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The oxidation of octacyanomolybdate(IV) and octacyanotungstate(IV) by nitrous acid

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Abstract—The kinetics of the oxidation of octacyanomolybdate(IV) by nitrous acid has been studied in aqueous perchloric acid medium. An equilibrium concentration of the nitrosonium ion, NO^+, has been proposed as the active oxidizing species. An acid dissociation constant for $H[Mo(CN)_8]^{3-}$, $K_a = 0.47 \pm 0.05$ M at 25°C and $I = 1.0$ M has been obtained from the kinetic data. © 1997 Elsevier Science Ltd

Kinetic studies on nitrous acid have been mainly concerned with nitrosation reactions in the older literature [1]. It was evident that a protonation step (eq. (1)) is a prerequisite for nitrosation of substrates (S) which is controlled by the rate law in eq. (2).

$$HNO_2 + H^+ \rightleftharpoons H_2O + NO^+ \qquad (1)$$
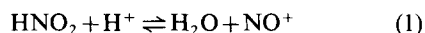
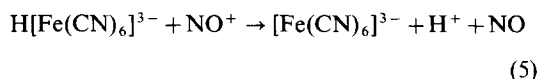$$\text{Rate} = k[S][HNO_2][H^+]. \qquad (2)$$

The same rate equation also seems to hold for the oxidation of a number of inorganic complexes by nitrous acid. Iridium(III) is oxidized by nitrous acid to an equilibrium with Ir^{IV} (eq. (3)) with a rate law [2] for the forward reaction which

$$IrCl_6^{3-} + HNO_2 + H^+ \rightleftharpoons IrCl_6^{2-} + NO + H_2O \quad (3)$$
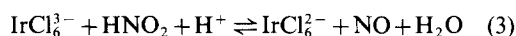
corresponds to eq. (2). A mechanistic investigation has revealed that a similar rate law applies to the redox indicator behavior of ferrocyphen, $[Fe(phen)_2(CN)_2]$, for nitrite titrations at low acidities [3]. The latter reactions were all considered as rate-limiting diffusion-controlled electron transfers from the substrate to NO^+, incorporating the prerequisite equilibrium (eq. (1)) and a rate determining step (eq. (4)).

$$S + NO^+ \rightarrow \text{products}. \qquad (4)$$
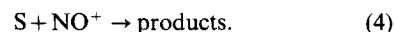
The oxidation of hexacyanoferrate(II) ions (eq. (5))

$$H[Fe(CN)_6]^{3-} + NO^+ \rightarrow [Fe(CN)_6]^{3-} + H^+ + NO \qquad (5)$$

involves only the monoprotonated form as the active participant [4]. The third-order rate constants for the latter and the oxidation of $IrCl_6^{3-}$ show reasonable correlations with calculated encountered-controlled rates [4,5] for the interaction between a tri-negatively charged species and NO^+.

Our interest in the nitrous acid oxidation of octacyanomolybdate(IV) and octacyanotungstate(IV) originates from preparative procedures [6] for the respective octacyanometalate(V) species using HNO_3 as oxidant. We found that the yields of oxidized product varied according to the ageing and daylight exposure of the concentrated nitric acid used. This was indicative of nitrous acid, a known photochemical decomposition product [7,8] of nitric acid, being the active oxidizing agent. Further investigation resulted in an improved preparation method [9] using sodium nitrite in mineral acid medium as oxidizing agent. A kinetic study [10] to this effect has indeed shown that $H[W(CN)_8]^{3-}$ is more reactive than $[W(CN)_8]^{4-}$ and that the rate of this reaction is comparable to that of the hexacyanoferrate(II) oxidation. The present kinetic study of the oxidation of the $[Mo(CN)_8]^{4-}$ by

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HNO_2 is complimentary to that of the octacyanotungstate(IV) complex which allows comparison of the reaction mechanisms and reactivities.

EXPERIMENTAL

Potassium octacyanomolybdate(IV)dihydrate, $K_4[Mo^{IV}(CN)_8] \cdot 2H_2O$, was prepared as described by Leipoldt *et al.* [11] and was used as a primary standard [12] after recrystallization. Stock solutions of sodium nitrite were freshly prepared daily using a Merck 'Pro Analysi' reagent. A sodium perchlorate solution was prepared by neutralizing sodium carbonate with concentrated perchloric acid. The solution was neutralized to pH = 7, using a sodium hydroxide solution and then standardized gravimetrically. All other reagents used were analytical grade and redistilled water was used throughout.

The kinetics were followed by stopped-flow spectrophotometry at 390 nm using a Durrum D-110 instrument. The temperature of reaction mixtures was controlled to within 0.1°C. All experiments were carried out in perchloric acid medium with $[NO_2^-]$ a tenfold excess relative to $[Mo^{IV}(CN)_8^{4-}]$, to obtain pseudo-first-order reaction conditions. Reaction mixtures were maintained at constant ionic strength by the addition of sodium perchlorate.

RESULTS AND DISCUSSION

The oxidation of octacyanomolybdate(IV) by aqueous nitrous acid shows first-order kinetics in $[Mo^{IV}(CN)_8^{4-}]$ and $log(A_\infty - A_t)$ *vs* time plots were linear for several half-lives of the reaction. The results in Table 1 show that the reaction is linearly dependent on $[N^{III}]_T$ and that variation in the initial concentration of the product, $[Mo^V(CN)_8]^{3-}$ have no significant effect on the reaction rate.

Since the pK_a [13] for HNO_2 at $I = 1.0$ M is 3.002 and the equilibrium constant [14] for reaction (1) is 3×10^{-7} M^{-1}, the main N^{III} species at the experimental acidity conditions is HNO_2. For many years there was a dispute in the literature as to whether the active nitrosating species in aqueous nitrous acid solutions was the nitrous–acidium ion, $H_2NO_2^+$, or an equilibrium concentration of the nitrosonium ion, NO^+ [15]. Anbar and Taube [16], in their kinetic and isotopic study of the reaction between nitrous acid and hydrogen peroxide, produced evidence that the nitrosonium ion is the active oxidizing species.

Kinetic measurements with variation in $[H^+]$ (Fig. 1) show the pH dependence of the oxidation of $[Mo^{IV}(CN)_8]^{4-}$ by nitrous acid. Considering the acid dissociation constant of HNO_2 (*v. sup.*) these results could be an indication that two cyanomolybdate species are operative over the pH range studied.

We have previously shown [10] (see also Fig. 1) that $H[W(CN)_8]^{3-}$ ($pK_a^{24} = 1.6$) is in equilibrium with $[W(CN)_8]^{4-}$ and that both species are oxidized by nitrous acid in the acidity range employed. A similar observation is also valid for the hexacyanoferrate(II) oxidation but with the exception that the $H_2[Fe(CN)_6]^{2-}$ ion was not active [4]. The results in both cases however allowed a kinetic determination of the appropriate dissociation constant which correspond very well with those determined by potentiometric methods.

Values for the acid dissociation constants of $H[Mo^{IV}(CN)_8]^{3-}$ could however not be found in the

Table 1. Observed rate constants for the oxidation of octacyanomolybdate(IV) by nitrite ions [$T = 25.0°C$ and $[H^+] = 0.20$ M ($HClO_4$)]

$10^4[Mo^{IV}(CN)_8^{4-}]$ M	$10^3[NO_2^-]$ M	$10^4[Mo^V(CN)_8^{3-}]$ M	$I(NaClO_4)$ M	k_{obs} s^{-1}
2.0	4.0		1.0	38.4
3.0	4.0		1.0	40.2
4.0	4.0		1.0	39.1
5.0	4.0		1.0	37.6
4.0	3.0		1.0	29.7
4.0	4.0		1.0	39.9
4.0	5.0		1.0	48.7
4.0	6.0		1.0	58.2
4.0	8.0		1.0	77.7
4.0	10.0		1.0	94.3
4.0	4.0	1.0	1.0	38.3
4.0	4.0	2.0	1.0	39.6
4.0	4.0	3.0	1.0	39.9
4.0	4.0	4.0	1.0	40.9
4.0	4.0		0.9	37.7
4.0	4.0		0.9	37.7
4.0	4.0		0.7	36.7
4.0	4.0		0.6	37.3
4.0	4.0		0.5	36.6
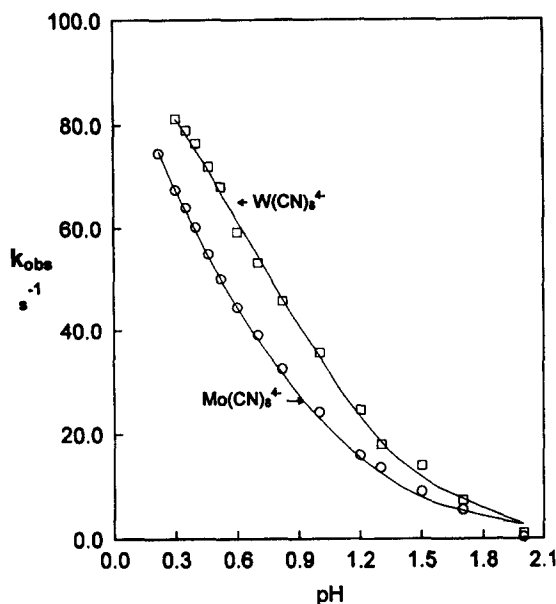
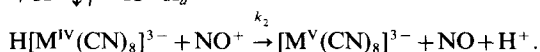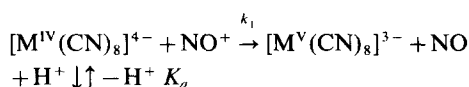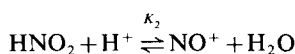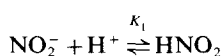Fig. 1. The hydrogen ion dependence for the oxidation of octacyanometalate(IV) by nitrous acid. $[M^{IV}(CN)_8^{4-}] = 4 \times 10^{-4}$ M, $[NO_2^-] = 4 \times 10^{-3}$ M, $I = 1.0$ M (NaClO₄) and $T = 25.0°C$. ($W^{IV}(CN)_8^{4-}$ data from ref. [10]).

literature. Although there is a substantial difference in the reduction potential [17] of the $[Mo^V(CN)_8]^{3-}/$ $[Mo^{IV}(CN)_8]^{4-}$ and $[W^V(CN)_8]^{3-}/[W^{IV}(CN)_8]^{4-}$ couples their physical and chemical properties [18,19,20,21,22] are almost identical. Both these octacyanometalate(IV) and -(V) ions are spheres with the same negative charge and therefore a similar effective ion charge must be operative. It has been established [21,22] that the metal–nitrogen distance for both ions is approximately 3.3 Å. This resulted in similar ionic radii for these ions. It has also been established that hydrogen ions in the direct vicinity of $[M(CN)_8]^{4-}$ (M = Mo, W) are stabilized by ion-dipole bonds [19,20,21,22]. Coulombic interaction between H⁺ and the nitrogens of the CN-ligand are similar for both complex ions. Considering the above it is reasonable to expect the acid dissociation constant for $H[Mo(CN)_8]^{3-}$ to be of the same order of magnitude as that for the corresponding tungsten complex.

From the available data an appropriate reaction pathway for the oxidation of $[M(CN)_8]^{4-}$ (M = Mo, W) by aqueous nitrous acid could be as proposed in the following scheme:

$$NO_2^- + H^+ \overset{K_1}{\rightleftharpoons} HNO_2$$

$$HNO_2 + H^+ \overset{K_2}{\rightleftharpoons} NO^+ + H_2O$$

$$[M^{IV}(CN)_8]^{4-} + NO^+ \overset{k_1}{\rightarrow} [M^V(CN)_8]^{3-} + NO$$
$$+ H^+ \downarrow\uparrow - H^+ \quad K_a$$

$$H[M^{IV}(CN)_8]^{3-} + NO^+ \overset{k_2}{\rightarrow} [M^V(CN)_8]^{3-} + NO + H^+ .$$

A product study with relatively high reactant concentrations, confirmed the product, NO, by the effervescence of a colourless gas which turned quickly to the characteristic brown fumes of NO_2 in the atmosphere directly above the reaction mixture. The proposed reaction mechanism corresponds with the rate law:

$$R = \frac{K_1 K_2 (k_1 K_a + k_2[H]^+)[H^+]^2 [M^{IV}(CN)_8^{4-}]_T [N^{III}]_T}{(K_a + [H]^+)(1 + K_1[H^+] + K_1 K_2[H^+]^2)}$$

where

$$[M^{IV}(CN)_8^{4-}]_T = [M(CN)_8^{4-}] + [HM(CN)_8^{3-}]$$

and

$$[N^{III}]_T = [NO_2^-] + [HNO_2] + [NO^+].$$

Since $K_2 \ll K_1$ the rate law for the acidity range $0.6 > [H^+] > 0.01$ mol dm⁻³ can be rearranged to a form consistent with nucleophilic attack upon the nitrosonium ion [15].

$$\frac{-d[M(CN)_8^{4-}]}{dt} = \left(\frac{k_1 K_a + k_2[H^+]}{K_a + [H]^+}\right)$$
$$\times [M^{IV}(CN)_8^{4-}]_T [N^{III}]_T. \quad (6)$$

A non-linear least squares fit of the hydrogen ion dependent data for the $[Mo^{IV}(CN)_8]^{4-}$ reaction as well as similar data for the $[W^{IV}(CN)_8]^{4-}$ reaction in our previous report [10] (Fig. 1) to rate law (6) yielded values for k_1, k_2 and K_a at $I = 1.0$ M and $T = 25°C$ (Table 2). The value of k_2 corresponds very well with the calculated [4] encounter-controlled reaction rate for the reaction of triply charged anions such as $H[Mo(CN)_8]^{3-}$ and $H[W(CN)_8]^{3-}$ with the nitrosonium ion, NO⁺. The K_a values at zero ionic strength were calculated by using the Davies equation [23]:

$$\log K = \log K_0 + Z_A Z_B[I^{1/2}/1 + I^{1/2}) - 0.3I]. \quad (7)$$

As expected, the K_a values obtained from the octacyanomolybdate(IV) and the octacyanotungstate(IV) data, $7.4 \pm 0.6 \times 10^{-2}$ and $3.5 \pm 0.3 \times 10^{-2}$ M, respectively, are of the same order in magnitude. As previously reported [10], the value of K_a for $H[W^{IV}(CN)_8]^{3-}$ is in agreement with the value reported by Samotus et al. [24]. It is thus reasonable to believe that the value obtained from the $[Mo^{IV}(CN)_8]^{4-}$ data is the acid dissociation constant for the equilibrium

$$H[Mo^{IV}(CN)_8]^{3-} \overset{K_a}{\rightleftharpoons} [Mo^{IV}(CN)_8]^{4-} + H^+. \quad (8)$$
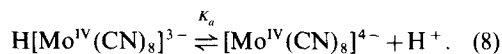
The mechanism for the oxidation of octacyanomolybdate(IV) and octacyanotungstate(IV) by nitrous acid is thus basically the same as those of $[Fe(CN)_6]^{4-}$, $[Fe(phen)_2(CN)_2]$ and $[IrCl_6]^{3-}$. For the cyano complexes of Fe^{II}, Mo^{IV} and W^{IV} the monoprotonated species are more reactive (Table 2) in the order $H[W(CN)_8]^{3-} \sim H[Mo(CN)_8]^{3-} > H[Fe(CN)_6]^{3-}$.

Table 2. Rate and acid dissociation constants for the oxidation of the octacyano-molybdate(IV), octacyanotungstate(IV) and hexacyanoferrate(II) complexes by nitrous acid [$T = 25.0°C$ and $I = 1.0$ M $(NaClO_4)$]

	$H[W^{IV}(CN)_8]^{3-\,a}$	$H[Mo^{IV}(CN)_8]^{3-}$	$H[Fe^{II}(CN)_6]^{3-}$
k_1, $M^{-1}.s^{-1}$	$0 \pm 3 \times 10^2$	$0 \pm 2 \times 10^2$	
k_2, $M^{-1}.s^{-1}$	$3.0 \pm 0.1 \times 10^4$	$3.3 \pm 0.2 \times 10^4$	$2.6 \times 10^{3\,b}$
K_a, M	$2.2 \pm 0.2 \times 10^{-1}$	$4.7 \pm 0.5 \times 10^{-1}$	
K_a^0, M	$3.5 \pm 0.3 \times 10^{-2}$	$7.4 \pm 0.6 \times 10^{-2}$	
pK_a^0	1.46 ± 0.04	1.13 ± 0.03	4.17^c

^{a} Recalculated with data from ref. [10].
^{b} Calculated from ref. [4].
^{c} A literature value in ref. [4].

In the case of molybdenum and tungsten the depro-tonated species react much slower—a situation which is reminiscent of alkali metal ion catalysis found for several redox reactions of these complexes where ion association occurred in the form of a first-order dependency on alkali metal ion concentrations [22]. We thus suggest that the electron flow is facilitated by a bridging H^+ between the cyano ligand and the NO^+ in the transition state as a possible explanation for the rate enhancement of k_2 over k_1.

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