Kinetic Study of Ruthenium(III)-catalysed Oxidation of 2-Methylpentane-2,4-diol by Alkaline Hexacyanoferrate(III)

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A concerted hydrogen-atom transfer one-electron transfer mechanism is proposed for the ruthenium(III)-catalysed oxidation of 2-methylpentane-2,4-diol by alkaline hexacyanoferrate(III).

Some substrates like alcohols, organic acids *etc.*, which are not easily oxidized by common oxidants, can be oxidized in the presence of transition metal ions. Owing to the fact that these methods are expensive, the use of transition metals in catalytic quantities in combination with an inexpensive cooxidant is an attractive alternative.[1,2]

Here, we describe the first reported study for the ruthenium(III)-catalysed oxidation of 2-methylpentane-2,4-diol by alkaline hexacyanoferrate(III).

Experimental

All the reagents used were of A.R. grade, except for the catalyst which was 100% in Ru^{III}. The aqueous solutions handled were prepared in water obtained by a Millipore-Milli Q Water Purification System. The ionic strength was kept constant at 0.5 M by adding sodium perchlorate. The progress of the reaction was followed spectrophotometrically by measuring the optical absorbance of hexacyanoferrate(III) at 420 nm on a Perkin Elmer Lambda 3B spectrophotometer equipped with a thermostated cell holder which kept the temperature constant at 30.0 ± 0.1 °C. The initial rates method[17] was used for kinetic analysis. The initial rates were obtained by fitting the absorbance versus time data, for a small percentage of the reaction (5% or less)[17] to a straight line, $A = \alpha_0 + \alpha_1 t$, by the least-squares method; the slope provides the initial rate, $v_0 = \alpha_1 = -(\mathrm{d}A/\mathrm{d}t)_0$, given in absorbance units. The initial rate, v_0, expressed in M min^{-1} is given by $v_0 = -1/\varepsilon(\mathrm{d}A/\mathrm{d}t)_0 = -(\mathrm{d}[\mathrm{Fe(CN)_6}^{3-}]/\mathrm{d}t)_0$, where $\varepsilon = 1000\ \mathrm{M^{-1}\,cm^{-1}}$ at 420 nm. Under kinetic conditions 4-hydroxy-4-methylpentan-2-one was the only reaction product found by gas chromatography. Moreover, under the conditions $[\mathrm{Fe(CN)_6}^{3-}] \gg [\mathrm{diol}]$, the reaction was allowed to go to completion and the residual oxidant concentration was determined spectrophotometrically. These measurements indicated that 1 mole of alcohol reacted with 2 moles of oxidant.

Results

Fig. 1 shows that the initial rate, v_0, varies linearly with the hexacyanoferrate(III) concentration at low concentrations (first-order kinetics) and becomes independent of hexacyanoferrate(III) concentration (zero-order kinetics) at high concentrations.

It has been observed that at low concentration of 2-methylpentane-2,4-diol the initial rate is proportional to [diol] (first-order kinetics); at a higher concentration of 2-methylpentane-2,4-diol the initial rate becomes independent of that concentration (zero-order kinetics).

It has been observed that on increasing $[\mathrm{OH^-}]$ the initial rate increases and then decreases showing a maximum value. The variation of the experimental initial rate with the medium basicity is complicated and obeys eqn. (5).

$$v_0 = \frac{A_1[\mathrm{OH^-}] + A_2[\mathrm{OH^-}]^2}{1 + B_1[\mathrm{OH^-}] + B_2[\mathrm{OH^-}]^2} \qquad (5)$$

This equation was fitted by a non-linear regression method. The average error was found to be 4.5%.

The plots of v_0 versus catalyst concentration gave straight lines with zero intercept. Hence, the kinetics are first order in catalyst concentration and the rate of the uncatalysed reaction is negligible in comparison with the catalysed reaction.

The hydrogen on the α-carbon of the alcohol is necessary for the reaction to occur,[19] since tertiary alcohol (2,3-dimethylbutane-2,3-diol) was unreactive under kinetic conditions.

When acrylonitrile[22] (0.01 M) was added to the reaction mixture in a typical kinetic experiment, the reaction rate decreased (15%), while no difference in the reaction rate was observed when acetonitrile (0.01 M) was added. Moreover when, in a typical kinetic experiment, 2,4,6-*triert*-butylphenol[23] (1.6×10^{-4} M) was added to the reaction mixture the reaction rate decreased (40%). These facts indicate the generation of free radicals in the reaction.

The oxidation of cyclobutanol[24] under kinetic conditions yields butyraldehyde as the main product.

Discussion

Optical behaviour of an aqueous solution 4.0×10^{-5} M $\mathrm{RuCl_3}$ in the $[\mathrm{OH^-}] = 10^{-3}$–0.4 M range may involve the existence of several hydroxo-aquo ruthenium complexes in the equilibrium as follows:

$$\mathrm{Ru(H_2O)_6}^{3+} + \mathrm{OH^-} \overset{K_0}{\rightleftharpoons} \mathrm{Ru(H_2O)_5OH^{2+}} + \mathrm{H_2O} \qquad (6)$$

$$\mathrm{Ru(H_2O)_5OH^{2+}} + \mathrm{OH^-} \overset{K_1}{\rightleftharpoons} \mathrm{Ru(H_2O)_4(OH)_2}^{+} + \mathrm{H_2O} \qquad (7)$$

$$\mathrm{Ru(H_2O)_4(OH)_2}^{+} + \mathrm{OH^-} \overset{K_2}{\rightleftharpoons} \mathrm{Ru(H_2O)_3(OH)_3} + \mathrm{H_2O} \qquad (8)$$

As no evidence for the existence of oxo-bridged ruthenium(III) complexes was obtained, we propose a mechanism involving catalytic paths by the hydroxo-aquo ruthenium complexes. $\mathrm{Ru(H_2O)_4(OH)_2}^{+}$ and $\mathrm{Ru(H_2O)_3(OH)_3}$, because equilibrium (6) is shifted forward considerably under the experimental conditions ($K_0 = 1.26 \times 10^{11}$ at 25 °C[26]).

The dependence of reaction rate on [diol] observed suggests the formation of an intermediate complex between the alcohol and the active species of the catalyst. Thus for the species $\mathrm{Ru(H_2O)_4(OH)_2}^{+}$ the following can be written:

$$\mathrm{Ru(H_2O)_4(OH)_2}^{+} + \mathrm{RR'CHOH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C_1}^{+} + \mathrm{H_2O} \qquad (9)$$

MO analysis[31] has shown that the activation energy for hydride transfer from methanol to the oxo ligand of $\mathrm{Ru(HN{=}CH{-}CH{=}NH)_2(NH_3)O^{2+}}$ would be substantially lowered by prior coordination of the substrate to the metal *via* the hydroxylic oxygen. Such an intermediate complex in

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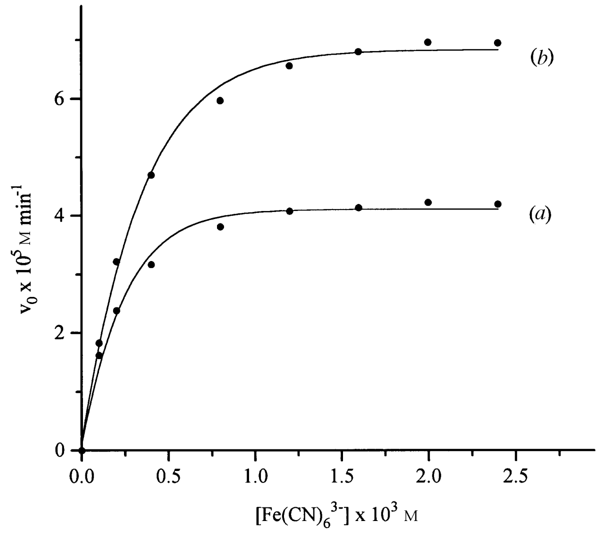
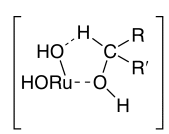


Fig. 1 Effect of $[Fe(CN)_6^{3-}]$ on the initial rate. [2-Methylpentane-2,4-diol] = 0.08 M; $[RuCl_3] = 2.40 \times 10^{-6}$ M; $I = 0.5$ M and $T = 30$ °C, (a) [NaOH] = 0.28 M; (b) [NaOH] = 0.1 M

the $Ru(H_2O)_4(OH)_2^+$ reaction with 2-methylpentane-2,4-diol would have the following structure.



C_1^+

R is CH_3—$C(CH_3)OH$—CH_2, and R′ is CH_3

To explain the dependence of v_0 on hexacyanoferrate(III) concentration we propose that the ruthenium-substrate complex is attacked by hexacyanoferrate(III) in a slow step (10). This attack involves an outer-sphere one-electron transfer from ruthenium to oxidant and a hydrogen atom transfer from the α-C—H bond to the oxygen of the hydroxo ligand of ruthenium:

$$C_1^+ + Fe(CN)_6^{3-} \xrightarrow{k_2} RR'\dot{C}OH + Fe(CN)_6^{4-} + Ru(H_2O)_5OH^{2+} \qquad (10)$$

The moderate primary isotope effect observed ($v_{0,H}/v_{0,D} = 5.9$) for $[^2H_6]$ethane-1,2-diol[14] supports the direct involvement of the carbon—hydrogen bond in the rate determining step. The experimentally observed presence of free radicals in the reaction mixture and the observation that the oxidation of cyclobutanol produces butyraldehyde, would support a hydrogen-atom transfer mechanism.

Finally, hexacyanoferrate(III) reacts rapidly with the ketyl radical to yield the reaction products, *i.e.* 4-hydroxy-4-methylpentan-2-one and hexacyanoferrate(II):

$$Fe(CN)_6^{3-} + RR'\dot{C}OH \rightarrow Fe(CN)_6^{4-} + RR'\overset{+}{C}OH \qquad (11)$$

$$RR'\overset{+}{C}OH + OH^- \rightarrow RR'CO + H_2O \qquad (12)$$

In addition to eqn. (10) we can write for the other active species of the catalyst:

$$Ru(H_2O)_3(OH)_3 + RR'CHOH \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} C_2 + H_2O \qquad (13)$$

$$C_2 + Fe(CN)_6^{3-} \xrightarrow{k_4} RR'\dot{C}OH + Fe(CN)_6^{4-} + Ru(H_2O)_4(OH)_2^+ \qquad (14)$$

The next step would be similar to that reported above. Hence the disappearance rate of hexacyanoferrate(III) is given by:

$$\frac{-d[Ox]}{dt} = 2k_2[C_1^+][Ox] + 2k_4[C_2][Ox] \qquad (15)$$

where [Ox] is the potassium hexacyanoferrate(III) concentration.

By applying steady-state hypothesis for both C_1^+ and C_2 complexes we obtain:

$$[C_1^+] = \frac{k_1[S][Ru(H_2O)_4(OH)_2^+]}{k_{-1} + k_2[Ox]} \qquad (16)$$

$$[C_2] = \frac{k_3[S][Ru(H_2O)_3(OH)_3]}{k_{-3} + k_4[Ox]} \qquad (17)$$

where [S] is the 2-methylpentane-2,4-diol concentration.

The total ruthenium(III) concentration may be obtained from the mass balance:

$$[Ru^{III}]_T = [Ru(H_2O)_5OH^{2+}] + [Ru(H_2O)_4(OH)_2^+] + [Ru(H_2O)_3(OH)_3] + [C_1^+] + [C_2] \qquad (18)$$

Because of the Hammond postulate,[34] it is reasonable to assume that $k_2/k_{-1} \approx k_4/k_{-3}$, that is $k_{-1} + k_2[Ox] \approx \beta(k_{-3} + k_4[Ox])$. Substitution of the expressions for $[C_1^+]$ and $[C_2]$ in terms of $[Ru^{III}]_T$ into eqn. (15) leads to the reaction rate:

$$\frac{-d[Ox]}{dt} = \frac{2\{k_1k_2K_1[OH^-] + \beta k_3k_4K_1K_2[OH^-]^2\}[Ox][S][Ru^{III}]_T}{\{1 + K_1[OH^-] + K_1K_2[OH^-]^2\} \times \{k_{-1} + k_2[Ox]\} + [S]\{k_1K_1[OH^-] + \beta k_3K_1K_2[OH^-]^2\}} \qquad (26)$$

All experimental results are in complete agreement with the rate eqn. (26).

Techniques used: UV, gas chromatography

References: 35

Figs: 5

Equations: 26

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