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Kinetic study of ruthenium (VI)-catalyzed oxidation of 2-propanol by alkaline hexacyanoferrate (III)

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ABSTRACT: The kinetics of Ru(VI)-catalyzed oxidation of 2-propanol by hexacyanoferrate(III) was investigated in alkaline media using a spectrophotometric technique. The reaction shows first order in [Ru(VI)], a Michaelis–Menten-type dependence on [2-propanol], a fractional order in [$Fe(CN)_6^{3-}$] and a complicated variation on [OH^-]. A reaction mechanism which involves two active catalytic species is proposed. Each of these species forms an intermediate complex with the substrate. These complexes decompose slowly, producing ruthenium(IV) complexes, which are reoxidized by hexacyanoferrate(III) in subsequent steps. The theoretical rate law obtained is in complete agreement with all the experimental observations. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: 2-propanol; oxidation; hexacyanoferrate(III); ruthenium(VI) catalysis

INTRODUCTION

The oxidation of alcohols is one of the fundamental transformations in organic synthesis. Various reactions using transition metal oxo complexes such as oxidants are well known. The most frequently used reagents are permanganate,[1] chromic acid,[2] pentavalent vanadium,[3] ferrate[4] and, more recently, high oxidation state ruthenium oxo complexes.[5–8] For several reasons (e.g. economic, environmental), the development of catalytic processes for alcohol oxidation is an important goal. In this context, the use of these higher oxides of ruthenium as catalysts in combination with different co-oxidants has become increasingly important in the oxidation of alcohols.[9–11] It would be particularly useful if the catalytic species effected such reactions without attacking sensitive linkages in the R groups of alcohols. Ruthenate ion, RuO_4^{2-}, is sufficiently selective to be able to tolerate such linkages; for example, RuO_4^{2-} does not appear to oxidize isolated double bonds at room temperature.[12]

So far it is recognized that sodium ruthenate-catalyzed oxidation of primary and secondary alcohols, in aqueous alkaline media, proceeds via the formation of an Ru(VI)–substrate complex, which dissociates in the rate-determining step to give the corresponding products of reaction and hydrated ruthenium dioxide (Scheme 1).

$$R_2CHOH + RuO_4^{2-} \overset{K}{\rightleftharpoons} \text{complex}$$

$$\text{complex} \xrightarrow[\text{slow}]{k} R_2CO + RuO_2 \cdot xH_2O$$

$$RuO_2 \cdot xH_2O + 2Fe(CN)_6^{3-} + 4OH^- \xrightarrow{\text{fast}} RuO_4^{2-} + 2Fe(CN)_6^{4-} + (x+2)H_2O$$

Scheme 1

The role of the co-oxidant appears to be solely the regeneration of the catalyst in a fast step. This reaction mechanism has been suggested in several studies using hexacyanoferrate(III) as the co-oxidant in a basic medium.[13–16]

This paper reports a study of the kinetics of oxidation of 2-propanol by hexacyanoferrate(III) in an aqueous alkaline medium, in the presence of catalytic amounts of Ru(VI), showing original results hitherto unreported. In particular, we found that the oxidation rate varies with the initial hexacyanoferrate(III) concentration. Such behavior led us to the proposal of a plausible reaction mechanism which involves oxidation of the substrate by RuO_4^{2-}, which is followed by the catalyst reoxidation by the co-oxidant. In this way, when [$Fe(CN)_6^{3-}$] is high the catalyst reoxidation is fast relative to substrate oxidation and the rate does not depend on [$Fe(CN)_6^{3-}$]. At low [$Fe(CN)_6^{3-}$], however, the two consecutive reactions have

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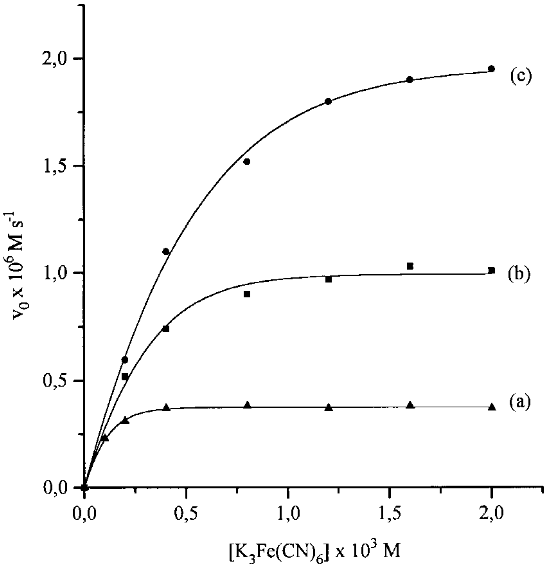


Figure 1. Dependence of v_0 on [$K_3Fe(CN)_6$]. [Ru(VI)] = 4 × 10^{-6} M, I = 0.5 M and T = 30 °C; (a) [NaOH] = 0.3 M, [2-propanol] = 0.2 M; (b) [NaOH] = 0.2 M, [2-propanol] = 0.4 M; (c) [NaOH] = 0.1 M, [2-propanol] = 0.5 M

comparable rates and the rate depends on [$Fe(CN)_6^{3-}$]. Moreover, this mechanism, which is more detailed than those described in the literature, involves a hydride transfer from the α-C—H bond of the alcohol to the oxoligand of ruthenium.

EXPERIMENTAL

Reactants. Potassium hexacyanoferrate (III), potassium hexacyanoferrate (II), 2-propanol, ethanol, sodium hydroxide and sodium perchlorate, all of analytical-reagent grade from Merck, were used without further purification. Acrylonitrile, 2,4,6-tri-*tert*-butylphenol, 2-propanol-d_8, *tert*-butanol hydrated ruthenium dioxide and sodium metaperiodate (analytical-reagent grade) were provided by Aldrich Chemical. Water used for solutions was obtained from an OSMO BL-6 from SETA Purification Systems.

Sodium ruthenate solution was obtained by the oxidation of hydrated ruthenium dioxide with sodium metaperiodate and reducing the ruthenium tetraoxide produced by the action of sodium hydroxide, following the literature procedure.[10] The orange solution obtained was heated slightly for ~24 h to ensure complete reduction of Ru(VIII) to Ru(VI). Stock solutions of sodium ruthenate were prepared by adding a small quantity of the above solution to 25 cm^3 of 1 M NaOH. The concentration was calculated by photometric determination, measuring the absorbance at 465 nm, with molar absorptivity 1820 l mol^{-1} cm^{-1}.[17] The purity of these solutions was checked by measuring the ratio of the absorbance at 465 and 385 nm as 2.07 corresponding to pure ruthenate.[18]

General. All experiments were initiated by the addition of 2-propanol to other reagents and were performed at 30.0 ± 0.1 °C. The ionic strength was kept constant at 0.5 M by adding sodium perchlorate. An excess of 2-propanol and hydroxide ions over hexacyanoferrate(III) was used.

The reaction kinetics were studied using a Shimadzu UV-160 spectrophotometer equipped with a multiple cell carrier with temperature regulated by circulating water. The consumption of hexacyanoferrate(III) was followed by recording the absorbance at 420 nm.

Absorbance–time data for all the kinetic runs were fitted for a small percentage of reaction (about 5% or less)[19] to a straight line, $A = \alpha_0 + \alpha_1 t$, by the least-squares method. The slope provides the initial rate, $v_0 = \alpha_1 = (dA/dt)_0$, given in absorbance units. The initial rate, v_0, expressed in l mol^{-1} s^{-1}, is given by $v_0 = -1/\epsilon\,(dA/dt)_0 = -(d[Fe(CN)_6^{3-}]/dt)_0$, where ϵ = 1000 l mol^{-1} cm^{-1} at 420 nm. The method of initial rates was used because of the advantages it offers (e.g. the presence of competitive reactions is considerably less important when the initial rates method is employed and the time necessary for carrying out experiments decreases appreciably).[19]

Product determinations were performed by gas chromatography using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a BP-21 polyethylene glycol column (50 m × 0.22 μm i.d., 25 μm film thickness). For the kinetic conditions [NaOH] = 0.2 M, [2-propanol] = 0.5 M, [Ru(VI)] = 4 × 10^{-6} M, [$K_3Fe(CN)_6$] = 1.2 × 10^{-3} M and I = 0.5 M, it was found that 2-propanone was the only oxidation product of 2-propanol. Hexacyanoferrate(II) was also identified spectrophotometrically as the reduction product of hexacyanoferrate(III).

The stoichiometry of the net reaction was determined spectrophotometrically by measuring, at 420 nm, the hexacyanoferrate(III) remaining after completion of an experiment performed at [NaOH] = 0.2 M, [2-propanol] = 5 × 10^{-4} M, [Ru(VI)] = 5 × 10^{-5} M, [$K_3Fe(CN)_6$] = 2 × 10^{-3} M, I = 0.5 M and T = 30 °C, yielding a ratio of oxidant to substrate of 2:1. The above results support the following stoichiometric reaction:

$$\begin{aligned}&(CH_3)_2CHOH + 2Fe(CN)_6^{3-} + 2OH^- \\ &\quad\rightarrow (CH_3)_2CO + 2Fe(CN)_6^{4-} + 2H_2O \qquad (1)\end{aligned}$$

RESULTS

Influence of [hexacyanoferrate(III)]

The plot of the initial rates, v_0, versus [$Fe(CN)_6^{3-}$] (Fig. 1) shows a first-order dependence with respect to [$Fe(CN)_6^{3-}$] when the latter concentration is low and a

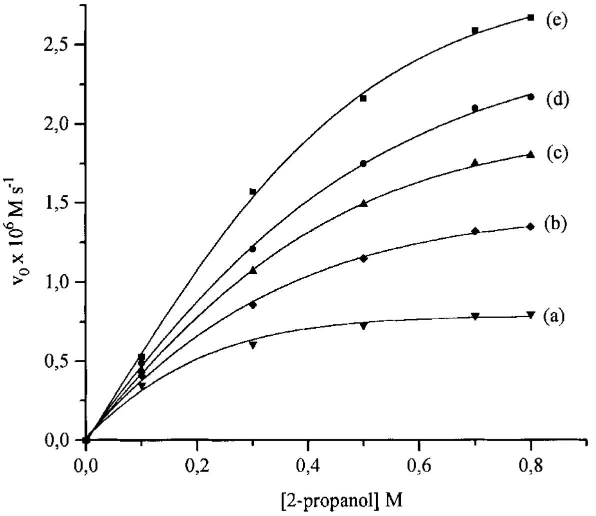


Figure 2. Dependence of v_0 on [2-propanol] at different $[K_3Fe(CN)_6]$. [Ru(VI)] = 4 × 10^{-6} M, [NaOH] = 0.1 M, *I* = 0.5 M and *T* = 30 °C; $[K_3Fe(CN)_6]$ = (a) 0.2 × 10^{-3}; (b) 0.4 × 10^{-3}; (c) 0.8 × 10^{-3}; (d) 1.2 × 10^{-3}; (e) 1.6 × 10^{-3} M

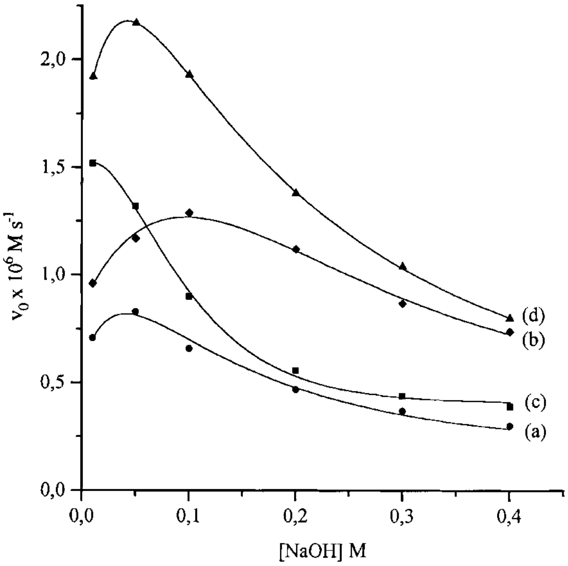


Figure 3. Variation of v_0 with respect to [NaOH]. [Ru(VI)] = 4 × 10^{-6} M, I = 0.5 M and *T* = 30 °C $[K_3Fe(CN)_6]$ = 0.4 × 10^{-3} M: (a) [2-propanol] = 0.2 M; (b) [2-propanol] = 0.6 M. $[K_3Fe(CN)_6]$ = 1.2 × 10^{-3} M: (c) [2-propanol] = 0.2 M; (d) [2-propanol] = 0.6 M

zero-order dependence at high concentrations. This variation was studied for different initial concentrations of NaOH and 2-propanol. The variation of v_0 as a function of $[Fe(CN)_6^{3-}]$ is given by the equation

$$v_0 = \frac{[\mathrm{Ox}]}{k_1' + k_2'[\mathrm{Ox}]} \tag{2}$$

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

Dependence on [2-propanol]

We observed the same dependence of the initial rate on [2-propanol] (Fig. 2) as in the case of hexacyanoferrate(III). The plots of $1/v_0$ versus 1/[2-propanol] gave straight lines with positive slopes and intercepts, which correspond to the equation

$$\frac{1}{v_0} = a + \frac{b}{[\mathrm{S}]} \tag{3}$$

where [S] is the concentration of 2-propanol.

Table 1. Parameters *a* and *b* of the plot of $1/v_0$ versus 1/[S] at different $[K_3Fe(CN)_6]$

$[K_3Fe(CN)_6]$ (10^{-3} M)	*a* (10^5 l mol^{-1} s^{-1})	*b* (10^5 s)	*r*
0.2	10.08 ± 0.09	1.85 ± 0.01	0.9998
0.4	4.91 ± 0.01	1.95 ± 0.01	0.9996
0.8	2.88 ± 0.01	1.98 ± 0.01	0.9998
1.2	2.21 ± 0.01	1.82 ± 0.01	0.9999
1.6	1.17 ± 0.03	1.76 ± 0.01	0.9983

[Ru(VI)] = 4 × 10^{-6} M; [NaOH] = 0.1 M; *I* = 0.5 M; *T* = 30 °C.

Dependence on both [hexacyanoferrate(III)] and [2-propanol]

In order to obtain a rate equation that combines the dependence of v_0 on both $[Fe(CN)_6^{3-}]$ and [2-propanol] we studied the variation of v_0 with [2-propanol] at different hexacyanoferrate(III) concentrations, maintaining $[OH^-]$ and $[RuO_4^{2-}]$ constant (Fig. 2). The parameters *a* and *b* were obtained from the plot of $1/v_0$ versus 1/[S] (Table 1). A straight line with a zero slope and positive intercept [intercept = (1.85 ± 0.07) × 10^5 s] was obtained by plotting *b* versus $1/[Fe(CN)_6^{3-}]$. The plot of *a* versus $1/[Fe(CN)_6^{3-}]$ was linear [*r* = 0.9976; slope = 194.96 ± 0.08 s and intercept = (2.71 ± 0.02) × 10^4 l mol^{-1} s]. According to this, the experimental rate equation that collects the dependence of v_0 on $[Fe(CN)_6^{3-}]$ and [2-propanol] can be expressed as

$$v_0 = \frac{[\mathrm{Ox}][\mathrm{S}]}{k_3'[\mathrm{S}] + k_4'[\mathrm{Ox}] + k_5'[\mathrm{Ox}][\mathrm{S}]} \tag{4}$$

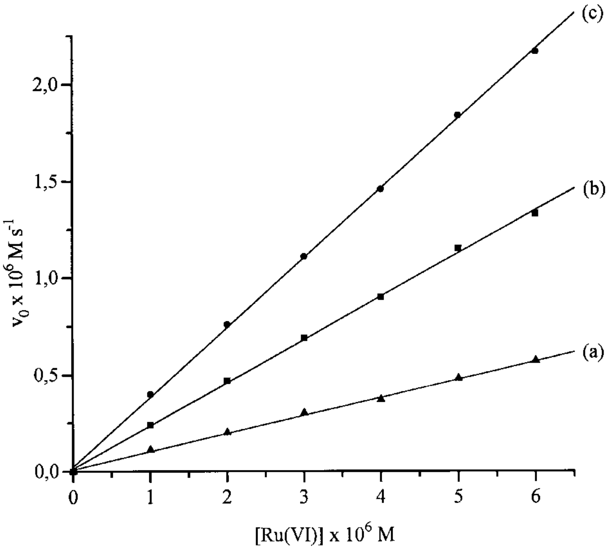


Figure 4. Plot of v_0 versus [Ru(VI)]. $I = 0.5$ M and $T = 30$ °C; (a) $[K_3Fe(CN)_6] = 1.2 \times 10^{-3}$ M, [2-propanol] = 0.2 M, [NaOH] = 0.3 M; (b) $[K_3Fe(CN)_6] = 0.8 \times 10^{-3}$ M, [2-propanol] = 0.4 M, [NaOH] = 0.2 M; (c) $[K_3Fe(CN)_6] = 0.8 \times 10^{-3}$ M, [2-propanol] = 0.5 M, [NaOH] = 0.1 M

Influence of the alkaline medium

It was observed (Fig. 3) that the initial rate passes through a maximum as $[OH^-]$ is varied. Moreover, the initial rate does not tend to zero at very low $[OH^-]$. This may be due to the possible existence of other oxo species of ruthenium in neutral or acid medium (pH 5–8)[20] because the ruthenate species is only stable in alkaline media.[10]

No simple mathematical relationship that might justify the dependence of v_0 on $[OH^-]$ was found. This indicates that the variation of the initial rate with the basicity of the medium is complicated, and obeys the general equation

$$v_0 = \frac{A_0 + A_1[OH^-] + A_2[OH^-]^2 + \ldots}{1 + B_1[OH^-] + B_2[OH^-]^2 + \ldots} \qquad (5)$$

The experimental values were fitted to Eqn. (5) by means of a non-linear regression program, obtaining the best average error (1.7%) for the expression

$$v_0 = \frac{A_0 + A_1[OH^-]}{1 + B_1[OH^-] + B_2[OH^-]^2} \qquad (6)$$

Effect of Ru(VI) concentration

By plotting v_0 versus $[Ru(VI)]_T$ (Fig. 4), straight lines with zero intercepts were obtained. Hence the initial rate shows first-order kinetics with respect to [Ru(VI)], and the uncatalyzed reaction is negligible in comparison with the catalyzed reaction.

Influence of product concentration

Several experiments were carried out in order to find out whether the addition of different initial amounts of hexacyanoferrate(II) ions to the reaction mixture modified the values of v_0. The results showed that the initial rate of the reaction was totally unaffected by $Fe(CN)_6^{4-}$ concentration. Also, the initial rate of a typical experiment at low $[Fe(CN)_6^{3-}]$ did not vary in presence of 1×10^{-4} M $(CH_3)_2CO$.

Substituent effects

A tertiary alcohol (0.2 M *tert*-butanol) was unreactive under kinetic conditions, implying the necessary presence of a hydrogen on the α-carbon of the alcohol for the reaction to occur.

Isotopic effect

The oxidation initial rates of $(CH_3)_2CHOH$ [$v_0 = (1.19 \pm 0.03) \times 10^{-6}$ l mol^{-1} s^{-1}] and $(CD_3)_2CDOD$ [$v_0 = (2.02 \pm 0.02) \times 10^{-7}$ l mol^{-1} s^{-1}] were obtained in H_2O, in order to determine the possible existence of an isotopic effect. The experimental conditions used were [2-propanol] = 0.5 M, [NaOH] = 0.2 M, $[K_3Fe(CN)_6] = 1.2 \times 10^{-3}$ M, $[Ru(VI)] = 4 \times 10^{-6}$ M, $I = 0.5$ M and $T = 30$ °C. A substantial primary kinetic isotope effect was observed [$v_0(H)/v_0(D) = 5.89$], which implies the breaking of the C—H bond in a slow step.

Detection of free radicals

Because the $Fe(CN)_6^{3-}$ species act as a one-electron transfer oxidant, the possible formation of free radicals as intermediates in the oxidation of organic compounds by hexacyanoferrate(III) should be tested. The results showed that neither the addition of acrylonitrile nor of 2,4,6-tri-*tert*-butylphenol (a stronger radical capturer) to the reaction mixture had any effect on the reaction rate.

Oxidation of cyclobutanol

We carried out the oxidation of cyclobutanol because the nature of the oxidation products for this alcohol depends on the mechanism. One-electron oxidation would produce acyclic four-carbon compounds which appear to be derived from the primary free radical $^{\cdot}CH_2CH_2CH_2CHO$, whereas two-electron oxidation would produce cyclobutanone directly.[21,22]

The reaction products were determined under the following kinetic conditions: [cyclobutanol] = 0.07 M, [hexacyanoferrate(III)] = 1.0×10^{-3} M, [Ru(VI)] = 4.6×10^{-6} M, [NaOH = 0.2 M, I = 0.5 M and T = 30 °C. After complete reduction of hexacyanoferrate(III), the organic products were separated from the reaction mixture by extraction with diethyl ether. The ether solution was analyzed by gas chromatography, cyclobutanone being found as the sole product. This result indicates that the oxidation of 2-propanol by RuO_4^{2-} occurs by a two-electron transfer mechanism.

Oxidation of 2-propanol by Ru(VI) and catalyst regeneration by $Fe(CN)_6^{3-}$

We also carried out some kinetic experiments to test whether the oxidation of 2-propanol by catalytic quantities of RuO_4^{2-} proceeds at a similar rate to that of the reoxidation of catalyst by $Fe(CN)_6^{3-}$.

The oxidation of 2-propanol by RuO_4^{2-} was followed spectrophotometrically. The initial rate was determined by monitoring the increase in absorbance at 320 nm. At this wavelength the product of the reaction [which appears to be a soluble form of ruthenium(IV) similar to the species formed during the electrochemical reduction of ruthenate(VI)] conforms to Beer's law with $\epsilon = 3370$[8] $l\,mol^{-1}\,cm^{-1}$. Under the conditions [2-propanol] = 1×10^{-3} M, [NaOH] = 0.5 M, T = 30 °C and $[RuO_4^{2-}] = 2 \times 10^{-4}$ M, the initial rate obtained was $v_0 = (4.5 \pm 0.02) \times 10^{-8}\ l\,mol^{-1}\,s^{-1}$. Assuming a first-order dependence with respect to 2-propanol and RuO_4^{2-}, the initial rate (under the kinetic experimental conditions $[RuO_4^{2-}] = 4 \times 10^{-6}$ M, [2-propanol] = 0.4 M and [NaOH] = 0.5 M) is $v_0 = (3.6 \pm 0.01) \times 10^{-7}\ l\,mol^{-1}\,s^{-1}$.

We also determined the initial rate of catalyst reoxidation in the following way. Ruthenate(VI) (12.5×10^{-3} mmol) was allowed to react at 30 °C with 2-propanol (12.5×10^{-3} mmol), both in 25 ml of 0.5 M NaOH. When the reaction had gone to completion (as indicated by the complete disappearance of any orange color), 0.08 ml of the reaction mixture was mixed with an appropriate volume of a 0.01 M solution $Fe(CN)_6^{3-}$ in 0.5 M NaOH, so that the final concentrations of Ru(IV) and $Fe(CN)_6^{3-}$ were 4×10^{-6} and 1.0×10^{-3} M respectively. Under these conditions, the initial rate obtained was $v_0 = (1.3 \pm 0.01) \times 10^{-7}\ l\,mol^{-1}\,s^{-1}$. The initial rate was determined by monitoring the decrease in absorbance at 420 nm.

Activation parameters

Under the conditions [2-propanol] = 0.5 M, $[K_3Fe(CN)_6] = 0.4 \times 10^{-3}$ M, [NaOH] = 0.1 M, [Ru(VI)] = 4×10^{-6} M, I = 0.5 M and temperature range 26–34 °C, the experimental activation parameters determined were $\Delta H^* = 19.02 \pm 0.13\ kJ\,mol^{-1}$ and $\Delta S^* = -261.91 \pm 0.45\ J\,mol^{-1}\,K^{-1}$.

DISCUSSION

It is known that the MO_4^{x-} species of the 3d transition metals do not expand their coordination shells in basic media.[23] However, such expansions can occur to a very small extent in 4d and 5d transition metal oxyanions.[24]

During a study of the reaction between perruthenate and manganate ions in aqueous alkaline medium, Luoma and Brubaker[25] suggested that one or more anions could possibly have hydroxide ions associated with them. This association with OH^- ions could be represented by the equilibrium

$$MO_4^{x-} + OH^- \rightleftharpoons (MO_4OH)^{(x+1)-} \tag{7}$$

where M is Ru or Mn and x = 1 or 2, depending on the state of oxidation.

Other transition metal oxyions have been postulated to form hydroxy–oxy complexes: the $OsO_4(OH)_2^{2-}$ species has been isolated[26] and mesoperrhenates $ReO_4(OH)_2^{3-}$ can be isolated, although their concentration in alkaline solutions of perrhenate must be small.[27,28]

Similarly, during the kinetic study of the decomposition of perruthenate ions in alkaline medium, Carrington and Symons[24] suggested that the coordination of OH^- ions with RuO_4^- occurred to a lower extent, because ruthenium represents an intermediate case between osmium and rhenium. Therefore, ruthenate ions, Ru(VI), may coordinate with hydroxide ions to a lower extent.

On the basis of literature data, we propose as the first step of the reaction the coordination of ruthenate ion to hydroxide ions, according to the equilibria:

$$RuO_4^{2-} + OH^- \overset{K_1}{\rightleftharpoons} RuO_4(OH)^{3-} \tag{8}$$

$$RuO_4(OH)^{3-} + OH^- \overset{K_2}{\rightleftharpoons} RuO_4(OH)_2^{4-} \tag{9}$$

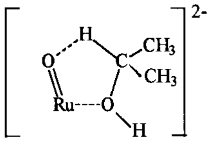
Moreover, in order to explain the v_0 dependence on $[OH^-]$, it is assumed that the active species of catalyst are RuO_4^{2-}, as the major species present, and $RuO_4(OH)^{3-}$, to a much lower extent.

The dependence of the initial rate on [2-propanol] suggests the formation of an intermediate complex, C_1^{2-}, between the catalyst active species and the organic substrate. Thus, we can write for RuO_4^{2-} species:

$$(CH_3)_2CHOH + RuO_4^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_1^{2-} \tag{10}$$

The results reported by Cundary and Drago[29] for an MO analysis of the interaction between *cis*-$[Ru(HN{=}CH{-}HC{=}NH)_2\,(NH_3)(O)]^{2+}$ and methanol show that the larger size of second-row transition metal atoms increases the possibility of coordination of the substrate to the metal via the hydroxylic oxygen. This coordination implies a large negative ΔS^*, indicating that a strongly associated complex exists in the rate-determining step. Furthermore, this complex undergoes further stabilization from the increase in the interaction between the C—H bond and the Ru—O π system. A similar intermediate has been proposed in the CrO^{2+} reaction with methanol.[30] Other authors[31] also suggest the formation of cyclic structures as transition states in other types of reactions, basing this on their observations of large isotope effects and high negative entropies of activation.

Therefore, C_1^{2-} could be a cyclic complex in which 2-propanol is coordinated to the metal via hydroxylic oxygen and a hydrogen bond between the Ru(VI) oxoligand and the hydrogen of α-C is formed:



C_1^{2-}

This coordination may explain why sterically hindered alcohols react more slowly.[30] Thus, under the same experimental conditions {[substrate] = 0.2 M, $[K_3Fe(CN)_6] = 1.2 \times 10^{-3}$ M, [NaOH] = 0.2 M, $[Ru(VI)] = 4 \times 10^{-6}$ M, $I = 0.5$ M and $T = 30\,°C$}, ethanol reacts more quickly [$v_0 = (7.25 \pm 0.05) \times 10^{-7}$ l mol^{-1} s^{-1}] than 2-propanol [$v_0 = (5.62 \pm 0.02) \times 10^{-7}$ l mol^{-1} s^{-1}].

The intermediate complex, C_1^{2-}, thus formed undergoes slow decomposition producing a reduced form of ruthenium as $RuO_3(OH)^{3-}$ and carbonium ion:

$$C_1^{2-} \xrightarrow{k_2} (CH_3)_2\overset{+}{C}OH + RuO_3(OH)^{3-} \qquad (11)$$

This decomposition involves a hydride transfer from the α-C—H bond to the oxoligand of ruthenium

The moderate isotope effect observed supports the direct involvement of the carbon–hydrogen bond in a slow step. A hydride-transfer mechanism would be supported by the following esperimental results: a) the absence of free radicals in the reaction medium [it has been reported[32,33] for the Ru(III)-catalyzed oxidations of alcohols and diols by hexacyanoferrate(III) that the presence of free radicals in the reaction mixture involves a hydrogen-atom transfer] and b) the observation that the oxidation of cyclobutanol produces cyclobutanone as the sole product.

The next fast step will be the formation of 2-propanone:

$$(CH_3)_2\,\overset{+}{C}OH + OH^- \rightarrow (CH_3)_2CO + H_2O \qquad (12)$$

We have previously described that the oxidation of 2-propanol by RuO_4^{2-}, using the catalytic concentration $[RuO_4^{2-}] = 4 \times 10^{-6}$ M, proceeds with a similar rate to that of the reoxidation of Ru(IV), at that same concentration, by 1×10^{-3} M $Fe(CN)_6^{3-}$. Hence, in order to explain the dependence of v_0 on $[Fe(CN)_6^{3-}]$, we propose that the oxidation of the substrate by RuO_4^{2-} is followed by the catalyst reoxidation by the co-oxidant:

$$RuO_3(OH)^{3-} + Fe(CN)_6^{3-} \xrightarrow{k_3} RuO_3(OH)^{2-} + Fe(CN)_6^{4-} \qquad (13)$$

$$RuO_3(OH)^{2-} + Fe(CN)_6^{3-} \rightarrow RuO_3(OH)^{-} + Fe(CN)_6^{4-} \qquad (14)$$

$$RuO_3(OH)^{-} + OH^- \rightarrow RuO_4^{2-} + H_2O \qquad (15)$$

In this way, when the $[Fe(CN)_6^{3-}]$ is high, the catalyst reoxidation is fast relative to substrate oxidation and the rate does not depend on $[Fe(CN)_6^{3-}]$. At low $[Fe(CN)_6^{3-}]$, however, the two consecutive reactions (11) and (13) have comparable rates and the rate depends on $[Fe(CN)_6^{3-}]$.

We can write a similar reaction mechanism for the other active species of catalyst:

$$(CH_3)_2CHOH + RuO_4(OH)^{3-} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} C_2^{3-} \qquad (16)$$

$$C_2^{3-} \xrightarrow{k_5} (CH_3)_2\overset{+}{C}OH + RuO_3(OH)_2^{4-} \qquad (17)$$

$$RuO_3(OH)_2^{4-} + Fe(CN)_6^{3-} \xrightarrow{k_6} RuO_3(OH)_2^{3-} + Fe(CN)_6^{4-} \qquad (18)$$

The next steps would be similar as those of reactions (12), (14) and (15).

Hence, according to the above reaction mechanism, the rate equation that accounts for the disappearance of hexacyanoferrate(III) is

$$-\frac{d[Ox]}{dt} = 2k_3[RuO_3(OH)^{3-}][Ox] + 2k_6[RuO_3(OH)_2^{4-}][Ox] \qquad (19)$$

As the amounts of $RuO_3(OH)^-$ and $RuO_3(OH)^{2-}$ present are negligible at any time (by forming a part of fast steps), the total ruthenium(VI) concentration can be expressed as

$$[Ru(VI)]_T = [RuO_4^{2-}] + [RuO_4(OH)^{3-}] + [RuO_4(OH)_2^{4-}] + [C_1^{2-}] + [C_2^{3-}] + [RuO_3(OH)^{3-}] + [RuO_3(OH)_2^{4-}] \qquad (20)$$

To approach a rate equation compatible with the experimental one, it is necessary to assume the following relations:

$$\frac{k_2}{k_{-1}} \approx \frac{k_5}{k_{-4}} \quad ; \quad \frac{k_3}{k_2} \approx \frac{k_6}{k_5} \qquad (21)$$

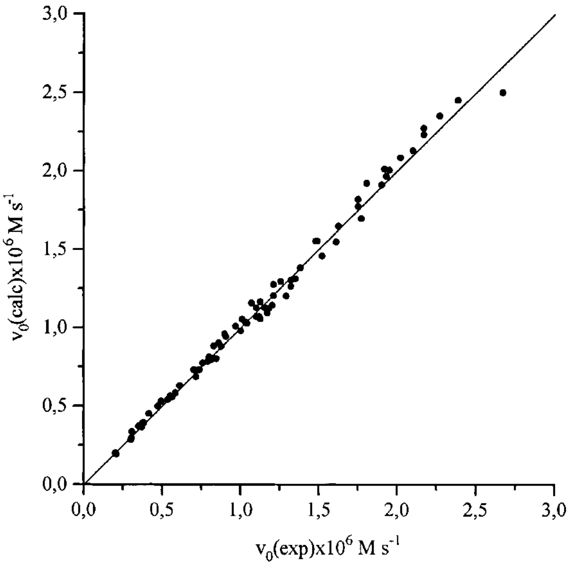


Figure 5. Plot of v_0 (calc) versus v_0 (exp)

that is,

$$k_{-1} + k_2 \approx \beta(k_{-4} + k_5)\ ;\ k_5 + k_6[\mathrm{Ox}] \approx \gamma(k_2 + k_3[\mathrm{Ox}]) \qquad (22)$$

where β and γ are constants independent of the experimental conditions.

In accordance with Hammond's postulate,[34] we can consider that the relations (21) for the parallel reaction sets (10), (11) and (16), (17), and (11), (13) and (17), (18) are not extremely affected, although the real rate constants may differ significantly from each set.

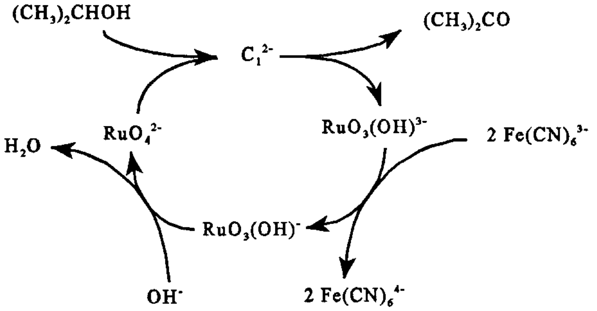
On applying the steady-state conditions with respect to C_1^{2-}, C_2^{3-}, $RuO_3(OH)^{3-}$ and $RuO_3(OH)_2^{4-}$, we obtained for the rate of disappearance of hexacyanoferrate(III) [Eqn. (19)], the following expression:

$$v_0 = \frac{2k_2k_6(k_1k_3 + \beta k_4k_6K_1[\mathrm{OH^-}])[\mathrm{S}][\mathrm{Ru(VI)}]_\mathrm{T}[\mathrm{Ox}]}{Zk_3k_6(k_{-1}+k_2)[\mathrm{Ox}] + [\mathrm{S}](k_2 + k_3[\mathrm{Ox}])(k_3k_4K_1[\mathrm{OH^-}] + k_1k_6)} \qquad (23)$$

where $Z = 1 + K_1[\mathrm{OH^-}] + K_1K_2[\mathrm{OH^-}]^2$. Equation (23) is in complete agreement with all the experimental results obtained, that is, the fractional dependence of v_0 on [2-propanol] and [$Fe(CN)_6^{3-}$], the first order in [Ru(VI)] and the complicated variation on [OH^-]. This equation can be expressed as

$$v_0 = \frac{(P_1 + P_2[\mathrm{OH^-}])[\mathrm{S}][\mathrm{Ox}][\mathrm{Ru(VI)}]_\mathrm{T}}{(1 + P_3[\mathrm{OH^-}] + P_4[\mathrm{OH^-}]^2)[\mathrm{Ox}] + [\mathrm{S}](P_5 + P_6[\mathrm{OH^-}] + P_7[\mathrm{Ox}][\mathrm{OH^-}] + P_8[\mathrm{Ox}])} \qquad (24)$$

The kinetic data were fitted to Eqn. (24) using a non-linear regression program based on the Marquardt algorithm.[35] The values obtained for the parameters of Eqn. (24) were $P_1 = 4.63$, $P_2 = 1.01 \times 10^2$, $P_3 = 2.09 \times 10^1$, $P_4 = 6.63 \times 10^2$, $P_5 = 1.02 \times 10^{-2}$, $P_6 = 1.09 \times 10^{-2}$, $P_7 = 4.27 \times 10^1$ and $P_8 = 1.00 \times 10^{-3}$. The agreement between v_0(calc) and v_0(exp) is satisfactory, as observed in Fig. 5. The average error of Eqn. (24) was 5.42%.



Scheme 2.

CONCLUSION

We have studied the ruthenium(VI)-catalyzed oxidation of 2-propanol by alkaline hexacyanoferrate(III). We observed a change of order from one to zero for both $Fe(CN)_6^{3-}$ and $(CH_3)_2$ CHOH species to increase their concentrations. The reaction shows first order in [Ru(VI)] and a complicated variation on [OH^-].

We tested experimentally that the substrate is oxidized by catalytic quantities of Ru(VI) at a rate similar to that of the reoxidation of intermediates Ru(IV) species by $Fe(CN)_6^{3-}$. Hence we propose a mechanism based on the catalytic cycle described in Scheme 2. The decomposition of intermediate complex C_1^{2-} involves a hydride transfer from the α-C—H bond to the oxoligand of ruthenium.

A similar cycle can be written for the other active species of Ru(VI), $RuO_4(OH)^{3-}$.

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