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REDUCTION OF OCTACYANOMOLYBDATE(V) ANION BY HYDROXYLAMMONIUM ION IN AQUEOUS HYDROCHLORIC ACID

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ABSTRACT. The stoichiometry and kinetics of the reduction of octacyanomolybdate(V) anion by hydroxylammonium ion has been studied in aqueous hydrochloric acid in the 0.01 - 0.10 mol dm^{-3} range. The rate shows a first order dependence on the substrate, an inverse second-order dependence on $[H^+]$ and a negative salt effect. One mol of the oxidant is consumed per mol of the reductant to give nitrogen as the gaseous product. a mechanism involving free radicals is proposed.

INTRODUCTION

The kinetics of the reduction of octacyanomolybdate(V) anion by a wide range of substrates have been investigated in aqueous solution (1-7). The results of these studies suggest that the anion is substitution inert since it does not readily undergo exchange of cyanide ions with the solvent and other ligands in solution. Thus Marcus theory was employed to show that its reactions with I^- (1), MnO_4^{2-} (2) and SO_3^{2-} (3) proceed by the outer-sphere mechanism.

We recently reported the outer-sphere reactions of hydroxylamine and 12-tungstocobaltate(III) anion (8), and the reductions of octacyanomolybdate(V) anion by some thiols (6,7). In view of our interest in hydroxylamine as a reductant and octacyanomolybdate(V) anion as an oxidant, the dynamics of their interaction in aqueous hydrochloric acid is reported below.

EXPERIMENTAL

Reagents. Potassium octacyanomolybdate(IV) dihydrate and potassium octacyanomolybdate(V) were prepared and standardised as described previously (7). Their stock solutions were prepared every week to prevent decomposition (9) and were stored and used under subdued lighting conditions. Hydroxylamine hydrochloride (BDH, Analar) was recrystallised from an H_2O - EtOH mixture and its solution was freshly prepared and standardised bromatometrically (10). Hydrochloric acid was prepared by dilution of Analar grade stock solution and was analysed by titration with NaOH. All other reagents were used without further purification.

Absorption spectra. The electronic spectra of octacyanomolybdate(V) anion solution (in the 1.0 - $7.5x10^{-5}$) mol dm^{-3} range in HCl (0.01 - 1.00 mol dm^{-3}) were recorded on a Unicam SP 8000 spectrophotometer. The spectra exhibited the characteristic absorption maximum at 388 nm (4,7,8) and their shapes were independent of $[Mo(CN)_8{}^{-3}]$ and $[H^+]$. Beer's law was valid in the concentration range studied.

Stoichiometry. The reaction stoichiometry was determined by spectrophotometric titrations. This was accomplished by measuring the absorbance of solutions containing varying hydroxylamine concentrations in the range (0.90 - 4.5 x 10^{-4}

mol dm^{-3}, $[Mo(CN)_8{}^{3-}]$ = (1.4×10^{-4}) mol dm^{-3}, $[H^+]$ = 0.05 mol dm^{-3} and I = 0.1 mol dm^{-3} (NaCl) at 388 nm after the reaction had gone to completion.

Kinetics. Kinetic studies were conducted in the presence of a large excess of hydroxylamine and at a constant ionic strength adjusted to 1.0 mol dm^{-3} (NaCl), unless otherwise indicated. Under these conditions the reactions were slow. Therefore, the rates were measured at 388 nm by monitoring absorbance changes due to octacyanomolybdate(V) anion on a Pye Unicam SP 1750 spectrophotometer using absorption cells maintained at 25 ± 0.2°C. Plots of log $(A_t - A_\infty)$ (A_t and A_∞ are the absorbances at time t and the end of the reaction respectively) versus time were rectilinear to about 70% of reaction. Duplicated measurements agreed within ± 5%.

RESULTS

Stoichiometry. Plots of absorbance at 388 nm after the reaction had been completed against the concentration of hydroxylamine were made. From the points of inflection of such plots, it was found that 1.03 ± 0.05 mol of NH_3OH^+ were consumed per mol of $Mo(CN)_8{}^{3-}$. Thus the overall reaction may be represented by equation (1).

$$2Mo(CN)_8{}^{3-} + 2NH_3OH^+ \rightarrow 2Mo(CN)_8{}^{4-} + N_2 + 4H^+ + 2H_2O \quad (1)$$

Octacyanomolybdate(IV) anion was characterised by its electronic spectra (4) and nitrogen was identified as described previously (8).

Dependence on NH_3OH^+ concentration. At a constant $[Mo(CN)_8{}^{3-}]$ = 5.0×10^{-5} mol dm^{-3}, varied $[NH_3OH^+]$ = 0.01 - 0.10 mol dm^{-3} and I = 1.0 mol dm^{-3} (NaCl) plots of k_{obs} versus $[NH_3OH^+]$ were linear with positive slopes (Fig. 1). The intercepts of the lines were found by the method of least squares to be insignificant, suggesting that the order with respect to NH_3OH^+ is unity.

Dependence on $[H^+]$. The concentration of hydrogen ion was varied in the range 0.01 - 0.10 mol dm^{-3} at 25 ± 0.2 °C. Values of the second order rate constant k_2 obtained from the slopes of the lines in Fig. 1 as a function of $[H^+]$ are presented in Table 1. A plot of k_2 versus $[H^+]^{-2}$ yielded a straight line passing through the origin. Thus the reaction appears to follow the rate equation (2).

$$-\frac{d[Mo(CN)_8{}^{-3}]}{dt} = \frac{k[Mo(CN)_8{}^{3-}][NH_3OH^+]}{[H^+]^2} \quad (2)$$

Under our experimental condition, the least square slope of this line (k) was evaluated to be 1.78×10^{-3} mol dm^{-3} s^{-1} at 25 ± 0.2 °C.

Table 1. Dependence of the second order rate constant k_2 on hydrogen ion concentration for the reaction of $Mo(CN)_8{}^{3-}$ and NH_3OH^+; $[Mo(CN)_8{}^{3-}]$ = 5.0×10^{-5} mol dm^{-3}; $[NH_3OH^+]$ = 1.0 - 25 $\times 10^{-3}$ mol dm^{-3}; I = 1.0 mol dm^{-3} (NaCl).

$10^2[H^+]$, mol dm^{-3}	1.00	1.50	2.50	5.00	7.50	1.00
k_2, mol dm^{-3-1}	18.30	7.33	2.69	1.47	0.55	0.33

Effect of $Mo(CN)_8{}^{4-}$. The deviations of the pseudo-first-order plots from linearity at higher extents of reaction and the kinetic data obtained in the presence of varied amounts of added $Mo(CN)_8{}^{4-}$ (Table 2) suggest that $Mo(CN)_8{}^{4-}$ retards the rate of the reaction.

Table 2. Dependence of k_{obs} on added [$Mo(CN)_8^{4-}$] at constant temperature [NH_3OH^+] = 5.0×10^{-3} mol dm^{-3}; [H^+] = 0.015 mol dm^{-3}; [$Mo(CN)_8^{3-}$] 5.0×10^{-5} mol dm^{-3} and I = 1.0 mol dm^{-3} (NaCl).

10^4[$Mo(CN)_8^{4-}$], mol dm^{-3}	0	1.00	5.00	10.00
$10^3 k_{obs}$, s^{-1}	60.11	49.50	44.12	42.50

Effect of acrylamide. Addition to 12% w/v acrylamide to a partially oxidized reaction mixture (3.0 cm^3) containing [$Mo(CN)_8^{3-}$] = 5×10^{-4} mol dm^{-3}, NH_3OH^+ (1.0 mol dm^{-3}) and [H^+] = 0.05 mol dm^{-3} followed by addition of a large excess of methanol gave a suspension of polyacrylamide. However, no polymerization was observed in control experiments in which either $Mo(CN)_8^{3-}$ or NH_3OH^+ were excluded.

The reaction was also studied in the presence of different concentrations of acrylamide. The pseudo-first-order rate constant increased by about 816% in *ca* 5% (w/v) acrylamide (Table 3). This result as well as the one reported above implicate the involvement of free radicals in the reaction mechanism.

Table 3. Dependence of k_{obs} on acrylamide at 25 ± 0.2 °C [$Mo(CN)_8^{3-}$] = 5.0×10^{-5} mol dm^{-3}; [NH_3OH^+] = 5.0×10^{-3} mol dm^{-3}; [H^+] = 0.015 mol dm^{-3} I = 1.0 mol dm^3 (NaCl).

% Acrylamide (w/v)	0.00	0.40	0.80	1.20	4.80
$10^3 k_{obs}$, s^{-1}	18.13	22.04	23.74	43.84	166.02

Effect of ionic strength. The ionic strength of the reaction mixture was varied between 0.1 - 1.0 mol dm^{-3} by the addition of sodium chloride. It is evident from the results in Table 4 that the rate of reduction of $Mo(CN)_8^{3-}$ by NH_3OH^+ decreases with increase in ionic strength, possibly suggesting a negative Bronsted - Debye (11) salt effect which would be expected in a reaction between oppositely charged ions.

Table 4. The variation of k_{obs} with ionic strength at 25 ± 0.2°C for the reaction of $Mo(CN)_8^{3-}$ and NH_3OH^+.
[NH_3OH^+] = 5.0×10^{-3} mol dm^{-3};
[$Mo(CN)_8^{3-}$] = 5.0×10^{-3} mol dm^{-3};
[H^+] = 0.025 mol dm^{-3}.

I(NaCl), mol dm^{-3}	0.10	0.40	0.60	0.80	1.00
$10^3 k_{obs}$, s^{-1}	24.90	15.03	13.7	13.30	11.20

DISCUSSION

On the basis of the various rate dependence, the reaction probably follows the mechanism represented by equations (3) and (4)

$$Mo(CN_8^{3-} + NH_3OH^+ \rightleftharpoons Mo(CN)_8^{4-} + NH_2O^{\bullet} + 2H^+ \qquad (3)$$

$$NH_2O^{\bullet} \xrightarrow{k_3} \tfrac{1}{2}N_2 + H_2O \qquad (4)$$

Octacyanomolybdate(V) anion is a one-electron oxidant. Therefore, the first step in the reaction is the formation of an intermediate radical which eventually decomposes to give the identified gaseous product. The observed polymerization of acrylamide is consistent with the postulation of $NH_2O^{\bullet}$ as an intermediate in this reaction, since the radical has been identified in methanolic solution (10) and is well established as an intermediate in other reactions of hydroxylamide (8, 13-15).

The large rate inhibiting effect of $Mo(CN)_8^{4-}$ and catalytic effect of acrylamide require equation (3) to be reversible. While the former suggests that a reverse reaction of $Mo(CN)_8^{4-}$ with $NH_2O^{\bullet}$ to form $Mo(CN)_8^{3-}$ and NH_3OH^+ occurs, the latter may be attributed to increase in the rate of the forward reaction (k_1 path) in order to offset the effect of the reaction of $NH_2O^{\bullet}$ with acrylamide on the equilibrium. The fact that a decrease in rate in the presence of 5% (w/v) acrylamide was observed in the reaction of $Au^{(III)}$ with hydroxylamine, which is not inhibited by the reaction products (13), is consistent with the above hypothesis.

If equilibrium steady state approximation (16) is applied to equations (3) and (4), a rate law analogous to equation (2) is obtained.

$$\frac{-\,d\,Mo(CN)_8^{3-}}{dt} = \frac{k_3k_1[Mo(CN)_8^{3-}]\,[BH_3OH^+]}{k_{-1}[Mo(CN)_8^{4-}]\,[H^+]^2} \tag{5}$$

This equation is analogous to that reported for the reduction of Pu(IV) (15) and Fe(III) (17) by hydroxylamine, and it is in accord with the kinetic results displayed in Table 1 and Fig. 1.

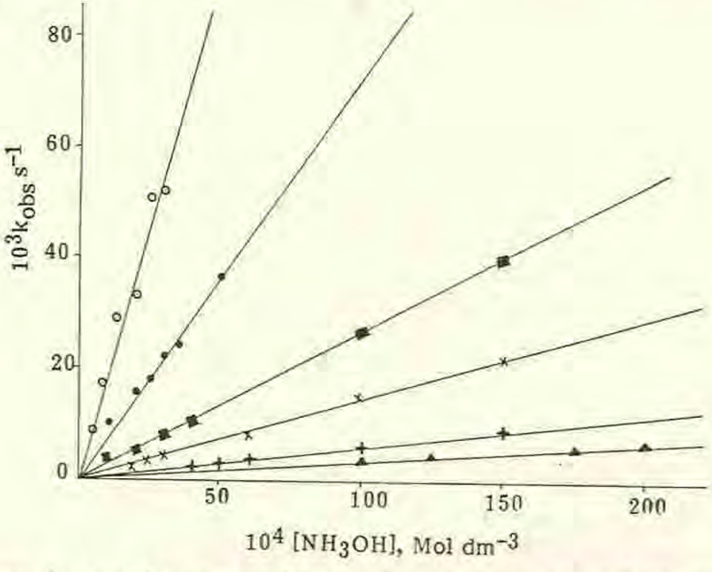

Fig. 1. Dependence of k_{obs} versus $[NH_3OH^+]$ for the reaction of $Mo(CN)_8^{3-}$ and NH_3OH^+ at 25°C. $Mo(CN)_8^{3-} = 5.0 \times 10^{-5}$ mol dm^{-3}; I = 1.0 ml dm^{-3} $[H^+] = 0.01$ mol dm^{-3} (⊙); 0.015 mol dm^{-3} (●); 0.025 mol dm^{-3} (■); 0.05 mol dm^{-3} (X); 0.075 mol dm^{-3} (+); 0.10 mol dm^{-3} (▲).

Our observed pattern of variation of the reaction rate with $[H^+]$ may be interpreted in three ways. First, it may suggest that NH_2OH^+ is the reactive species of the reductant as in analogous reactions of hydroxylamine with $Fe(CN)^{3-}$ (13) and Pu(IV) (15). Secondly, NH_3OH^+ may be assumed to be the reactive species of the reductant while the square inverse $[H^+]$ dependence is rationalised in terms of the reversible reaction (3). Thirdly, the $[H^+]$ dependence term may be attributed to the hydrolysis of oxidant with the hydrolysed species as the reactive form of the oxidant. We believe that the second possibility is the most plausible under the conditions employed for the investigation because (a) the experiments were conducted at $[H^+] = 0.01 - 0.10$ mol dm^3 whereas the dissociation constant of hydroxylammonium ion is in the range $8.7 \times 10^{-7} - 2.0 \times 10^{-6}$ mol dm^{-3} (18). Thus the substrate would largely be in its protonated form; (b) the hydrolysis of the oxidant is unprecedented in similar acidity (1,6,7) and the invariance of its electronic spectra with varying acidity in the range 0.01 - 1.0 mol dm^{-3} suggest that $Mo(CN)_8{}^{3-}$ is the only reactive species of the oxidant under the reaction conditions; (c) the observed reaction stoichiometry and kinetic results cannot be reconciled on the basis of the first and their possibilites but are effectively accommodated by the second proposal; and (d) the observed variation of reaction rate with the ionic strength is reminiscent of a negative general salt effect arising from the interaction of oppositely charged reactive species, possibly $Mo(CN)_8{}^{3-}$ and NH_3OH^+ in the titled reaction.

Distinction between the inner or outer-sphere mechanism, for at least, the first step in the $Mo(CN)_8{}^{3-}$ reduction of NH_3OH^+ cannot be made unequivocally from our data. However, the oxidant has displayed a consistent reluctance to substitution in its oxidation by various inorganic and organic substrates such as I^-(1) $MnO_4{}^{2-}$(2), $SO_3{}^{2-}$ (3), Se(IV) (4), As(III) (5) and some thiols (6,7). The reaction of $Mo(CN)_8{}^{3-}$ and NH_3OH^+ may proceed via a similar mechanism.

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REFERENCES

1. M.H. Ford-Smith and J.H. Rawsthrone, J. Chem. Soc., (A), 160 (1969).
2. J.G. Leipoldt, C.R, Dennis, E.G. Grobler, Inorg. Chim. Acta, **77**, L47 (1983).
3. C.R. Dennis, S.S. Basson and J.G. Leipoldt, Polyhedron, **2**, 1357 (1983).
4. (a) J.G. Leipoldt, C.R. Dennis, A.J. Van Wyk and L.D.C. Bok, Inorg. Chim. Acta, **31**, 187 (1978).
5. J.G. Leipoldt, L.D.C. Bok and C.R, Dennis, J. Inorg. Nucl. Chem., **38**, 1655 (1976).
6. M.A. Olatunji and R.C. Okechykwu, Transition Met. Chem., **12**, 205, 1987).
7. M.A. Olatunji and R.C. Okechykwu, Inorg. Chim. Acta, **89**, 131 (1987).
8. G.A. Ayoko and M.A. Olatunji, Transition Met. Chem., **10**, 218 (1985).
9. H.H. Willard and R.C. Thielke, J. Am. Chem. Soc., **57**, 2609 (1935).
10. J. Bassett, R.C. Denney, G.H. Jeffery and J. Mendham, "Vogel's Textbook of Quantitative Inorganic Analysis", 4th Ed., Longman, London, p. 394, (1978).
11. J.N. Bronsted, Z. Phys. Chem., **102**, 160 (1922).
12. C.J.W. Gutch and W.A. Waters, J. Chem. Soc., 751 (1965).
13. K.K. Sengupta and B. Basu, Transition Met. Chem., **8**, 6 (1983).
14. V.K. Jindal, M.C. Agarwal and S.P. Mushran, J. Chem. Soc. (A), 2060 (1970).
15. G.S. Barney, J. Inorg. Nucl. Chem., **38**, 1677 (1976).
16. C.W. Pyun, J. Chem. Educ., **48**, 194, (1971).
17. G. Bengtson, Acta Chem. Scand., **27**, 1717 (1973).
18. R.A. Scott, G.P. Haight and J.N. Cooper, J. Am. Chem. Soc., **96**, 4136 (1974).