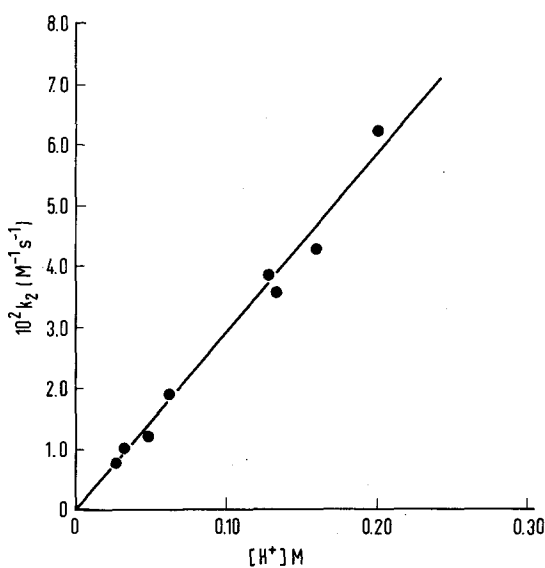
The dependence of k_2 on $[\text{H}^+]$ was investigated over the 0.65–1.55 pH range. The reaction rate decreases with increas-

* Author to whom all correspondence should be directed.

Table 1. Kinetic data for the oxidation of $[\text{Mo}(\text{CN})_8]^{4-}$ by IO_4^- ^{a)}

Temp (°C)	pH	$10^2[\text{IO}_4^-]$ (M)	$10^3 k_{\text{obs}}$ (s ⁻¹)	$10^2 k_2$ (M ⁻¹ s ⁻¹)		
25.0	0.70	1.0	1.24	6.20 ^{b)}		
			1.26	6.30 ^{c)}		
			1.26	6.30		
			1.30	6.50 ^{d)}		
			1.23	6.15 ^{e)}		
			2.0	2.38		
			3.0	3.45		
			4.0	4.76		
			5.0	6.26		
			0.70	1.0	1.24	6.20
			0.79	3.0	2.58	4.30
			0.87	1.0	0.71	3.55
			0.89	3.0	2.31	3.85
			1.21	1.0	0.38	1.90
			1.31	3.0	0.70	1.17
			1.48	1.0	0.20	1.0
			1.55	3.0	0.47	0.78
20.0	0.83	1.0	0.57	2.85		
30.0			1.63	8.15		
35.0			2.56	12.8		
40.0			3.87	19.35		

^{a)} Unless otherwise stated $[\{\text{Mo}(\text{CN})_8\}^{4-}] = 3.75 \times 10^{-4} \text{M}$, $I = 0.70 \text{M}$ and $[\text{CDTA}] = 10^{-3} \text{M}$; ^{b)} $[\{\text{Mo}(\text{CN})_8\}^{4-}] = 7.5 \times 10^{-4} \text{M}$; ^{c)} $[\{\text{Mo}(\text{CN})_8\}^{4-}] = 6.0 \times 10^{-4} \text{M}$; ^{d)} $[\{\text{Mo}(\text{CN})_8\}^{4-}] = 3.0 \times 10^{-4} \text{M}$; ^{e)} $[\{\text{Mo}(\text{CN})_8\}^{4-}] = 1.5 \times 10^{-4} \text{M}$.

**Figure 1.** Variation of k_2 (M⁻¹s⁻¹) with $[\text{H}^+]$.**Table 2.** Effect of ionic strength on k_3 (M⁻²s⁻¹)^{a)}

I (M)	pH	$10^4 k_{\text{obs}}$ (s ⁻¹)	$10^2 k_2$ (M ⁻¹ s ⁻¹)	k_3 (M ⁻² s ⁻¹)
0.20	1.01	10.0	5.0	0.51
0.50	1.02	8.8	4.4	0.46
0.70	1.21	3.8	1.9	0.31
1.20	0.90	6.6	3.3	0.26

^{a)} $[\text{IO}_4^-] = 0.010 \text{M}$, $[\{\text{Mo}(\text{CN})_8\}^{4-}] = 3.75 \times 10^{-4} \text{M}$, $T = 25.0^\circ \text{C}$.

ing pH as shown in Table 1; a plot of k_2 versus $[\text{H}^+]$ is linear and is shown in Figure 1.

From these results the rate law for the oxidation of $[\text{Mo}(\text{CN})_8]^{4-}$ by IO_4^- in aqueous acid is in accordance with Equation (2).

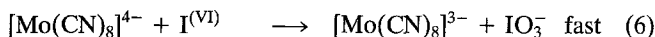
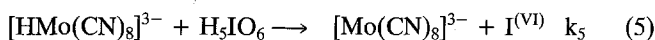
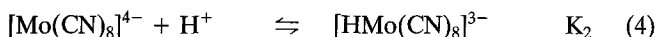
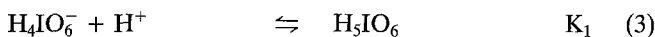
$$d[\{\text{Mo}(\text{CN})_8\}^{3-}]/dt = 2k_3 [\{\text{Mo}(\text{CN})_8\}^{4-}][\text{IO}_4^-][\text{H}^+] \quad (2)$$

The influence of ionic strength on the reaction rate was investigated over the 0.20–1.20 M range, and the results are given in Table 2, which shows that the magnitude of k_3 decreases with increasing ionic strength.

The effect of temperature on k_2 , at constant pH and ionic strength, was studied over the 20.0–40.0°C range. The enthalpy, ΔH^\ddagger , and entropy, ΔS^\ddagger , of activation were calculated from the linear plot of $\ln(k_2/T)$ vs. $1/T$ as $70.6 \pm 2.9 \text{ kJ mol}^{-1}$ and $-31.4 \pm 8.4 \text{ J mol}^{-1} \text{K}^{-1}$.

The $[\text{Mo}(\text{CN})_8]^{4-} - \text{IO}_4^-$ reaction, unlike the $[\text{Fe}(\text{CN})_6]^{4-} - \text{IO}_4^-$ and $[\text{W}(\text{CN})_8]^{4-} - \text{IO}_4^-$ reactions, does not show a $[\text{H}^+]$ independent pathway which seems to reflect redox potential differences between these reductants. Hexacyanoferrate(II) and octacyanotungstate(IV) have redox potentials of 0.36 V and 0.57 V respectively⁽¹⁷⁾, i.e. lower than the 0.80 V reported for octacyanomolybdate(IV)⁽¹⁸⁾. The periodate ion thus seems to have a redox potential of $< 0.80 \text{V}$, and this is in agreement with the reported potential 0.70 V for periodate in neutral and alkaline media.

A mechanism consistent with the kinetics is given in Equations (3–6):



The rate law given in Equation (7) is derived from the above mechanism:

$$\frac{d[\{\text{Mo}(\text{CN})_8\}^{4-}]}{dt} = \frac{2k_5 K_1 K_2 [\{\text{Mo}(\text{CN})_8\}^{4-}][\text{IO}_4^-][\text{H}^+]^2}{1 + K_1 [\text{H}^+]} \quad (7)$$

Equation (7) reduces to Equation (8), which is identical to the experimental rate law, if $K_1 [\text{H}^+] \gg 1$.

$$d[\{\text{Mo}(\text{CN})_8\}^{3-}]/dt = 2k_5 K_2 [\{\text{Mo}(\text{CN})_8\}^{4-}][\text{IO}_4^-][\text{H}^+] \quad (8)$$

This is not unreasonable considering the thermodynamic value of K_1 of $1.8 \times 10^3 \text{M}^{-1}$ at 25°C ⁽¹⁹⁾, and the $[\text{H}^+]$ employed. Protonation of $[\text{Mo}(\text{CN})_8]^{4-}$ has not been reported before, and without assuming it, the derived rate law given by Equation (8) would not be obtained. However, by analogy with $[\text{Fe}(\text{CN})_6]^{4-}$ which is known to be extensively protonated in acidic solution, protonation of $[\text{Mo}(\text{CN})_8]^{4-}$ is likely, except when K_2 is very small.

The oxidation mechanism for $[\text{Mo}(\text{CN})_8]^{4-}$ by periodate may be inferred, because of the lack of any direct evidence, from the behaviour of periodate as an inner-sphere oxidant^(1-4, 6). The two reactants, Mo^{IV} and I^{VII} could be bridged through the cyanide ligand, with substitution occurring in the inner coordination sphere of the labile I^{VII} .

The catalysis observed, when CDTA was omitted, seems to be due to trace metal impurities. Several metal ions are known to catalyse periodate oxidations^(15, 16).

The decrease in the reaction rate with increasing ionic strength may be attributed to a decrease in the magnitude of K_1 and K_2 . From the proposed mechanism and the derived

rate law, the ionic strength effect may be due to K_2 more than to K_1 as the latter cancels, as shown in Equation (8).

Acknowledgement

This research was supported by the University of Kuwait under Grant No. SC09.

References

- (1) Y. Sulfab and A. I. Abu-Shadi, *Inorg. Chim. Acta*, **21**, 115 (1977).
 – (2) A. Y. Kasim and Y. Sulfab, *Inorg. Chim. Acta*, **24**, 247 (1977). –
 (3) F. R. El-Eziri and Y. Sulfab, *Inorg. Chim. Acta*, **25**, 15 (1977). –
 (4) A. A. Abd El-Khalek and Y. Sulfab, *J. Inorg. Nucl. Chem.*, in press (1981). – (5) Y. Sulfab, *J. Inorg. Nucl. Chem.*, **38**, 2270 (1976). –
 (6) A. Y. Kassim and Y. Sulfab, *Inorg. Chem.*, **20**, 506 (1981). – (7) P. Guardado, A. Maestra and M. Baton, *J. Inorg. Nucl. Chem.*, **43**, 1392 (1981). – (8) I. Pechet and Z. Luz, *J. Am. Chem. Soc.*, **87**, 4068 (1965). – (9) A. Indelli, F. Ferranti and F. Secco, *J. Phys. Chem.*, **70**, 631 (1966). – (10) G. J. Buist, in C. H. Bamford and C. F. H. Tripper, (Eds.), *Comprehensive Chemical Kinetics*, Elsevier, Vol. 6, pp. 435. (11) J. van der Poel and H. M. Neumann, *Inorg. Synth.*, **1**, 53 (1968). – (12) M. H. Ford-Smith and J. H. Rawsthorne, *J. Chem. Soc. A.*, 160 (1969). – (13) F. S. H. Head and H. A. Standing, *J. Chem. Soc.*, 1457 (1952). – (14) R. P. Mitra, B. K. Sharma and H. Mohan, *Aust. J. Chem.*, **25**, 499 (1972). – (15) H. A. Mottola and H. Freiser, *Anal. Chem.*, **39**, 1294 (1967). – (16) A. Y. Kasim and Y. Sulfab, *Inorg. Chim. Acta*, **22**, 169 (1977). – (17) W. Latimer, *Oxidation Potentials*, Prentice-Hall, Englewood Cliffs, N. J., 2nd Edit. 1952. – (18) R. J. Campion, N. Purdie and N. Sutin, *Inorg. Chem.*, **3**, 1091 (1964). – (19) S. H. Laurie, J. M. Williams and C. J. Nyman, *J. Phys. Chem.*, **68**, 1311 (1964).

(Received October 26th, 1981)

TMC 725

Initial State and Transition State Contributions to Reactivity in Mercury(II)-catalysed Aquation of the *trans*-[Rh(en)₂Cl₂]⁺, [Cr(NH₃)₅Cl]²⁺, and *cis*-[Cr(NH₃)₄(OH₂)Cl]²⁺ Cations in Binary Aqueous Solvent Mixtures

A. Olabode Adeniran, Gareth J. Baker, Gabriel J. Bennett, Michael J. Blandamer, John Burgess*, Nilam K. Dhammi and Philip P. Duce

Chemistry Department, University of Leicester, Leicester LE1 7RH, U.K.

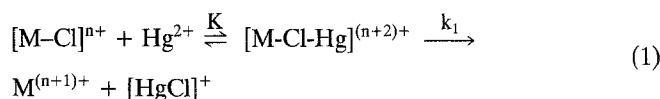
Summary

Rate constants are reported for mercury(II)-catalysed aquation of the *trans*-[Rh(en)₂Cl₂]⁺, [Cr(NH₃)₅Cl]²⁺, and *cis*-[Cr(NH₃)₄(OH₂)Cl]²⁺ cations in water and in methanol-, ethanol-, and acetonitrile-water solvent mixtures. In the case of *trans*-[Rh(en)₂Cl₂]⁺, the dependence of rate constants on mercury(II) concentration indicates reaction through a binuclear (Rh-Cl-Hg bridged) intermediate. The dependence of the equilibrium constant for the formation of this intermediate and of its rate constant for dissociation (loss of HgCl⁺) on solvent composition have been established. With the aid of measured solubilities, published ancillary thermodynamic data, and suitable extrathermodynamic assumptions, the observed reactivity trends for these mercury(II)-catalysed aquations are dissected into initial state and transition state components. The reactivity patterns for these three complexes are compared with those for mercury(II)-catalysed aquation of other chloro-transition metal complexes, particularly *cis*-[Rh(en)₂Cl₂]⁺, [Co(NH₃)₅Cl]²⁺, and [ReCl₆]²⁻.

Introduction

During the last few years there has been considerable interest in resolving solvent effects on reactivity in inorganic sys-

tems into their initial state and transition state components⁽¹⁻³⁾. For technical reasons connected with the required kinetic and thermodynamic measurements, such analyses are more readily carried out on bimolecular than on unimolecular reactions. However, there are relatively few examples of the former type amongst substitutions of octahedral complexes. One well documented reaction of this type is the mercury(II)-catalysed aquation of chloro-complexes^(4, 5). Though dissociative as far as the central metal ion is concerned, these reactions are in fact bimolecular S_E2 processes; Equation (1):



The dinuclear [M-Cl-Hg]⁽ⁿ⁺²⁾⁺ species of Equation (1) may be a genuine intermediate or may be the transition state for a one-step S_E2 process; the general dependence of k_{obs} (Hg²⁺ in large excess) on mercury(II) concentration is shown in Figure 1. When [M-Cl-Hg]⁽ⁿ⁺²⁾⁺ is a transition state, then second-order kinetic behaviour is observed (Section A, Figure 1). When this dinuclear species has much greater stability, being formed rapidly and completely from reactants, k_{obs} is constant (Section C, Figure 1). In intermediate circumstances, plots of k_{obs} versus [Hg²⁺] are curved (Section B, Figure 1). All three types of kinetic behaviour have been reported for this type of reaction in aqueous solution. We have undertaken an initial

* Author to whom all correspondence should be directed.