Oxidation of 2,3-butanediol by alkaline hexacyanoferrate(III) using Ru(III) or Ru(VI) as catalyst[†]

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ABSTRACT: The reactions of 2,3-butanediol by hexacyanoferrate(III) in alkaline medium using ruthenium compounds as catalysts have been studied spectrophotometrically. The effect on the reaction rate of concentration of substrate, oxidant, catalyst and basicity of the medium leads to similar experimental rate equations for both catalysts, Ru(III) and Ru(VI). The reaction mechanism involves the formation of a catalyst–substrate complex that yields a carbocation for Ru(VI) or a radical for Ru(III) oxidation. Hexacyanoferrate(III)'s role is the catalyst regeneration. The rate constants of complex decomposition and catalyst regeneration have been determined. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: alcohol oxidation; catalysed; Ruthenium(III) and (VI) and hexacyanoferrate(III).
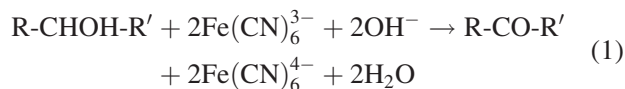
INTRODUCTION

The oxidation of organic compounds such as alcohols and organic acids is a topic of great interest, especially if the organic substrates are not easily oxidised by common oxidants.[1–3] Thus an alternative to solve this problem is the addition of catalytic quantities of transition-metal ions and a soft cooxidant to the reaction.[4] The catalytic activity of these ions is attributed to their capacity to exist in more than one oxidation state, their capacity to form complexes and their capacity to change their coordination number.[5] These facts justify that actually the ruthenium complexes were employed in the homogeneous alcohol oxidations. Moreover, the use of a catalyst allows the existence of sensitive linkages in the alcohol molecule.[6] Although numerous kinetic studies have been made using Ru(III) or Ru(VI) as catalysts,[7–10] the catalytic behaviour has rarely been compared. Thus, this work focuses on the comparative study of both catalysts in the oxidation of 2,3-butanediol with alkaline hexacyanoferrate(III) in order to predict which of the two is the best catalyst.

EXPERIMENTAL

All the reagents used, that is, hexacyanoferrate(III), sodium hydroxide, 2,3-butanediol and sodium perchlor-

ate, were purchased from Merck (A.R. grade) and ruthenium trichloride (Johnson–Matthey). The solutions were prepared using water from an OSMO BL-6 deionizer from SETA. A stock solution of ruthenium trichloride (0.0024 M) was prepared by dissolving the sample in very dilute hydrochloric acid 0.1638 M. Sodium ruthenate solution was prepared following the Lalitha–Sethuram procedure.[8] The purity of ruthenate stock solutions was assessed by taking into account that the ratio between the absorbance at 465 nm and 386 nm should be equal to 2.07 for pure ruthenate.[11]

All kinetic runs were initiated by the addition of substrate to a mixture containing the other reagents. The oxidation kinetics of 2,3-butanediol were followed by measuring the absorbance of hexacyanoferrate(III) at 420 nm ($\varepsilon = 1000 \, \mathrm{M^{-1} \, cm^{-1}}$) on a Simadzu UV-160 spectrophotometer. The initial rates method was used for kinetic analysis.[12] The ionic strength was kept constant at 0.5 M by the addition of sodium perchlorate. The only organic reaction product detected for the oxidation of 2,3-butanediol was 3-hydroxy-2-butanone, which was identified using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a BP-21 polyethylene glycol column (50 m long × 0.22 µm i.d., 25 µm film thickness). The stoichiometry obtained showed that one mole of diol consumed two moles of hexacyanoferrate(III):

$$\begin{aligned} \text{R-CHOH-R}' + 2\text{Fe(CN)}_6^{3-} + 2\text{OH}^- &\rightarrow \text{R-CO-R}' \\ &+ 2\text{Fe(CN)}_6^{4-} + 2\text{H}_2\text{O} \end{aligned} \quad (1)$$

where
R = CH$_3$—CHOH— and R′ = CH$_3$—

Correspondence to: F. J. Poblete, Departamento de Química Física, Universidad de Castilla-La Mancha, Avda. Camilo José Cela, 10, 13071 Ciudad Real, Spain.
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RESULTS

Figure 1 shows the variation of initial rate with respect to $[Fe(CN)_6^{3-}]_0$ (Fig. 1A) and $[diol]_0$ (Fig. 1B) for both catalysts. These results have led to the following expression at constant concentrations of catalyst and hydroxide ions:

$$v_0 = \frac{[Fe(CN)_6^{3-}]_0[diol]_0}{k'[diol]_0 + k''[Fe(CN)_6^{3-}]_0 + k'''[diol]_0[Fe(CN)_6^{3-}]_0} \quad (2)$$

where the parameters obtained by non-linear regression fit are shown in Table 1.

This equation justifies the change of order from one to zero for both hexacyanoferrate(III) and diol species upon increasing their concentrations.

The variation of v_0 with $[catalyst]_0$ was linear (Fig. 2), being negligible the uncatalysed process. Thus, the rate equation would be:

$$v_0 = k_c[catalyst]_0 \quad (3)$$

where the values of k_c are $50.57 \pm 0.02 \, min^{-1}$ for Ru(III) and $62.47 \pm 0.9 \, min^{-1}$ for Ru(VI).

As shown in Fig. 3, the plots of v_0 *versus* $[OH^-]$ reach a maximum for both catalysts. In the case of Ru(VI), v_0 does not tend to be zero at very low $[OH^-]$, whereas it does for Ru(III). The variation of v_0 with the basicity of the medium is complicated and obeys the following equation:

$$v_0 = \frac{A_0 + A_1[OH^-] + A_2[OH^-]^2}{1 + B_1[OH^-] + B_2[OH^-]^2} \quad (4)$$

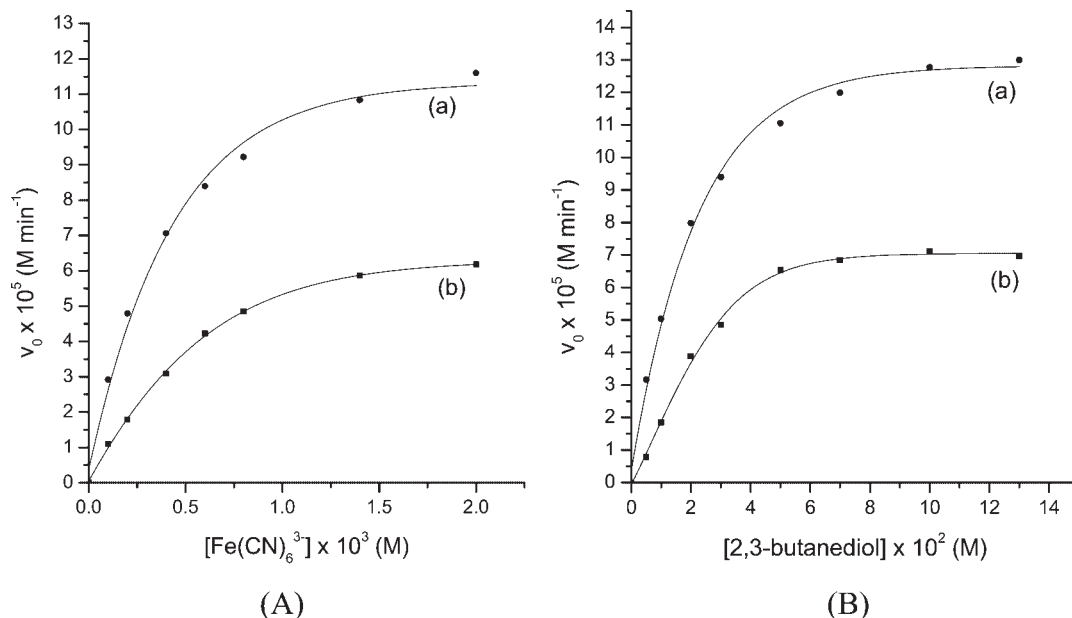The best average error was obtained for Ru(III) when $A_0 = 0$ and for Ru(VI) when $A_2 = 0$.

Table 1. Kinetic parameters obtained by non-linear regression fitting from Eqn 2

	k'/min	$k''/10^2 \, min$	$k'''/10^3 \, min \, M^{-1}$
For Ru(III)	2.83 ± 0.09	1.25 ± 0.06	3.03 ± 0.09
For Ru(VI)	7.01 ± 0.10	3.02 ± 0.04	1.72 ± 0.20

$[Ru] = 1.0 \times 10^{-6} \, M$, $[NaOH] = 0.15 \, M$, $I = 0.5 \, M$ and $T = 30 \, ^\circ C$.

The possible formation of free radicals as intermediates was investigated by adding radical scavengers to the reaction mixture. In Ru(III) case, polymeric species has been obtained by the addition of $0.7 \, M$ acrylonitrile indicating that radicals are present in the reaction medium. However, for Ru(VI), no effect has been observed when $0.01 \, M$ acrylonitrile or $1.6 \times 10^{-4} \, M$ 2,4,6-tri-*tert*-butylphenol (a stronger radical scavenger) has been added.

The oxidation of cyclobutanol was carried out because the nature of its oxidation products depends on the reaction mechanism. One-electron oxidation produces acyclic four-carbon compounds, which appear to be derived from the primary free radical $\cdot CH_2CH_2CH_2CHO$, whereas two-electron oxidation produces cyclobutanone directly.[13,14] Under the kinetic conditions (cyclobutanol] = $0.08 \, M$, [hexacyanoferrate(III)] = $2.0 \times 10^{-3} \, M$, [catalyst] = $2.5 \times 10^{-6} \, M$, $[OH^-] = 0.1 \, M$, $I = 0.5 \, M$ and $T = 30 \, ^\circ C$) the reaction yields butanal as the major product in the case of Ru(III) and cyclobutanone in the case of Ru(VI).

The presence of a hydrogen on the α-carbon of the alcohol is necessary for the reaction progress[15] because tertiary alcohols ($0.1 \, M$ *tert*-butanol) do not react under kinetic conditions[16] for both catalysts.

The observed oxidation rate of CD_3—$CDOD$—CD was compared with that of CH_3—$CHOH$—CH_3 in order

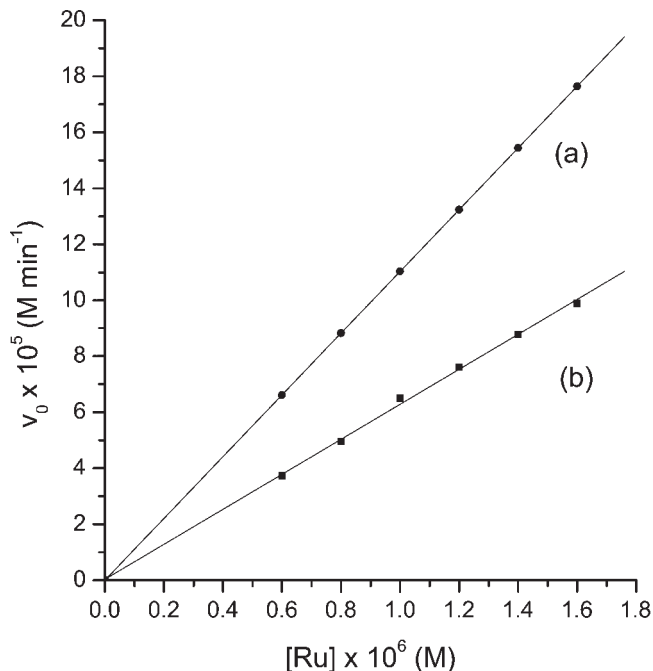**Figure 1.** Plots of v_0 *versus* $[Fe(CN)_6^{3-}]_0$, [2,3butanediol] = $0.03 \, M$ (A) and plots of v_0 *versus* [2,3-butanediol]$_0$, $[Fe(CN)_6^{3-}]_0 = 8.0 \times 10^{-4} \, M$ (B). $[Ru]_0 = 1.0 \times 10^{-6} \, M$, $[NaOH] = 0.15 \, M$, $I = 0.5 \, M$ and $T = 30 \, ^\circ C$. Ru(III) (a) and Ru(VI) (b).

Figure 2. Effect of [catalyst]$_0$ on the initial rate. [2,3-butanediol]$_0 = 0.05$ M, [Fe(CN)$_6^{3-}$]$_0 = 8.0 \times 10^{-4}$ M, [OH$^-$] = 0.15 M, $T = 30\,^\circ$C, $I = 0.5$ M. Ru(III) (a) and Ru(VI) (b).
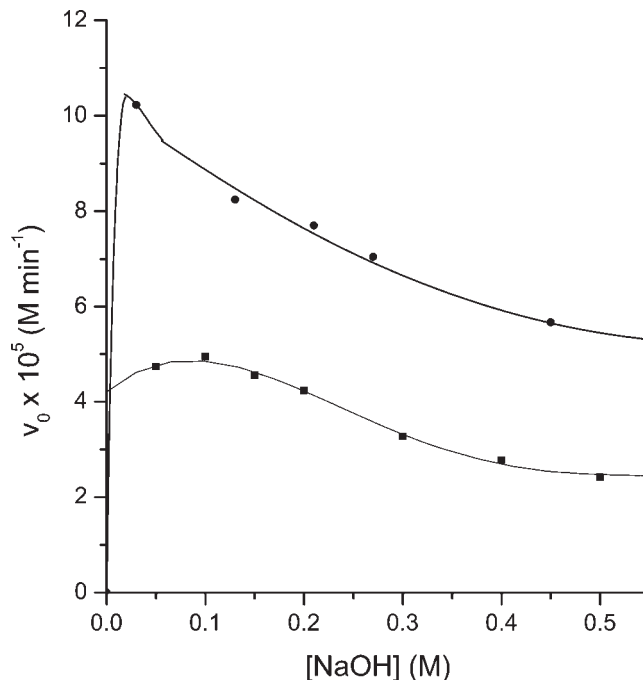
Figure 3. Variation of v_0 with respect to [NaOH]. [Fe(CN)$_6^{3-}$]$_0 = 8.0 \times 10^{-3}$ M, [2,3-butanediol]$_0 = 0.02$ M, [Ru]$_0 = 1.0 \times 10^{-6}$ M, $I = 0.5$ M and $T = 30\,^\circ$C. Ru(III) (a) and Ru(VI) (b).
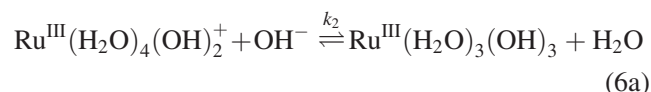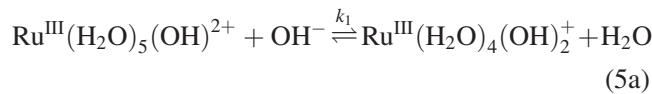
to verify the existence of a kinetic isotope effect. A substantial primary kinetic isotope effect was indeed observed [$(v_{0,H}/v_{0,D}) = 5.9$] for both catalysts under the following kinetic conditions: [catalyst] $= 2.0 \times 10^{-6}$ M, [Fe(CN)$_6^{3-}$] $= 1.2 \times 10^{-3}$ M, [alcohol] $= 0.5$ M, [OH$^-$] $= 0.2$ M, $I = 0.5$ M and $T = 30\,^\circ$C.
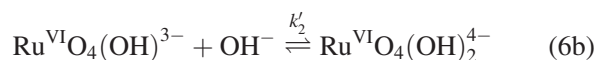
DISCUSSION

Before formulating the probable oxidation mechanism, it may be helpful to select the ruthenium species that may act as catalyst in the reaction.

The dependence of v_0 on [OH$^-$] in the process catalysed by Ru may be justified by assuming the existence of two active species of catalyst with similar reactivity in equilibrium.
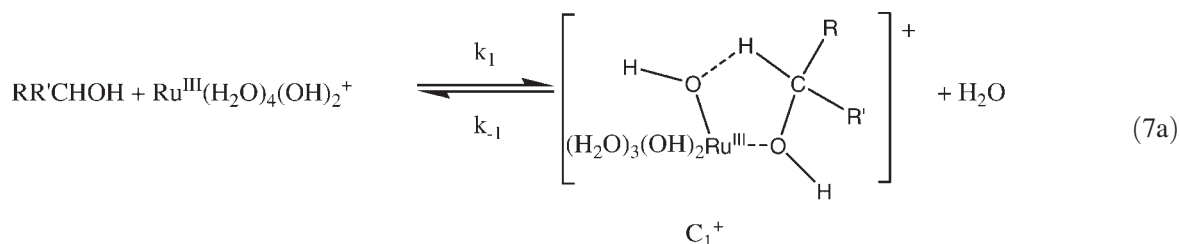
Thus, in the process catalysed by Ru(III) the active catalytic species are Ru(H$_2$O)$_4$(OH)$_2^+$ and Ru(H$_2$O)$_3$(OH)$_3$.[17]

$$Ru^{III}(H_2O)_5(OH)^{2+} + OH^- \overset{k_1}{\rightleftharpoons} Ru^{III}(H_2O)_4(OH)_2^+ + H_2O \tag{5a}$$

$$Ru^{III}(H_2O)_4(OH)_2^+ + OH^- \overset{k_2}{\rightleftharpoons} Ru^{III}(H_2O)_3(OH)_3 + H_2O \tag{6a}$$

And, for Ru(VI) process, RuO$_4^{2-}$ and RuO$_4$(OH)$^{3-}$ are the catalytic species[18]:

$$Ru^{VI}O_4^{2-} + OH^- \overset{k_1'}{\rightleftharpoons} Ru^{VI}O_4(OH)^{3-} \tag{5b}$$

$$Ru^{VI}O_4(OH)^{3-} + OH^- \overset{k_2'}{\rightleftharpoons} Ru^{VI}O_4(OH)_2^{4-} \tag{6b}$$

Both in the case of the oxidation catalysed by Ru(III) as in the case of the process catalysed by Ru(VI), the dependence of initial rate on substrate fits Michaelis–Menten model. Therefore, we suggest the existence of an intermediate complex formed from the organic substrate and the respective active catalytic species.

$$RR'CHOH + Ru^{III}(H_2O)_4(OH)_2^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[\begin{array}{c} \text{H} \\ \text{O} \cdots \text{H} \\ \text{(H}_2\text{O)}_3\text{(OH)}_2\text{Ru}^{III}\text{--O} \\ \text{H} \end{array} \begin{array}{c} \text{R} \\ \text{C} \\ \text{R'} \end{array} \right]^+ + H_2O \tag{7a}$$

$$C_1^+$$

$$RR'CHOH + Ru^{VI}O_4^{2-} \; \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} \; \left[\begin{array}{c} \text{structure} \end{array} \right]^{2-} \qquad (7b)$$

$$C_1^{2-}$$
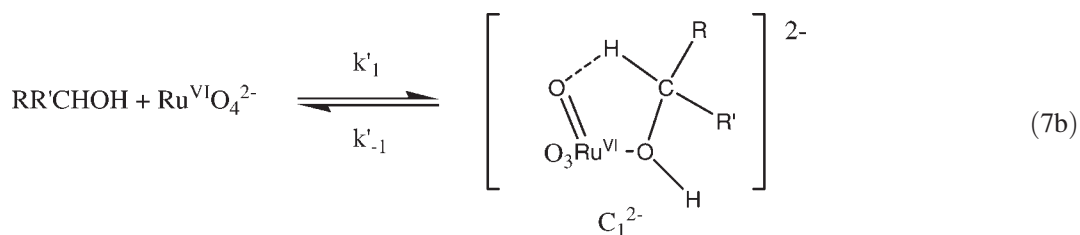
Both complexes, C_1^+ and C_1^{2-}, decompose slowly but in a different way.

In the case of Ru(III), the decomposition of C_1^+ yields a ketyl radical and Ru(II) and it takes place by means of a homolitic rupture and a hydrogen atom transfer from the α—CH bond of the alcohol to the oxygen of the hydroxo ligand of ruthenium. This transfer is experimentally guaranteed by the presence of free radicals in the reaction mixture and the presence of butanal as major product in the oxidation of cyclobutanol.

$$C_1^+ \xrightarrow{k_2} RR'\overset{\cdot}{C}OH + Ru^{II}(H_2O)_5OH^+ \qquad (8a)$$

However, in the case of catalyst Ru(VI), the complex C_1^{2-} decomposes by means of a heterolitic rupture and the subsequent hydride transfer from the α—CH bond of the substrate to the oxoligand of ruthenium as follows:

$$C_1^{2-} \xrightarrow{k'_2} RR'\overset{\oplus}{C}OH + Ru^{IV}O_3OH^{3-} \qquad (8b)$$
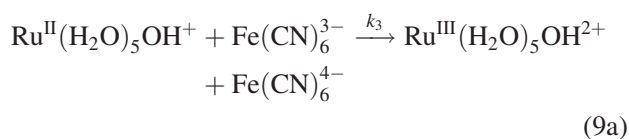
This process is favoured by the prior coordination of the organic substrate to the metal through the oxygen of the hydroxyl group and supported by the following experimental results: (a) a moderate kinetic isotope effect, which indicates cleavage of a C—H bond in the absence of free radicals in the reaction mixture, (b) the presence of cyclobutanone as the unique product in the oxidation of cyclobutanol and (c) the negative value of the Hammett reaction constant found for the oxidation of benzyl alcohol.[19]
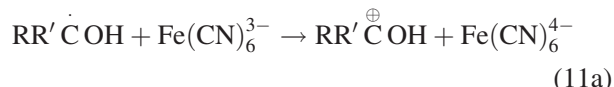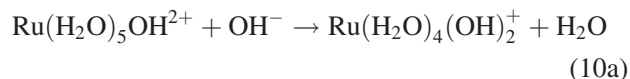
From the species involved in these decompositions, two new processes take place: the regeneration of the catalyst and the formation of final products.

The dependence of initial rate v_0 on $[Fe(CN)_6^{3-}]$, can be justified by the oxidation of the reduced species of catalyst precisely through hexacyanoferrate(III). For Ru (III):
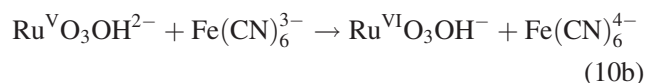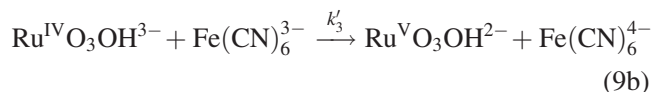
$$Ru^{II}(H_2O)_5OH^+ + Fe(CN)_6^{3-} \xrightarrow{k_3} Ru^{III}(H_2O)_5OH^{2+} + Fe(CN)_6^{4-} \qquad (9a)$$

$$Ru(H_2O)_5OH^{2+} + OH^- \rightarrow Ru(H_2O)_4(OH)_2^+ + H_2O \qquad (10a)$$

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

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

And for Ru (VI):

$$Ru^{IV}O_3OH^{3-} + Fe(CN)_6^{3-} \xrightarrow{k'_3} Ru^VO_3OH^{2-} + Fe(CN)_6^{4-} \qquad (9b)$$

$$Ru^VO_3OH^{2-} + Fe(CN)_6^{3-} \rightarrow Ru^{VI}O_3OH^- + Fe(CN)_6^{4-} \qquad (10b)$$

$$RR'\overset{\oplus}{C}OH + OH^- \rightarrow RR'CO + H_2O \qquad (11b)$$

In this way, the role of $Fe(CN)_6^{3-}$ is limited to regenerate catalysts, at least, in the case of Ru(VI).

A similar mechanism can be used for the other active catalyst species, $Ru(H_2O)_3 (OH)_3$ and $RuO_4(OH)^{3-}$.

Thus, the experimental rate equation can be written as:

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = 2k_3^{(')}[Ru(II \text{ or } IV)][Fe(CN)_6^{3-}] + 2k_3^{(')}[Ru'(II \text{ or } IV)][Fe(CN)_6^{3-}] \qquad (13)$$

where the concentrations of reduced species of the active catalytic species of ruthenium appear. Therefore, it was supposed that the constant of catalyst regeneration is the same for the two active species, k_3.

By the application of the steady-state conditions to the reduced species of catalyst and complexes, C, the theoretical rate equation of disappearance of $Fe(CN)_6^{3-}$ can be obtained.

For Ru(III):

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{2k_1k_2k_3k_A[Fe(CN)_6^{3-}][diol][Ru(III)]_T}{k_1k_2k_A[diol] + k_3(k_{-1} + k_2)k_B[Fe(CN)_6^{3-}] + k_1k_3k_A[Fe(CN)_6^{3-}][diol]} \qquad (14a)$$

Table 2. Rate constants of complex decomposition and catalyst regeneration

	Ru(VI)	Ru(III)
k_2 (min^{-1})	$2.9 \pm 0.1 \times 10^2$	$1.66 \pm 0.03 \times 10^2$
k_3 (l·mol^{-1}·min^{-1})	$7.1 \pm 0.8 \times 10^4$	$1.76 \pm 0.07 \times 10^5$

[NaOH] = 0.15 M, I = 0.5 M and T = 30 °C.

The $[\text{Ru(III)}]_T$ takes in account [Ru(III)] and [Ru(II)] and $k_A = k_1[\text{OH}^-] + k_1k_2[\text{OH}^-]^2$, $k_B = k_A + 1$.

For Ru(VI):

$$-\frac{d[\text{Fe(CN)}_6^{3-}]}{dt} = \frac{2k_1k_2k_3k_A[\text{Fe(CN)}_6^{3-}][\text{diol}][\text{Ru(VI)}]_T}{k_1k_2k_A[\text{diol}] + k_3(k_{-1} + k_2)k_B[\text{Fe(CN)}_6^{3-}] + k_1k_3k_A[\text{Fe(CN)}_6^{3-}][\text{diol}]} \tag{14b}$$

$[\text{Ru(VI)}]_T$ is the sum of [Ru(VI)] and [Ru(IV)] since [Ru(V)] is negligible because such species are only involved in fast steps and $k_A = 1 + k_1[\text{OH}^-]$, $k_B = k_A + k_1k_2[\text{OH}^-]^2$.

Both rate equations are consistent with experimental results obtained and justify the dependence of v_0 on $[\text{OH}^-]$, $[\text{Fe(CN)}_6^{3-}]$, [Substrate] and [Catalyst].

Since the parallelism that shows the dependence of v_0 on catalyst, substrate and hexacyanoferrate(III) in the process catalysed by Ru(VI) and Ru(III), both theoretical rate equations are very similar. The only difference in the equations is due to the slightly different behaviour of v_0 with respect to $[\text{OH}^-]$. The equation that summarizes the catalytic process is:

$$-\frac{d[\text{Fe(CN)}_6^{3-}]}{dt}$$

$$= \frac{A[\text{Fe(CN)}_6^{3-}][\text{diol}][\text{Ru(VI)}]_T}{B[\text{diol}] + C[\text{Fe(CN)}_6^{3-}] + D[\text{Fe(CN)}_6^{3-}][\text{diol}]} \tag{15}$$

By comparing both Eqns 14a and b with the respective experimental rate equations it is possible to estimate the rate constants for intermediate complex decomposition, k_2, and catalyst regeneration, k_3. These results are shown in Table 2.

CONCLUSION

The kinetics for the oxidation of 2,3-butanediol by Fe(CN)$_6^{3-}$, using Ru(VI) or Ru(III) as catalysts, are governed by similar experimental rate equations. These equations show a change of order from one to zero for both hexacyanoferrate(III) and diol concentrations. They

also show a first order with respect to catalyst concentrations. The reaction mechanism proposed involves oxidation of diol by Ru(VI) or Ru(III) through the formation of a substrate–catalyst complex, which subsequently decomposes to give Ru(IV) or Ru(II) species. Intermediate complex decomposition involves a hydrogen transfer from the α—C—H bond of the alcohol to the oxoligand of ruthenium in the case of Ru(VI), and a hydride transfer for the Ru(III) case. The role of Fe(CN)$_6^{3-}$ is the regeneration of the catalyst. For both oxidations the rate constants of complex decomposition and catalyst regeneration have been obtained (Scheme 1).
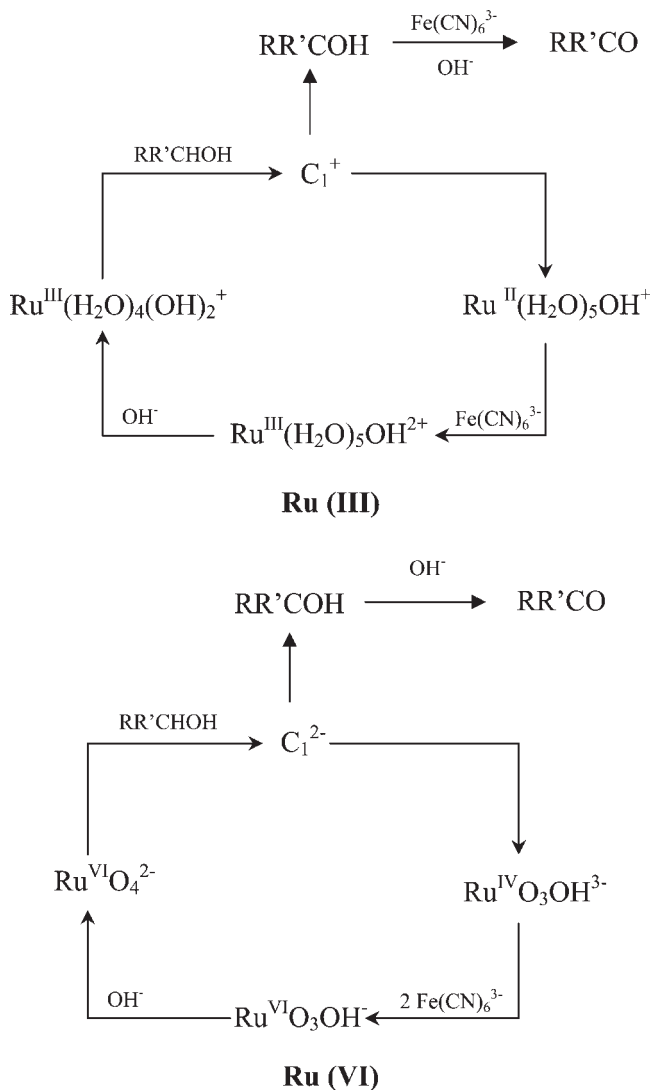
Scheme 1

The fact that Ru(III) reaches the maximum rate at lower concentrations of substrate and hexacyanoferrate(III) suggests that the catalysis of Ru(III) is better than Ru(VI).

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