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Kinetics of the Periodate Oxidation of Octacyanomolybdate(IV) in Ethanol—Water Solvent Mixtures

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The kinetics of the oxidation of $Mo(CN)_8^{4-}$ by IO_4^- has been studied in ethanol—water solvent mixtures over a temperature range of 15–35 °C. The effect of solvent composition on the reaction rate and the mechanism has been investigated. Activation parameters are given. An inner-sphere mechanism, consistent with the kinetic results, is proposed.

[Keywords: Periodate oxidation; Solvent effect; Reaction rate; Kinetics; Octacyanomolybdate (IV)]

Kinetik der Periodat-Oxidation von Octacyanomolybdat (IV) in Ethanol—Wasser

Die Kinetik der Oxidation von $Mo(CN)_8^{4-}$ mit IO_4^- wurde in Ethanol—Wasser über einen Temperaturbereich von 15—35 °C untersucht. Der Effekt der Lösungsmittelzusammensetzung auf die Reaktionsgeschwindigkeit und der Mechanismus der Reaktion werden diskutiert. Die Aktivierungsparameter sind angeführt. Es wird ein „Inner-Sphere"-Mechanismus vorgeschlagen, der mit den kinetischen Ergebnissen konsistent ist.

Introduction

Although electron transfer reactions have been studied extensively, the influence of changes of solvent on such reactions has received comparatively little attention[1]. The possibility to use solvent effects on reaction kinetics in diagnosis of mechanisms of inorganic substitution and redox reactions has been considered recently[2].

The alcohol—water solvent mixtures exhibit pronounced structural and dielectric changes at different component ratios[3]. According to the current theoretical treatments[4], changes in dielectric properties are expected to affect the reorganization of solvent molecules around the reactants and the intermediate activated complex. In the few studies reported, the solvent composition has been found to affect the reaction rates in somewhat different ways[5].

The oxidation of $Mo(CN)_8^{4-}$ has been studied recently in aqueous solutions[6], and the results show that the reaction is first-order with respect to both reactants and proceeds through an inner-sphere mechanism. In the present investigation, the effect of ethanol—water solvent mixtures of various compositions on the kinetics and mechanism of this reaction has been studied.

Experimental

Materials

The complex $K_4Mo(CN)_8 \cdot 2\,H_2O$ was prepared as described previously[7]. Its purity was checked spectrophotometrically $\varepsilon_{max}^{368} = 170\,M^{-1}\,cm^{-1}$ for $Mo(CN)_8^{4-}$. The complex was also oxidized to $Mo(CN)_8^{3-}$ and its absorption was found to be in excellent agreement with the molar absorption $\varepsilon_{max}^{388} = 1\,280\,M^{-1}\,cm^{-1}$ [8].

Reagent grades of $NaIO_4$, HNO_3, $NaNO_3$ and *CDTA* (*CDTA* = *trans*-1,2-diaminecyclohexane tetraacetate), were used without further purification. A solution of the ligand *CDTA* was prepared as the disodium salt by half neutralization of the acid form. Stock solutions of periodate and $Mo(CN)_8^{4-}$ complex, wrapped in aluminium foil to avoid photochemical decomposition[9, 10], were made up by weight. A stock solution of HNO_3 was prepared by dilution of the concentrated acid and standardized against NaOH solution. Pure ethanol of BDH quality was distilled before use. Its stability towards $Mo(CN)_8^{4-}$ complex and the product $Mo(CN)_8^{3-}$ was checked, no reaction was observed during the time taken for measurements. It is known[11] that ethanol is stable towards periodate and this was verified experimentally for the solutions used. All compositions were accurate to within ± 0.02 wt%. The dielectric constants of ethanol—water solvent mixtures were obtained from the data of *Åkerlof*[12].

Kinetic Measurements

The kinetic procedure was similar to that described for the $Mo(CN)_8^{4-}/IO_4^-$ reaction in aqueous solutions[6]. The rate of the reaction was monitored at 388 nm (on a Unicam SP 8000 spectrophotometer) at which the product $Mo(CN)_8^{3-}$ has an absorption maximum. The kinetic experiments were carried out in the presence of *CDTA* to inhibit any catalysis by trace amounts of metal-ion impurities[6]. *CDTA* is protonated in the $[H_3{}^+O]$ range employed. Our studies cover the solvent composition 0–62 wt% ethanol. However, attempts to measure in solvent mixtures containing 65 wt% ethanol or more failed hopelessly and reproducible results cannot be obtained. This is due to the precipitation of periodate.

Pseudo-first-order conditions were maintained in all runs by using a large excess of periodate concentration over that of the complex. The ionic strengths of the solutions were adjusted by the use of $NaNO_3$. The reaction was carried out in acid medium using HNO_3 to adjust [Acid]. The *pH* of the reaction medium was measured using a radiometer digital *pH*-meter model PHM 62.

Results and Discussion

The stoichiometric equation of the reaction is represented[6] by

$$2\,Mo(CN)_8^{4-} + IO_4^- + 2\,H^+ \longrightarrow 2\,Mo\,CN)_8^{3-} + IO_3^- + H_2O$$

The product of oxidation of $Mo(CN)_8^{4-}$ by IO_4^- was identified spectrophotometrically and found to be the same whether *CDTA* was added to reaction mixture or not[6]. This was verified experimentally in both aqueous and ethanol—water solvent mixtures, and it was found that there is no oxidizing effect for HNO_3 (up to 0.06 *M*) solution on the molybdate complex. During the reaction *pH* measurements proved that the *pH* stays constant, therefore there was no need to use a buffer solution.

Table 1. *Kinetics of the oxidation of* $Mo(CN)_8^{4-}$ *by* IO_4^- *in 34 wt% ethanol—water solvent mixture*[a] *at 25 °C*

10^2 [Acid] (M)	$10^2[IO_4^-]$ (M)	$10^4[Mo(CN)_8^{4-}]$ (M)	$10^3 k_{obs}$[b] (s^{-1})	$10^2 k_2$ ($M^{-1}\,s^{-1}$)
2.24	5.0	3.75	7.20	7.20
2.24	4.0	7.50	5.67	7.09
2.24	4.0	3.00	5.60	7.00
2.24	4.0	1.50	5.69	7.11
2.24	3.0	3.75	4.50	7.50
2.24	2.0	3.75	3.00	7.50
2.24	1.0	3.75	1.38	6.90
2.24	0.5	3.75	0.73	7.30

[a] $[CDTA] = 2 \cdot 10^{-3}\,M,\ I = 0.27\,M.$

[b] Standard deviations 4–8%.

The reaction proceeds with an apparent pseudo first-order rate constant k_{obs} determined from the slope of the straight lines obtained by plotting $-\ln(A_\infty - A_t)$ versus time, using a linear least-squares programme. These plots were linear up to ⩾ 90% of reaction.

In 34 wt% ethanol—water mixtures a number of runs were made to check the effect of solvent composition on the dependence of k_{obs} for both $[Mo(CN)_8^{4-}]$ and $[IO_4^-]$. The results, included in Table 1, show no effect for the solvent composition compared to aqueous solutions[6].

$$\text{Observed rate} = 2k_2[IO_4^-] \tag{1}$$

The factor 2 was included because $d[Mo(CN)_8^{3-}]/dt = -2\,d[IO_4^-]/dt$. The second-order rate constant k_2 is therefore obtained from eq. (2).

$$k_2 = \frac{k_{obs}}{2[IO_4^-]} \tag{2}$$

It is seen from Table 2 that the reaction rate increases gradually passing over a maximum at around 43 wt% ethanol and thereafter decreases with increasing ethanol content in the solvent mixture.

Starting from the point of maximum reaction rate (at around 43 wt% ethanol), the rate decreases on either increasing (0–43 wt% ethanol) or decreasing (43–62 wt% ethanol) the dielectric constant D of the medium. At any temperature, $\log k_{obs}$ was found to be linearly dependent on D^{-1} in both regions (Table 2).

The effect of solvent mixtures on the reaction rate may be examined in terms of changes in the activation parameters. These parameters are usually taken as a measure of the solvation effect. The effect of temperature on k_2 at constant [Acid] and ionic strength was studied over the range 15–35 ± 0.01 °C in various ethanol—water solvent mixtures (Table 2). The enthalpy, ΔH^*, entropy, ΔS^*, and free energy, ΔG^*, of activation for various solvent compositions were calculated from the linear plot of $\ln (k_2/T)$ versus $1/T$ and are collected in Table 3. It is seen that ΔG^* decreases gradually with successive ethanol addition up to about 43% by weight and then increases by further progressive addition of ethanol. According to the theory of absolute reaction rates, the increase of ΔG^* is a sign of solvation of the reacting species.

Some useful insight with regard to the changes in the structural aspects of the solvents may be obtained from the changes in the enthalpy and entropy, which contain important structural contributions[4]. The enthalpy change decreases gradually with increasing ethanol content up to about 43% by weight, and thereafter increases with progressive addition of ethanol. Non-polar solvents will be relatively unoriented and hence will have higher entropy of activation[13]. These solvents will therefore have a greater loss in entropy as a result of solvation and reactions in these solvents will consequently have a larger negative entropy of activation.

However ΔS^*, which has large negative values, increases with increasing ethanol content up to about 43% by weight, and thereafter decreases with further ethanol addition.

The sudden variation of thermodynamic parameters of activation noticed at around 43% by weight of ethanol reflects the variation of reaction kinetics with solvent composition.

In aqueous acidic solutions, over the [Acid] range, periodate exists in two forms, $H_4IO_6^-$, and H_5IO_6 which are in equilibrium[14]. However, by analogy with methanol—water mixtures[15], appreciable amounts of the undissociated acid H_5IO_6 were not formed in ethanol—water mixtures.

Proposed Mechanism

In acid medium one must consider the equilibrium[13] represented by eq. (3).

$$H_3^+O + S \rightleftharpoons SH^+ + H_2O \quad K_1 \tag{3}$$

Table 2. *Dependence of the rate constant on both temperature and dielectric constant for various ethanol—water solvent mixtures*[a, b]

Ethanol wt%	D at 25 °C	$[H_2O]$ (M)	[S] (M)	$10^3 k_{obs}$ (s^{-1})				
				15 °C	20 °C	25 °C	30 °C	35 °C
0	78.5	54.22	0.00	1.31	2.24	3.40	5.69	8.46
7	74.1	50.13	1.26	1.68	2.73	3.94	6.17	8.72
21	66.2	42.19	3.76	2.56	3.54	4.92	7.16	9.63
34	58.8	34.23	6.08	4.43	5.67	7.20	9.48	11.42
47	51.3	28.40	8.41	3.74	4.98	6.50	8.75	11.30
52	47.9	25.62	9.21	2.53	3.73	5.01	7.53	10.33
58	44.4	22.30	10.37	2.03	3.11	4.32	6.68	9.44
62	42.2	19.40	11.08	1.40	2.24	3.43	5.58	8.21

[a] $[Mo(CN)_8^{4-}] = 3.75 \cdot 10^{-4} M$, $[IO_4^-] = 0.05 M$, $[Acid] = 2.24 \cdot 10^{-2} M$.
[b] Standard deviations for k_{obs}: 2–4%.

Table 3. *Activation parameters for the oxidation of* $Mo(CN)_8^{4-}$ *by* IO_4^- *in ethanol—water solvent mixtures at 25 °C*

Ethanol wt%	ΔH^* $kJ\,mol^{-1}$	$-\Delta S^*$ $J\,mol^{-1}K^{-1}$	ΔG^* $kJ\,mol^{-1}$
0	68.0 ± 0.8	44.4 ± 2.8	81.2 ± 1.6
7	59.6 ± 1.0	71.6 ± 3.4	80.9 ± 2.0
21	48.2 ± 0.8	108.0 ± 2.7	80.4 ± 1.6
34	33.9 ± 0.8	153.1 ± 2.6	79.5 ± 1.6
47	39.4 ± 0.3	135.2 ± 1.1	79.7 ± 0.6
52	50.7 ± 0.6	99.4 ± 1.9	80.3 ± 1.2
58	55.5 ± 0.5	84.5 ± 1.3	80.8 ± 0.9
62	64.7 ± 0.6	55.6 ± 1.9	81.3 ± 1.2

It was reported, that the reaction is [Acid] dependent[6]. Accordingly, a proposed mechanism consistent with the kinetics is given in eqs. (4–7).

$$Mo(CN)_8^{4-} + H_3^+O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HMo(CN)_8^{3-} + H_2O \tag{4}$$

$$Mo(CN)_8^{4-} + SH^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HMo(CN)_8^{3-} + S \tag{5}$$

$$HMo(CN)_8^{3-} + H_4IO_6^- \xrightarrow{k_3} Mo(CN)_8^{3-} + I(VI) \text{ (slow)} \tag{6}$$

$$Mo(CN)_8^{4-} + I(VI) \longrightarrow Mo(CN)_8^{3-} + IO_3^- \text{ (fast)} \tag{7}$$

where S is an organic solvent molecule. The rate expression is

$$\mathrm{d}[\mathrm{Mo(CN)}_8^{3-}]/\mathrm{d}t = 2k_3\,[\mathrm{H_4IO_6^-}]\,[\mathrm{HMo(CN)}_8^{3-}] \qquad (8)$$

Using the steady state treatment of the species $\mathrm{HMo(CN)}_8^{3-}$ one gets

$$[\mathrm{HMo(CN)}_8^{3-}] = \frac{\{k_1[\mathrm{H_3^+O}] + k_2[S\mathrm{H^+}]\}}{k_{-1}[\mathrm{H_2O}] + k_{-2}[S] + k_3[\mathrm{H_4IO_6^-}]}\,[\mathrm{Mo(CN)}_8^{4-}]$$

Substituting into eq. (8) we obtain

$$\text{rate} = 2k_3[\mathrm{H_4IO_6^-}]\,[\mathrm{Mo(CN)}_8^{4-}]\left\{\frac{k_1[\mathrm{H_3^+O}] + k_2[S\mathrm{H^+}]}{k_{-1}[\mathrm{H_2O}] + k_{-2}[S] + k_3[\mathrm{H_4IO_6^-}]}\right\}$$

Assuming that $k_{-1}[\mathrm{H_2O}] + k_{-2}[S] \gg k_3[\mathrm{H_4IO_6^-}]$,

$$\text{rate} = 2k_3[\mathrm{H_4IO_6^-}]\,[\mathrm{Mo(CN)}_8^{4-}]\left\{\frac{k_1}{k_{-1}[\mathrm{H_2O}] + k_{-2}[S]}\,[\mathrm{H_3^+O}] + \frac{k_2}{k_{-1}[\mathrm{H_2O}] + k_{-2}[S]}\,[S\mathrm{H^+}]\right\} \qquad (9)$$

$$= 2k_3[\mathrm{H_4IO_6^-}]\,[\mathrm{Mo(CN)}_8^{4-}]\,\{k_4[\mathrm{H_3^+O}] + k_4'[S\mathrm{H^+}]\} \qquad (10)$$

Where $k_4 = k_1/k_{-1}[\mathrm{H_2O}] + k_{-2}[S]$ and $k_4' = k_2/k_{-1}[\mathrm{H_2O}] + k_{-2}[S]$. From eq. (3) it follows

$$K_1 = [S\mathrm{H^+}]\,[\mathrm{H_2O}]/[\mathrm{H_3^+O}]\,[S] \qquad (11)$$

and $[\text{Acid}] = [\mathrm{H_3^+O}] + [S\mathrm{H^+}]$

$$= [\mathrm{H_3^+O}]\,\{1 + K_1[S]/[\mathrm{H_2O}]\} \qquad (12)$$

also, $$[\text{Acid}] = [S\mathrm{H^+}]\,\{1 + [\mathrm{H_2O}]/K_1[S]\} \qquad (13)$$

Substitution of the value of $[\mathrm{H_3^+O}]$ and $[S\mathrm{H^+}]$ from eqs. (12) and (13) into eq. (10) one obtains

$$\text{rate} = 2k_3[\mathrm{H_4IO_6^-}]\,[\mathrm{Mo(CN)}_8^{4-}]\,[\text{Acid}]\left\{\frac{k_4}{1 + K_1[S]/[\mathrm{H_2O}]} + \frac{k_4'}{1 + [\mathrm{H_2O}]/K_1[S]}\right\} \qquad (14)$$

and

$$k_{\text{obs}} = 2k_3[\mathrm{H_4IO_6^-}]\,[\text{Acid}]\left\{\frac{k_4}{1 + K_1[S]/[\mathrm{H_2O}]} + \frac{k_4'}{1 + [\mathrm{H_2O}]/K_1[S]}\right\}$$

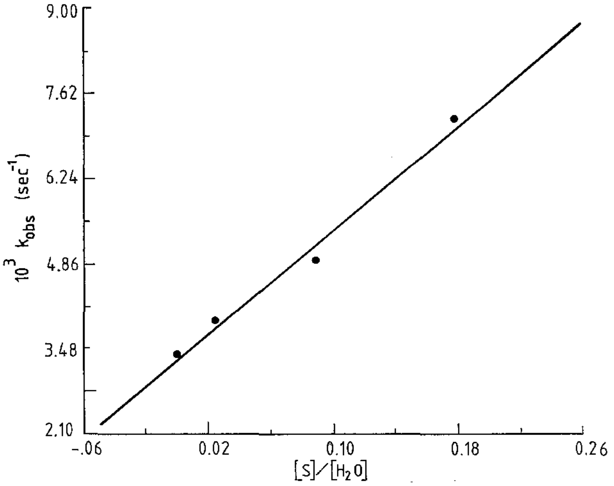

Fig. 1. Variation of k_{obs} with $[S]/[H_2O]$ at 25 °C in the range 0–34 wt% ethanol

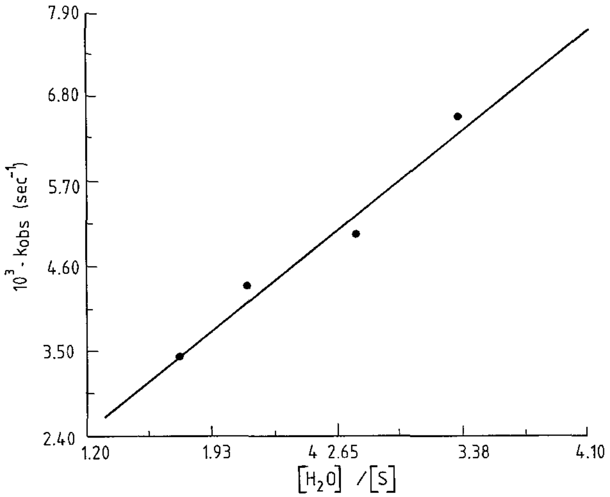

Fig. 2. Dependence of k_{obs} on $[H_2O]/[S]$ at 25 °C in the range 47–62 wt% ethanol

At constant $[H_4IO_6^-]$ and [Acid],

$$k_{obs} = A \left\{ \frac{k_4}{1 + K_1[S]/[H_2O]} + \frac{k_4'}{1 + [H_2O]/K_1[S]} \right\} \tag{15}$$

where A is a constant.

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It is obvious from eq. (15) that in the first region (0–43 wt% ethanol) the contribution of the second term in the bracket to the observed rate constant predominates, whereas the contribution of the first term predominates in the second region (43–62 wt% ethanol). The maximum of the reaction rate indicates a compensation of the two opposing factors affecting the reaction rate. Confirming this it was found that k_{obs} varies linearly with $[S]/[H_2O]$ and $[H_2O]/[S]$ in the first region and in the second region, as shown in Figs. 1 and 2, respectively.

In the former case, derived from the slope and intercept of Fig. 1 in comparison with eqs. (9–10), the k_2/k_1 ratio equals 6.00 at 25 °C. This indicates that the reaction is mainly catalysed by SH^+ in this region. Whereas in the latter case (Fig. 2) the k_1/k_2 ratio was found to be 5.67 which means that the reaction in this region is essentially catalysed by H_3O^+. The maximum of the reaction rate means that the reaction is equally catalysed by both SH^+ and H_3^+O.

The oxidation mechanism for $Mo(CN)_8^{4-}$ by IO_4^- may be inferred because of the lack of any direct evidence from the behaviour of periodate as an inner-sphere oxidant[6]. Two reactants, Mo(IV) and I(VII), could be bridged through the cyanide ligand with substitution occuring in the inner-coordination sphere of the labile I(VII)[6].

The values of the thermodynamic activation parameters for the oxidation of octacyanomolybdate(IV) by periodate are consistent with the above considerations and confirm our proposed mechanism for the reaction.

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