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Kinetics of the Ru(III) Catalyzed Oxidation of Formaldehyde and Acetaldehyde by Alkaline Hexacyanoferrate(III)

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The kinetics of ruthenium(III) catalyzed oxidation of formaldehyde and acetaldehyde by alkaline hexacyanoferrate(III) has been studied spectrophotometrically. The rate of oxidation of formaldehyde is directly proportional to $[\mathrm{Fe(CN)}_6^{3-}]$ while that of acetaldehyde is proportional to $k[\mathrm{Fe(CN)}_6^{3-}]/\{k' + k''[\mathrm{Fe(CN)}_6^{3-}]\}$, where k, k' and k'' are rate constants. The order of reaction in acetylaldehyde is unity while that in formaldehyde falls from 1 to 0. The rate of reaction is proportional to $[\mathrm{Ru(III)}]_T$ in each case. A suitable mechanism is proposed and discussed.

(Keywords: Kinetics; Mechanism; Oxidation; Ru(III) *catalyzed)*

Die Kinetik der Ru(III)-katalysierten Oxidation von Formaldehyd und Acetaldehyd mittels alkalischem Hexacyanoferrat(III)

Die Untersuchung der Kinetik erfolgte spektrophotometrisch. Die Geschwindigkeitskonstante der Oxidation von Formaldehyd ist direkt proportional zu $[\mathrm{Fe(CN)}_6^{3-}]$, währenddessen die entsprechende Konstante für Acetaldehyd proportional zu $k[\mathrm{Fe(CN)}_6^{3-}]/\{k' + k''[\mathrm{Fe(CN)}_6^{3-}]\}$ ist, wobei k, k' und k'' Geschwindigkeitskonstanten sind. Die Reaktionsordnung für Acetaldehyd ist eine erste, die für Formaldehyd fällt von erster bis zu nullter Ordnung. Die Geschwindigkeitskonstante ist in jedem Fall proportional zu $[\mathrm{Ru(III)}]_T$. Es wird ein passender Mechanismus vorgeschlagen.

Introduction

The oxidations by hexacyanoferrate(III) are generally slow. However, a small amount of osmium(VIII)[1] or ruthenium(III) ($\sim 10^{-6}\,M$) is sufficient to catalyze many such oxidations.

Ruthenium(III) catalyzed oxidation of some organic compounds by hexacyanoferrate(IIII)[2—4] generally proceeds via formation of a complex between the ruthenium(III) species and the substrate and its subsequent disproportionation (slow step) into oxidation products and the ruthenium(III)—hydride species. The ruthenium(III)—hydride species is rapidly reconverted to ruthenium(III) by hexacyanoferrate(III). Thus the order of above reactions in [hexacyanoferrata(III)] is zero. During the ruthenium(III) catalyzed oxidation of some organic compounds by IO_4^-[5], bis(tillurato) cuprate[6], the existence of ruthenium(II) or ruthenium(I) in place of ruthenium-hydride species has also been suggested.

The uncatalyzed oxidation of formaldehyde[7] and acetaldehyde by hexacyanoferrate(III) takes place in high alkaline solutions and at high ionic strength. However in presence of ruthenium(III) as a catalyst, the rate of oxidation of formaldehyde and acetaldehyde by alkaline hexacyanoferrate(III) has been found to be first order dependent in the [oxidant] and not zero order dependent as generally observed in the ruthenium(III) catalyzed oxidation of some organic compounds[2–6]. It was, therefore, imperative to study the title reaction in detail to understand the nature of the reactions.

Experimental

Aqueous solutions of formaldehyde and acetaldehyde were prepared from BDH reagent. Stock solutions of potassium ferricyanide and sodium hydroxide were prepared from analar BDH reagents. The solution of ruthenium(III) chloride was prepared by dissolving the sample in very dilute hydrochloric acid. The final strength of HCl and $RuCl_3$ were kept at $16.4 \cdot 10^{-2}$ *M* and $9.6 \cdot 10^{-3}$ *M* respectively. All other reagents used were of AR grade. Doubly distilled water was used throughout the investigations.

A thermostatic water bath was used to maintain the desired temperature within $\pm 0.1°$. The rates were measured spectrophotometrically by monitoring the absorbance due to hexacyanoferrate(III) as a function of time at 420 nm on a Bausch and Lomb spectronic-20 spectrophotometer. The absorbance due to hexacyanoferrate(II) and the catalyst was negligible at this wavelength. The concentration of hexacyanoferrate(III) was kept below $5.0 \cdot 10^{-4}$ *M* in order to obey *Beer*'s law.

Stoichiometry

The reaction mixtures containing a known excess of hexacyanoferrate(III) over aldehyde were kept at 40 °C in presence of 0.1 *M* NaOH and $1.92 \cdot 10^{-6}$ *M* Ru(III) for eight hours. The amount of hexacyanoferrate(III) left was consistent with the following stoichiometric equation,

$$RCHO + 2\,OH^- + 2\,Fe(CN)_6^{3-} = RCOOH + H_2O + 2\,Fe(CN)_6^{4-} \qquad (1)$$

The presence of corresponding acids as oxidation products was detected by suitable tests[8]. The corresponding acid as oxidation product has also been observed in earlier studies on uncatalyzed oxidation of formaldehyde by hexacyanoferrate(III)[7] and osmium(VIII) catalyzed oxidation of aldehydes by chloramine-*T*[9].

Results

The reactions were studied at different initial concentrations of the reactants. The log (absorbance) versus time plots in hexacyanoferrate(III) were found to be good straight lines and, therefore, the pseudo first order rate constants in hexacyanoferrate(III) (k_1) were evaluated from the slopes of these straight lines. The values of the rate constant in hexacyanoferrate(III) were nearly constant at all [hexacyanoferrate(III)] in case of formaldehyde (Table 1) and thus further established a first order dependence of rate in hexacyanoferrate(III).

Table 1. *Dependence of rate constants on initial concentration of reactants at 35 °C*

$[Fe(CN)_6^{3-}]$ $M \cdot 10^4$	[Aldehyde] $M \cdot 10^3$	$[Ru(III)]_T$ $M \cdot 10^6$	$k_1 \cdot 10^4$ (s^{-1}) Formaldehyde	$k_1 \cdot 10^4$ (s^{-1}) Acetaldehyde
3.0	4.0	1.92	15.8	22.0
3.5	4.0	1.92	16.0	17.0
4.0	4.0	1.92	15.6	14.5
4.5	4.0	1.92	15.5	12.1
5.0	4.0	1.92	15.0	10.5
5.0	1.6	1.92	8.0	—
5.0	2.4	1.92	11.5	6.7
5.0	3.2	1.92	13.4	8.6
5.0	6.0	1.92	16.3	14.4
5.0	8.0	1.92	17.5	20.2
5.0	4.0	0.96	7.6	7.7
5.0	4.0	2.88	20.5	13.4
5.0	4.0	3.84	30.7	15.4

$[OH^-] = 0.1\,M$ in case of formaldehyde and $0.05\,M$ in case of acetaldehyde.

However, an increase in the initial concentration of hexacyanoferrate(III) resulted in a decrease of the rate constant (k_1) in case of acetaldehyde. A plot of $1/k_1$ versus $1/[Fe(CN)_6^{3-}]$ in case of acetaldehyde gave a straight line with negative slope (Fig. 1). It appears, therefore, that the dependence of rate in hexacyanoferrate(III) in case of acetaldehyde may be represented as

$$\text{rate} \propto \frac{k\,[Fe(CN)_6^{3-}]}{k' + k''\,[Fe(CN)_6^{3-}]}$$

where k, k' and k'' are rate constants.

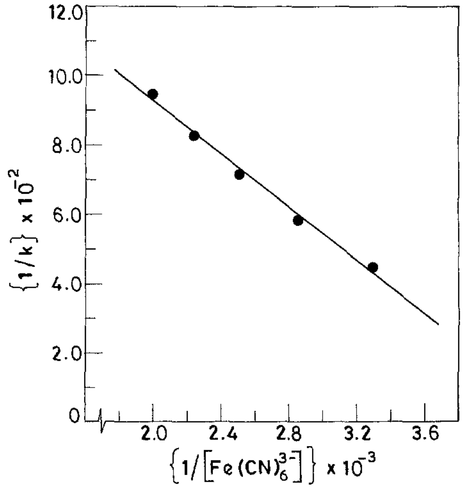


Fig. 1. Plot of $1/k_1$ versus $1/[Fe(CN)_6^{3-}]$ at 35° for acetaldehyde oxidation; $[OH^-] = 0.1\,M$, $[Ru(III)]_T = 1.92 \cdot 10^{-6}\,M$, $[\text{Acetaldehyde}] = 4.0 \cdot 10^{-3}\,M$

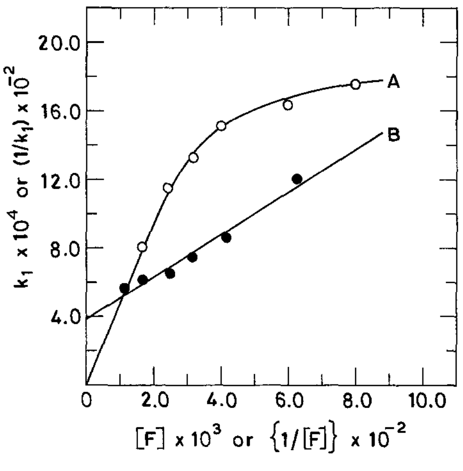


Fig. 2. *A* Plot of k_1 versus [Formaldehyde] at 35 °C; *B* Plot of $1/k_1$ versus 1/[Formaldehyde] at 35 °C; $[OH^-] = 0.10\,M$, $[Ru(III)]_T = 1.92 \cdot 10^{-6}\,M$, $[Fe(CN)_6^{3-}] = 5.0 \cdot 10^{-4}\,M$

The plot of k_1 versus [Formaldehyde] (Fig. 2 *A*) showed a deviation from linearity at higher formaldehyde concentrations while the plot of $1/k_1$ versus 1/[formaldehyde] (Fig. 2 *B*) was linear with an intercept. It is, therefore, clear that the order in formaldehyde falls from unity to zero at higher concentrations of formaldehyde. The plot of k_1 versus [Acetalde-

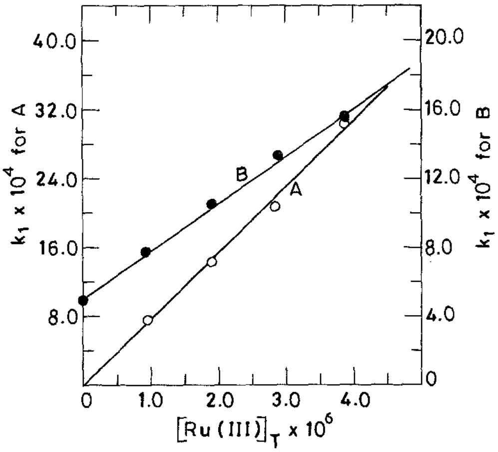


Fig. 3. Plots of k_1 versus $[Ru(III)]_T$ at 35 °C. *A* Formaldehyde; *B* Acetaldehyde; $[OH^-] = 0.10\,M$ in case of formaldehyde and $0.05\,M$ in case of acetaldehyde, $[Fe(CN)_6^{3-}] = 5.0 \cdot 10^{-4}\,M$, $[\text{Aldehyde}] = 4.0 \cdot 10^{-3}\,M$

hyde] was linear passing through the origin (figure not given) establishing first order dependence of rate in [Acetaldehyde].

The plots of k_1 versus $[Ru(III)]_T$ (Fig. 3) were linear suggesting that the rate is directly proportional to $[Ru(III)]_T$. It is also clear from Fig. 3 that the rate due to the uncatalyzed path is negligible in the case of formaldehyde.

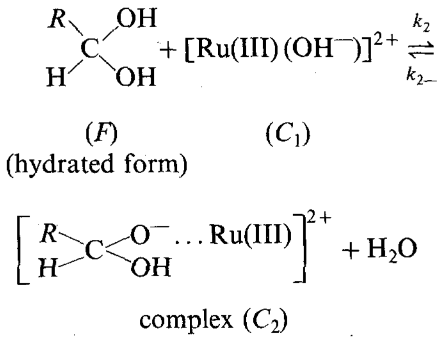
The effect of OH^- was studied at a fixed ionic strength ($\mu = 0.2\,M$) using sodium perchlorate. A change in the alkali concentration (0.04 to $0.2\,M$) had a negligible effect on the rate of reaction in each case. Addition of hexacyanoferrate(II) showed no effect on the reaction rate up to a concentration $5.0 \cdot 10^{-4}\,M$. Addition of sodium perchlorate up to $0.4\,M$ also showed a negligible effect on the rate of oxidation in each case.

The rates were also measured at 40, 45 and 50 °C to investigate the effect of temperature. The values of energy of activation calculated from *Arrhenius* plots were $\sim 8.1 \pm 0.1$ and 7.9 ± 1.0 kcal mol^{-1} for the oxidation of formaldehyde and acetaldehyde, respectively.

Discussion

Ruthenium(III) chloride exists in the hydrated form[10] as $[Ru(H_2O)_6]^{3+}$. Metal ions of the form $[Ru(H_2O)_6]^{3+}$ are also known to exist as $[Ru(H_2O)_5(OH^-)]^{2+}$ in the alkaline medium[11]. In the present investigations, the rate of oxidation is independent on the OH^- concentration, therefore the $[Ru(H_2O)_5(OH^-)]^{2+}$ species may be considered as the main reacting species. The studies on ruthenium(III) catalyzed oxidation of organic compounds[1—5] have shown that the oxidation proceeds by the abstraction of H^- by a Ru(III) species from the α-carbon atom of he substrate. The abstraction of α-hydrogen from 2-propanol by Ru(III) in acidic media was also reported[12]. In aqueous medium 99% of the formaldehyde exists[13] in the hydrated form as $CH_2(OH)_2$. A fast hydride ion transfer from the aldehyde in the oxidation of aldehydes by chromium (VI)[14,15] and chloramine[8]-*T* has also been suggested.

On the basis of the above facts and the experimental results the mechanism for the oxidation process may be suggested as follows:



(2)

$$(C_2)^{2+} + Fe(CN)_6^{3-} \xrightarrow{k_3} RCOOH + Ru(II) + Fe(CN)_6^{4-} + H^+ \quad (3)$$

$$Ru(II) + Fe(CN)_6^{3-} \xrightarrow{k_4} Fe(CN)_6^{4-} + Ru(III) \qquad \text{fast} \quad (4)$$

Ru(II) formed in step (3) is immediately reconverted into Ru(III) by $Fe(CN)_6^{3-}$ [step (4) being very fast] and thus the amount of Ru(II) present would be negligible. Therefore, at any time the total concentration of ruthenium (III) may be given as:

$$[Ru(III)]_T = [C_1] + [C_2] \quad (5)$$

By applying the steady state conditions with respect to C_2 in step (4) and (5), we get

$$[C_2] = \frac{k_2[C_1]}{k_{2-} + k_3[Fe(CN)_6^{3-}]} \quad (6)$$

By substituting the value of $[C_2]$ in equation (5) and solving it for $[C_2]$, $[C_2]$ in terms of $[Ru(III)]_T$ is obtained as

$$[C_2] = \frac{k_2[F][Ru(III)]_T}{k_{2-} + k_3[Fe(CN)_6^{3-}] + k_2[F]} \quad (7)$$

and, therefore, the rate of disappearance of hexacyanoferrate(III) may be represented as

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{Fe(CN)}_6^{3-}] = \frac{2k_2k_3[F][\mathrm{Ru(III)}]_T[\mathrm{Fe(CN)}_6^{3-}]}{k_{2-} + k_2[F] + k_3[\mathrm{Fe(CN)}_6^{3-}]} \qquad (8)$$

Now, if complex C_2 is stable, i.e. step (3) is slow, $(k_{2-} + k_2[F]) \gg k_3[\mathrm{Fe(CN)}_6^{3-}]$ may be taken as a suitable approximation and the rate law equation (8) reduces to

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{Fe(CN)}_6^{3-}] = \frac{2K_2k_3[F][\mathrm{Ru(III)}]_T[\mathrm{Fe(CN)}_6^{3-}]}{1 + K_2[F]} \qquad (9)$$

where $K_2 = k_2/k_{2-}$

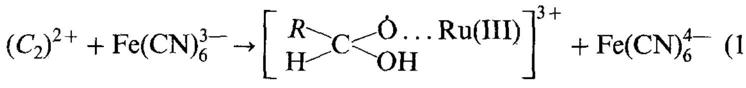
According to above rate law equation (9) the rate of reaction is first order in [hexacyanoferrate (III)] and $[\mathrm{Ru(III)}]_T$ while a plot of $1/k_{\mathrm{obs}}$ versus $1/[F]$ should give a straight line with an intercept, which was found to be true in case of formaldehyde.

On the other hand if complex C_2 is less stable so that the rate of step (3) is not small compared with the reverse rate of step (2) and the inequality $(k_{2-} + k_3[\mathrm{Fe(CN)}_6^{3-}]) \gg k_2[F]$ holds good, rate law equation (8) reduces to

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{Fe(CN)}_6^{3-}] = \frac{2k_2k_3[F][\mathrm{Ru(III)}]_T[\mathrm{Fe(CN)}_6^{3-}]}{k_{2-} + k_3[\mathrm{Fe(CN)}_6^{3-}]} \qquad (10)$$

According to equation (10) the rate of reaction is first order in $[F]$ and $[\mathrm{Ru(III)}]_T$, while a plot of $1/k_{\mathrm{obs}}$ versus $1/[\mathrm{Fe(CN)}_6^{3-}]$ should give a straighzt line with negative slope. The experimental results for the oxidation of acetaldehyde are in agreement with the rate law equation (10).

Thus the complex C_2 is more stable in case of formaldehyde. An alternative mechanism may also be suggested by replacing step (3) and (4) by the following steps.



$$(C_2)^{2+} + \mathrm{Fe(CN)}_6^{3-} \rightarrow \left[\begin{smallmatrix} R \\ H \end{smallmatrix} \!>\! C \!<\! \begin{smallmatrix} \dot{O}\ldots\mathrm{Ru(III)} \\ OH \end{smallmatrix} \right]^{3+} + \mathrm{Fe(CN)}_6^{4-} \qquad (11)$$

(X_T)

and

$$(X_T) + \mathrm{Fe(CN)}_6^{3-} \rightarrow R\mathrm{COOH} + \mathrm{H}^+ + \mathrm{Fe(CN)}_6^{4-} + \mathrm{Ru(III)}\ \text{(fast)} \qquad (12)$$

The rate law equation in this case would be same as given by equation (8) and thus the results can be explained in a similar manner.

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References

[1] *Upadhyay S. K., Agrawal M. C.,* Journal of Sci. and Ind. Research **42**, 508 (1983).
[2] *Singh H. S., Singh R. K., Singh S. M., Sisodia A. K.,* J. Phys. Chem. **81**, 1044 (1977).
[3] *Narendra N., Singh L. P., Singh R. P.,* J. Ind. Chem. Soc. **58**, 1204 (1981).
[4] *Dwivedi R. K., Verma M., Kumar P., Behari K.,* Tetrahedron **39**, 815 (1983).
[5] *Rao M. D., Prasada, Padmanabha J.,* Ind. J. Chem. **19 A**, 984 (1980).
[6] *Reddy K. B., Sethuram B., Rao, T. N.,* Bull. Soc. Chem., Belg. **90**, 1017 (1981).
[7] *Singh V. N., Gangwar M. C., Saxena B. B. L., Singh M. P.,* Cand. J. Chem. **47**, 1051 (1969).
[8] *Feigl F.,* Spot Test in Organic Analysis, p. 118, 131. London: Elsevier. 1960.
[9] *Sanehi R., Agrawal M. C., Mushran S. P.,* Ind. J. Chem. **12**, 311 (1974).
[10] *Connick R. E., Fine D. A.,* J. Amer. Chem. Soc. **82**, 4187 (1960).
[11] *Cotton F. A., Wilkinson G.,* Advanced Inorganic Chemistry, 2nd ed., p. 153. New York: Wiley. 1966.
[12] *Charman H. B.,* J. Chem. Soc. B **1967**, 629.
[13] *Bieber R., Trumpler G.,* Helv. Chim. Acta **30**, 1860 (1947).
[14] *Goswami C., Banerji K. K.,* Bull. Chem. Soc. Japan **43**, 2644 (1970).
[15] *Subbaraman L. R., Santappa M.,* Z. Phys. Chem. **210**, 172 (1966).