SHORT PAPER

J. Chem. Research (S),
2001, 182–184

Ruthenium (VI) catalysed oxidation of diols by alkaline hexacyanoferrate(III) ion – a kinetic study[†]

Kunj Behari, Roli Srivastava and Veena

Department of Chemistry, University of Allahabad, Allahabad-211002, India

The kinetics of Ru(VI) catalysed oxidation of 1,5 pentane diol; 1,6-hexane-diol, 1-pentanol and 1-hexanol by hexacyanoferrate (III) ion in an aqueous alkaline medium at constant ionic strength shows zero order dependence on hexacyanoferrate (III) and first order dependence on Ru(VI) and substrate. The result suggest that a complex is formed between Ru(VI) and diol, which slowly decomposes to give a reduced form of ruthenium, which is reoxidised to Ru(VI) in a fast step be alkaline hexacyanoferrate(III). A plausible reaction mechanism is proposed.

Keywords: ruthenium catalysed oxidation, alkaline hexacyanoferrate

Introduction

Among the platinum metals, osmium tetroxide[1] has been extensively used as a catalyst during the oxidation of organic compounds by alkaline hexacyanoferrate (III) , but has largely been replaced by ruthenium compounds because it is toxic[2] in acidic medium. However, when ruthenium tetroxide is dissolved in alkali, it gives ruthenate ion.[3] Recently Os (VIII) catalysed oxidation of glycols[4] by alkaline hexacyanoferrate (III) has been reported. Such studies have prompted us to study Ru (VI) catalysis during the oxidation of pentane-1,5 diol, hexane-1,6 diol, 1-pentanol and 1-hexanol by alkaline hexacyanoferrate (III) ion.

Experimental

Materials and methods: All chemicals used were of standard grade (A.R., B.D.H. or E. Merck). Diols were distilled before use, Na_2RuO_4 was prepared by reducing the RuO_4 with alkali[3] and its purity was checked by measuring the absorbance ratio at 460 and 385 nm. This ratio, 2.07 is diagnostic of pure ruthenate ion.[5] The concentration of ruthenate ion was calculated by measuring the absorbance of the solution at 460 nm with a Beckmann spectrophotometer model-26, taking $\in = 1820 M^{-1} cm^{-1}$ as its molar absorbance coefficient.[6]

Reaction mixture for kinetic measurements: The reaction was started by mixing the required amount of diol, Na_2RuO_4, alkali and hexacyanoferrate(III) at constant temperature and residual hexacyanoferrate(III) was determined by measuring the absorbance at 420 nm. After the completion of reaction when [hexacyanoferrate (III)] >> (substrate) the products were extracted repeatedly with ether. The ether extract was treated with 2,4-dinitrophenyl hydrazine solution prepared in 85% (H_3PO_4).[7] The purified hydrazones gave a single TLC spot indicating that only one aldehydic product is formed during the oxidation. The product, *i.e.* yield based on isolated hydrazone was 90–92%, The difference in the recovered hydrazone can be ascribed to the loss during purification. In the cases of 1,5-pentane diol, 1,6-hexane diol, 1-pentanol and 1-hexanol, the oxidation product was identified as their 2,4-dinitrophenyl hydrazone (m.p 97°C, lit[8a] 99°C), (m.p. 114°C, lit[8b] 112°C), (m.p. –109°C, lit[8c] 110°C), (m.p. 120°C, lit[8d] 122°C) respectively.

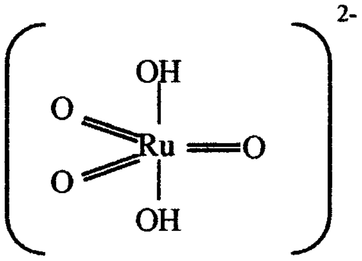
Results and discussion

Variation of the catalyst concentration: Ruthenium (VI) catalysed oxidation of diols by alkaline hexacyanoferrate(III) has been studied at constant ionic strength by addition of sodium perchlorate and followed zero order kinetics up to a reaction extent of more than 80%. The k_{obs} values reported are the averages obtained from duplicate runs. The results (Table 1) clearly indicate that the k_{obs} values are constant for different initial concentration of hexacyanoferrate (III). The results cover more than six fold change in [Ru(VI)] and are presented in Fig.1. A plot of k_{obs} versus [Ru(VI)] passes through the origin indicating that there is no reaction between $Fe(CN)_6^{-3}$ and the diols in the absence of ruthenium (VI).

Variation of the substrate concentration: The reaction velocity increases linearly with increasing substrate concentration in the lower concentration range, but deviation occurs at high concentration. A plot of k_{obs}^{-1} versus $[substrate]^{-1}$ is linear with positive intercept is presented in Fig. 2 this plot shows Michaelis-Menton behaviour suggesting thereby that complex formation between ruthenate ion and substrate occurs.

Variation of the concentration of OH^-: The reaction velocity decreases with increasing $[OH]^-$ (Fig. 3). The data can be represented in the form of $Y = mx+C$, and the regression coefficient is found to be 0.998.

Before discussing the mechanism, it is worthwhile considering the probable species of ruthenium (VI). The electronic spectral studies have confirmed that the lower oxidation state of ruthenium exists in the hydrated form,[9] but the higher oxidation states are not solvated to a lesser extent, since 5d metal oxoanions have the ability to increase their co-ordination shell. The Mossbauer spectrum of $[RuO_4]$ has been reported[10] as of $[RuO_3.\ (OH)_2]^{2-}$.



The retarding effect of hydroxide can be explained by assuming that some of the ruthenate ions exists as $[RuO_3\ (OH)_3]$. Therefore the following equilibrium may be considered.

$$[RuO_3\ (OH)_2]^{2-} + OH^- \rightleftharpoons [RuO_3(OH)_3]^{3-} \qquad (1)$$

As a result of decomposition of perruthenate ions in an alkaline medium Symons and Carrington[11] have suggested that coordination of hydroxide ions to perruthenate occurred to a lesser extent because ruthenium represents an intermediate case between osmium and rhenium. Similar results have also been reported by Loma and Brubakee.[12] Therefore ruthenate

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* To receive any correspondence. E-mail: kubehari@nde.vsnl.net.in

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

ions RuO_4^{2-} may coordinate with hydroxide ions to a lesser extent than does osmium (VIII). In view of the above argument the following reaction sequence based on the experimental results is proposed.

$$\underset{(A_1)}{[RuO_3(OH)_2]^{2-}} + OH^- \overset{K}{\rightleftharpoons} \underset{(A_2)}{[RuO_3(OH)_3]^{3-}} \qquad (2)$$

$$RCH_2OH+[RuO_3(OH)_2]^{2-} \overset{K_1}{\rightleftharpoons} \underset{(A_3)}{[RCH_2\text{-}O\text{-}RuO_2(OH)_3]^{2-}} \qquad (3)$$

$$[RCH_2\text{-}O\text{-}RuO_2(OH_3)]^{2-} \xrightarrow[k]{\text{Slow}} RCHO+Ru_2OH_2O+2OH^- \qquad (4)$$

$$RuO_2H_2O+4OH^-+2Fe(CN)_6^{3-} \xrightarrow{\text{fast}} [RuO_3(OH)_2]^{2-} + 2Fe(CN)_6^{4-}+2H_2O \qquad (5)$$

[where R represents the carbon chain attached to – CH_2OH].

The first step (eqn (2)) in the above scheme is arrived at on the basis of equilibrium(1) and values of *K* from the kinetic study

Table 1 Dependenxe of K_{obs} on hexacyanoferrate (III) ion on the rate (I = 0.25 mol/dm^3 and 30°C)

$10^4[K_4\{Fe(CN)_6\}]$ (mol/dm^3)	10^6K_{obs} (mol/dm^3)			
	$HO[CH_2]_5$ OH[a]	$HO[CH_2]_6$–OH[b]	$CH_3[CH_2]_4OH$[c]	$CH_3[CH_2]_5OH$[d]
2.50	16.06	39.61	27.90	27.80
2.00	16.10	38.96	27.24	26.38
1.67	16.15	34.28	26.98	25.40
1.25	15.92	39.08	27.42	26.80
0.635	15.04	38.71	26.84	27.20

[a] $10^2[HO(CH_2)_5\text{-}OH]$ = 2.00 mol/dm^3, $10^1[OH^-]$ = 1.00 mol/dm^3, $10^7[Ru^{VI}]$ = 4.25 mol/dm^3.
[b] $10^2[HO(CH_2)_6\text{-}OH]$ = 6.50 mol/dm^3, $10^1[OH^-]$ = 1.00 mol/dm^3, $10^7[Ru^{VI}]$ = 8.72 mol/dm^3.
[c] $10^2[CH_3(CH_2)_4\text{-}OH]$ = 2.50 mol/dm^3, $10^1[OH^-]$ = 5.00 mol/dm^3, $10^7[Ru^{VI}]$ = 6.82 mol/dm^3.
[d] $10^2[CH_3(CH_2)_5\text{-}OH]$ = 1.25 mol/dm^3, $10^1[OH^-]$ = 0.50 mol/dm^3, $10^7[Ru^{VI}]$ = 9.86 mol/dm^3.

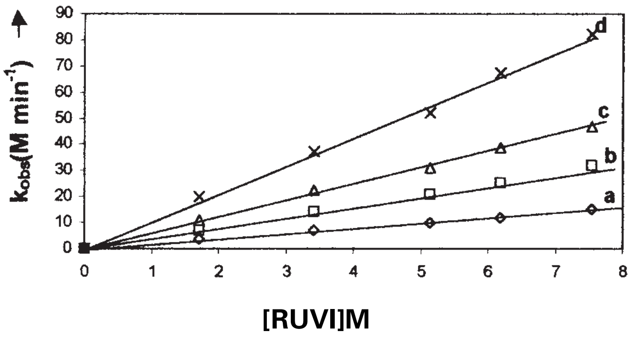

Fig. 1 Effect of $[Ru^{VII}]$ on the reaction rate, temp. 30°C. $10^3[K_3Fe(CN)_6]$ = 2.00 mol/dm^3, $10^2[OH^-]$ = 10.00 mol/dm^3 and I = 0.25 mol/dm^3. (a) $10^2[HO\text{–}(CH_2)_5OH]$ = 2.00 mol/dm^3; (b) $10^2[HO(CH_2)_6OH]$ = 6.25 mol/dm^3; (c) $10^2[CH_3(CH_2)_4OH]$ = 1.25 mol/dm^3; (d) $10^2[CH_3(CH_2)_5OH]$ = 8.33 mol/dm^3;

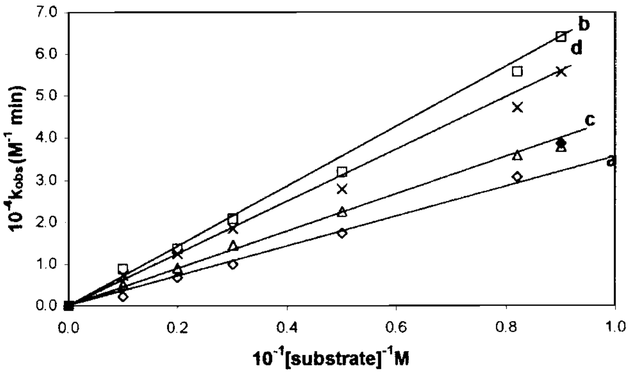

Fig. 2 Effect of [substrate] on the reaction rate, temp. 30°C. $10^3[K_3Fe(CN)_6]$ = 2.00 mol/dm^{-3}, $10^2[OH^-]$ = 10.00 mol/dm^{-3} and I = 0.25 mol/dm^3. (a) $[HO\text{–}(CH_2)_5OH]$, $10^7[Ru^{VI}]$ = 6.85 mol/dm^3; (b) $[HO\text{–}(CH_2)_6OH]$, $10^7[Ru^{VI}]$ = 7.20 mol/dm^3; (c) $[CH_3(CH_2)_4OH]$, $10^7[Ru^{VI}]$ = 6.82 mol/dm^3; (d) $[CH_3(CH_2)_5OH]$, $10^7[Ru^{VI}]$ = 9.86 mol/dm^3.

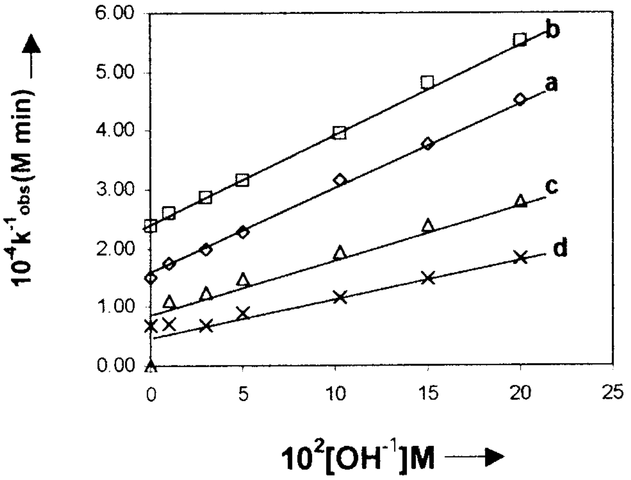

Fig. 3 Effect of $[OH^-]$ on the reaction rate, temp. 30°C. $10^3[K_3Fe(CN)_6]$ = 2.00 mol/dm^3, and I = 0.25 mol/dm^3. (a) $10^2[HO(CH_2)_5OH]$ = 2.00 mol/dm^3, $10^7[Ru^{VI}]$ = 6.85 mol/dm^3; (b) $10^2[HO(CH_2)_6OH]$ = 1.00 mol/dm^3, $10^7[Ru^{VI}]$ = 8.75 mol/dm^3; (c) $10^2[CH_3(CH_2)_4OH]$ = 2.50 mol/dm^3, $10^7[Ru^{VI}]$ = 6.82 mol/dm^3; (d) $10^2[CH_3(CH_2)_5OH]$ = 8.33 mol/dm^3, $10^7[Ru^{VI}]$ = 9.86 mol/dm^3.

Table 2 Values of *k* and *K* in proposed mechanism at 30 ± 1°C

Substrate	*K*	*k*
1.5 Pentane diol	2.88	24.88
1.6 Hexane diol	2.84	20.27
1-pentanol	3.20	73.30
1-hexanol	3.00	50.71

are more or less similar for all substrates, confirming the validity of first step. In step (3) an inner orbital d^2sp^3 hybridised complex may be formed which slowly disproportionates into the product and the reduced form of ruthenium (step 4). The latter is then reoxidised to ruthenate ion in a fast reaction (step 5) by the action of hexacyanoferrate (III) and alkali. The concetration of total ruthenate ions can be obtained as:

$$[RuO_4^{2-}]_T = [A_1]+[A_2]+[A_3] \qquad (6)$$

Considering the above steps, the final rate law in terms of decreasing concentration of hexacyanoferrate (III) ion would be

$$-[d\ Fe(CN)_b^{3-}]/dt = \frac{2kK_1[S][RuO_4^{2-}]_T}{1+K_1[S]+K[OH^-]} \qquad (7)$$

Further verification of the above rate law (equation (7)) can be done on rearranging as:

$$1/K_{obs} = \frac{1}{2kK_1[S][RuO_4^{2-}]_T} + \frac{1}{2k[RuO_4^{2-}]_T} + \frac{K[OH^-]}{2kK_1[S][RuO_4^{2-}]_T} \qquad (8)$$

Where rate = –d $[Fe(CN)_6^{3-}]/dt$ can be taken as to be equal to K_{obs} (standard zero order rate constant) which means that a plot of K^{-1}_{obs} versus $[S]^{-1}$ (Fig. 2) and K_{obs}^{-1} versus $[OH^{-1}]$ (Fig. 3) gives a straight line. The K and k values which have been obtained with the help of Figs 1, 2 and 3 are given in Table 2. The value of K in each case is more or less the same, which supports the first step of proposed mechanism, hence eqn (7) is valid.

The financial assistance from U.G.C. New Delhi in the form of a research project and a fellowship to R.S. is thankfully acknowledged.

Received 13 November 2000; accepted 22 March 2001
Paper 00/631

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