

A kinetic study of the oxidation of formaldehyde by the octacyanomolybdate(V) ion in aqueous alkaline medium

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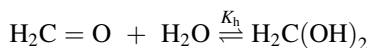
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Abstract The kinetics of the oxidation of formaldehyde by octacyanomolybdate(V) ions has been studied in aqueous alkaline medium. A formaldehyde-dependent and -independent reaction has been observed. The HCHO-dependent reaction displays first order kinetics in $[\text{Mo}(\text{CN})_8^{3-}]$, $[\text{HCHO}]$, $[\text{OH}^-]$ and alkali metal ion catalysis was observed. The rate law is consistent with: $\frac{-d[\text{Mo}(\text{CN})_8^{3-}]}{dt} = 2K_h K_1 K_2 k_3 [\text{Mo}(\text{CN})_8^{3-}] [\text{HCHO}] [\text{OH}^-] [\text{A}^+]$. Activation parameters for both the formaldehyde-dependent and -independent reaction have been obtained. The activation parameters for the HCHO-independent reaction provide evidence for the identification of the reaction. A reaction mechanism is proposed.

Keywords Kinetics · Redox · Aqueous medium · Activation parameters

Introduction

The carbonyl group, $-\text{C}=\text{O}$, is a structural characteristic of a wide range of compounds. The reactivity of this functional group is mainly due to the difference in the electronegativity between the carbon and oxygen atoms. Formaldehyde belongs to this group of compounds. Hydration of formaldehyde is a spontaneous process.



In aqueous medium, formaldehyde exists more than 99% in the hydrated form [1, 2] with a K_h value of 2×10^3 .

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Ferricyanide ($E^\circ = 0.36 \text{ V}$ [3]) and potassium permanganate ($E^\circ = 0.57 \text{ V}$ [3]) are the most common reagents used as oxidants for organic functional groups in alkaline medium. Speakman and Waters [4] reported the oxidation of aldehydes, ketones and nitroparaffins with ferricyanide while Holluta and Mutshin [5] reported the oxidation of formaldehyde by neutral permanganate and found the reaction to be base catalyzed.

$\text{W}(\text{CN})_8^{3-}$ ($E^\circ = 0.54 \text{ V}$ [6]) and $\text{Mo}(\text{CN})_8^{3-}$ ($E^\circ = 0.8 \text{ V}$ [6]) exhibit approximately similar redox potentials as the above mentioned oxidants. Furthermore, these $\text{M}(\text{CN})_8^{3-}$ ($\text{M}=\text{W}, \text{Mo}$) complexes are relatively substitution inert. This prompted the kinetic study of these complexes with some organic compounds.

Kinetic studies of the oxidation of formaldehyde (HCHO) with ferricyanide ($\text{Fe}(\text{CN})_6^{3-}$) [7] and octacyanotungstate(V) ($\text{W}(\text{CN})_8^{3-}$) [8] have been reported. In both studies, the reactions are first order with respect to the metal cyanide complex, formaldehyde and the hydroxide ion and correspond to the rate law:

$$R = \frac{K_h k}{[\text{H}_2\text{O}]} [\text{Mo}(\text{CN})_n^{3-}] [\text{HCHO}] [\text{OH}^-] \quad (1)$$

Experimental

Cesium octacyanomolybdate(V)dihydrate, $\text{Cs}_3\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$, was prepared as described by Leipoldt et al. [9–11] and was used as primary standard [12] after recrystallization. A stock solution of formaldehyde was prepared from Merck ‘‘Pro Analisi’’ 35% formaldehyde solution and was standardized by the method of Kolthoff and Belcher [13]. A stock solution of carbonate free sodium hydroxide was also prepared and standardized with potassium phthalate [14, 15]. All other reagents used were analytical grade and redistilled water was used throughout.

Kinetic measurements were made at constant ionic strength using sodium chloride as an electrolyte. Experiments were carried out in diffuse laboratory light because $\text{Mo}(\text{CN})_8^{3-}$ is sensitive to light [16], although in the dark at a pH between 1 and 12 the radiation effect is insignificant [17]. Rate data have been obtained by monitoring the absorbance decrease of $\text{Mo}(\text{CN})_8^{3-}$ on a Pye Unicam SP 1700 double beam spectrophotometer at 390 nm (Fig. 1). The temperature of reaction mixtures was controlled within 0.1 °C.

The extinction coefficients of $\text{Mo}(\text{CN})_8^{3-}$ and $\text{Mo}(\text{CN})_8^{4-}$ at 390 nm are $1,400 \text{ M}^{-1}\text{cm}^{-1}$ and $140 \text{ M}^{-1}\text{cm}^{-1}$, respectively [18]. Both the reagent, $\text{Mo}(\text{CN})_8^{3-}$, and the product, $\text{Mo}(\text{CN})_8^{4-}$, absorbed light at this wavelength. Beer’s law thus cannot be used directly to determine the concentration of $\text{Mo}(\text{CN})_8^{3-}$ at a time t . If the initial concentration of the $\text{Mo}(\text{CN})_8^{3-}$ equals ‘‘ a ’’ mol dm^{-3} then the total absorbance at a time t is given by:

$$A_t = \varepsilon_{\text{Mo}(\text{CN})_8^{3-}} \cdot x + \varepsilon_{\text{Mo}(\text{CN})_8^{4-}} \cdot (a - x)$$

and

$$\left[\text{Mo}(\text{CN})_8^{3-} \right] = x = \frac{A_t - \varepsilon_{\text{Mo}(\text{CN})_8^{4-}} \cdot a}{\varepsilon_{\text{Mo}(\text{CN})_8^{3-}} - \varepsilon_{\text{Mo}(\text{CN})_8^{4-}}}$$

This equation was used throughout to calculate $[\text{Mo}(\text{CN})_8^{3-}]$ at a time t .

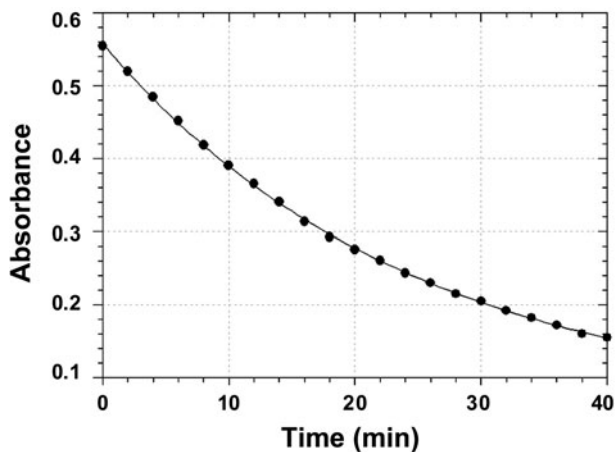


Fig. 1 Reaction trace of absorbance versus time. $[\text{Mo}(\text{CN})_8^{3-}] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{HCHO}] = 0.100 \text{ mol dm}^{-3}$; $[\text{OH}^-] = 0.050 \text{ mol dm}^{-3}$; $T = 25 \pm 0.1 \text{ }^\circ\text{C}$; $\mu = 0.1 \text{ mol dm}^{-3}$

Results and discussion

Pseudo-first order plots of $\ln[\text{Mo}(\text{CN})_8^{3-}]$ versus time were linear for more than two half-lives of the reaction. This as well as the results in Table 1 indicate that the reaction is first order with respect to $[\text{Mo}(\text{CN})_8^{3-}]$, $[\text{HCHO}]$, and $[\text{OH}^-]$. The plot of k_{obsd} versus $[\text{HCHO}]$ (Fig. 2) for the variation of the formaldehyde concentration in the reaction mixture yields a non-zero intercept. This is indicative of a second reaction independent of the $[\text{HCHO}]$ taking place. The hydroxide ion concentration range for this study could have the consequence that the $\text{Mo}(\text{CN})_8^{3-}$ oxidation of the hydroxide ion [19] become significant.

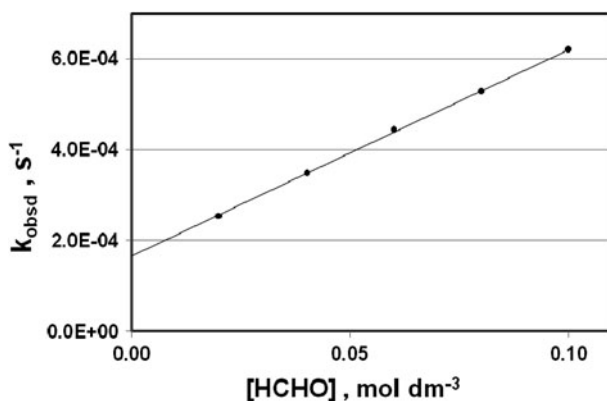
Alkali metal ion catalysis was significant in previous redox studies [20, 21] of the $\text{Mo}(\text{CN})_8^{3-}$ complex ion. The influence of added alkali metal ions on the reaction rate has also been studied by varying the alkali metal ion concentration with the addition of the alkali metal chloride to the reaction mixture and the ionic strength of the reaction mixture was kept constant with tetramethylammonium chloride. The plot of the first order rate constant versus alkali metal ion concentration is linear (Fig. 3) and indicates a very strong alkali metal ion catalysis and also that the reaction is first order in alkali metal ion concentration ($[\text{A}^+]$). The effectivity of the A^+ ion on the reaction rate is in the order $\text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$.

The observed first order dependence of k_{obsd} in $[\text{Mo}(\text{CN})_8^{3-}]$, $[\text{HCHO}]$, $[\text{OH}^-]$ and $[\text{A}^+]$ show the rate law to be of the form:

$$\frac{-d[\text{Mo}(\text{CN})_8^{3-}]}{dt} = k [\text{Mo}(\text{CN})_8^{3-}] [\text{HCHO}] [\text{OH}^-] [\text{A}^+] \quad (2)$$

Table 1 Observed rate constants for the oxidation of formaldehyde by $\text{Mo}(\text{CN})_8^{3-}$. $T = 25.0 \pm 0.1$ °C, $\mu = 0.10$ mol dm^{-3}

$[\text{Mo}(\text{CN})_8^{3-}]$ $\times 10^4$ (M)	$[\text{Mo}(\text{CN})_8^{4-}]$ $\times 10^4$ (M)	$[\text{HCHO}]$ (M)	$[\text{OH}^-]$ (M)	$k_{\text{obsd}} \times 10^4$ s $^{-1}$
2.50		0.100	0.050	6.37 ± 0.04
3.00		0.100	0.050	6.57 ± 0.03
3.50		0.100	0.050	6.50 ± 0.04
4.00		0.100	0.050	6.59 ± 0.03
4.50		0.100	0.050	6.53 ± 0.03
5.00		0.100	0.050	6.25 ± 0.03
5.00	2.50	0.100	0.050	6.22 ± 0.03
5.00	3.50	0.100	0.050	6.53 ± 0.04
5.00	3.00	0.100	0.050	6.66 ± 0.04
5.00	5.00	0.100	0.050	6.38 ± 0.03
5.00		0.100	0.050	6.20 ± 0.03
5.00		0.080	0.050	5.28 ± 0.01
5.00		0.060	0.050	4.43 ± 0.02
5.00		0.040	0.050	3.48 ± 0.03
5.00		0.020	0.050	2.55 ± 0.04
5.00		0.100	0.100	12.4 ± 0.2
5.00		0.100	0.080	9.74 ± 0.06
5.00		0.100	0.060	7.45 ± 0.05
5.00		0.100	0.040	4.87 ± 0.03
5.00		0.100	0.020	2.48 ± 0.04
5.00		0.100	0.010	1.23 ± 0.02

**Fig. 2** k_{obsd} versus the variation in $[\text{HCHO}]$. $[\text{Mo}(\text{CN})_8^{3-}] = 5.0 \times 10^{-4}$ mol dm^{-3} ; $[\text{OH}^-] = 0.050$ mol dm^{-3} ; $T = 25 \pm 0.1$ °C; $\mu = 0.1$ mol dm^{-3}

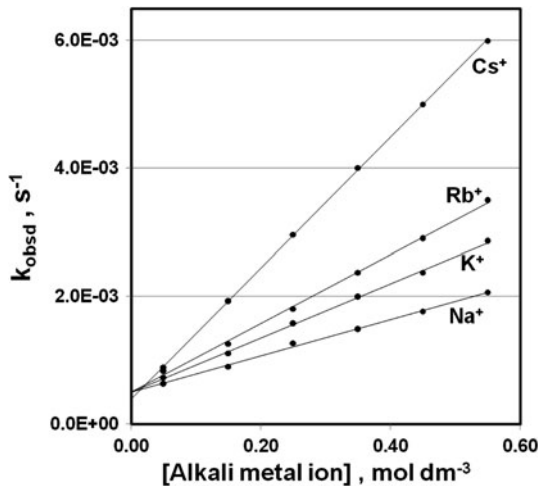
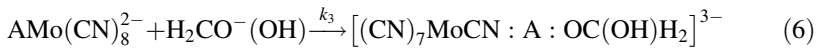
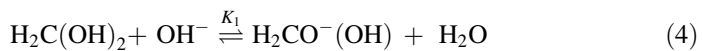
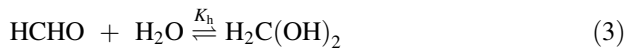


Fig. 3 First order rate constant, k_{obsd} , versus [Alkali metal ion]. $[Mo(CN)_8^{3-}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$; $[HCHO] = 0.10 \text{ mol dm}^{-3}$; $[OH^-] = 0.050 \text{ mol dm}^{-3}$; $T = 25 \pm 0.1 \text{ }^\circ\text{C}$; $\mu = 0.6 \text{ mol dm}^{-3}$. The intercept value is the first order rate constant without added alkali metal ions plus the first order rate constant of the formaldehyde independent reaction under the reaction conditions

The experimental results may be explained by the reaction mechanism:



The equilibria, Eqs. 3 [1, 2] and 5 [21] exist in solution and equilibrium 4 explains the OH^- dependence. The results of the variation of the alkali metal ion in the reaction mixture (Fig. 3) show a strong alkali metal ion catalysis and that the cation (A^+) should be a constituent of the activated complex. The formation of the activated complex (Eq. 6) is the rate determining step followed by a fast decomposition for the formation of the products. Tests to establish the formation of a free radical intermediate using vinyl acetate were negative. This is in agreement with previous ferricyanide oxidations of similar functional groups, where it is concluded that the free radical had no independent existence [7].

With Eq. 6 proposed as the rate determining step the rate of decrease of the $Mo(CN)_8^{3-}$ is given by:

$$\frac{-d[\text{Mo}(\text{CN})_8^{3-}]}{dt} = k_3 \left[\text{AMo}(\text{CN})_8^{2-} \right] [\text{H}_2\text{CO}^-(\text{OH})] + k_4 \left[(\text{CN})_7\text{MoCN} : \text{A} : \text{OC}(\text{OH})\text{H}_2 \right]^{3-} \quad (8)$$

Steady state treatment to $\text{H}_2\text{C}(\text{OH})_2$, $\text{H}_2\text{CO}^-(\text{OH})$, $\text{AMo}(\text{CN})_8^{2-}$ and $[(\text{CN})_7\text{MoCN}:\text{A}:\text{OC}(\text{OH})\text{H}_2]^{3-}$ yield the rate law:

$$\frac{-d[\text{Mo}(\text{CN})_8^{3-}]}{dt} = 2K_h K_1 K_2 k_3 \left[\text{Mo}(\text{CN})_8^{3-} \right] [\text{HCHO}] [\text{OH}^-] [\text{A}^+] \quad (9)$$

The total rate law under experimental conditions, as a HCHO-dependent reaction and a HCHO-independent reaction was observed (Fig. 2), is thus given by:

$$\frac{-d[\text{Mo}(\text{CN})_8^{3-}]}{dt} = 2K_h K_1 K_2 k_3 \left[\text{Mo}(\text{CN})_8^{3-} \right] [\text{HCHO}] [\text{OH}^-] [\text{A}^+] + k' \left[\text{Mo}(\text{CN})_8^{3-} \right] [\text{OH}^-]$$

The rate constant for the HCHO-dependent reaction has been determined as. $R = 0.91 \pm 0.02 \text{ M}^{-3} \text{ s}^{-1}$ and for the HCHO-independent reaction $R' = 3.32 \pm 0.06 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$.

The activation parameters for both the HCHO-dependent and -independent reactions were obtained by variation of $[\text{HCHO}]$ at various temperatures between 22 and 35 °C (Table 2). The parameters ΔH^\ddagger and ΔS^\ddagger were obtained from the Eyring equation:

$$k = \frac{k_B T}{h} e \left[\frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \right] \quad (10)$$

The equation converted to the logarithmic form yield a linearized form, [22]

$$\ln \left(\frac{k}{T} \right) = - \left(\frac{\Delta H^\ddagger}{RT} \right) + \left(\frac{\Delta S^\ddagger}{R} \right) + \ln \left(\frac{k_B}{h} \right) \quad (11)$$

where ΔH^\ddagger can be obtained from the slope, $-\frac{\Delta H^\ddagger}{R}$, and ΔS^\ddagger from the intercept

$$\frac{\Delta S^\ddagger}{R} + \ln \left(\frac{k_B}{h} \right)$$

Non-linear least-squares fits of the results in Table 2 to Eqs. 10 and 11 yield an activation enthalpy, $\Delta H^\ddagger = 54 \pm 3 \text{ kJ mol}^{-1}$, and an activation entropy,

Table 2 Observed rate constants for the reduction of $\text{Mo}(\text{CN})_8^{3-}$ by formaldehyde at various temperatures. $[\text{Mo}(\text{CN})_8^{3-}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{OH}^-] = 0.050 \text{ mol dm}^{-3}$; $\mu = 0.10 \text{ mol dm}^{-3}$

Temperature (°C)	Gradient $K_{\text{obsd}} \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$	Intercept $k_{\text{obsd}} \times 10^4 \text{ s}^{-1}$
22.6	3.6 ± 0.3	1.4 ± 0.2
25.1	4.6 ± 0.3	1.7 ± 0.3
27.5	5.4 ± 0.2	1.9 ± 0.2
30.3	6.3 ± 0.3	2.0 ± 0.3
35.0	9.3 ± 0.4	2.2 ± 0.3

$\Delta S^* = -110 \pm 9 \text{ J K}^{-1} \text{ mol}^{-1}$, for the HCHO-dependent reaction and an activation enthalpy, $\Delta H^\ddagger = 21 \pm 4 \text{ kJ mol}^{-1}$, and an activation entropy, $\Delta S^* = -245 \pm 15 \text{ J K}^{-1} \text{ mol}^{-1}$, for the HCHO-independent reaction. All the obtained values have been validated by using: [22]

$$\sigma \Delta S^* = \frac{1}{T_{av}} \sigma \Delta H^\ddagger$$

The activation parameters for the HCHO-independent reaction is similar to that of the $\text{Mo}(\text{CN})_8^{3-}$ oxidation of the hydroxide ion [19]. This is a means of identification for the HCHO-independent reaction.

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