

# KINETIC STUDY OF THE OXIDATION OF PROPAN-1-OL BY ALKALINE HEXACYANOFERRATE(III) CATALYZED BY RUTHENIUM TRICHLORIDE

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**The oxidation kinetics of propan-1-ol by alkaline hexacyanoferrate(III) catalyzed by ruthenium trichloride were studied spectrophotometrically. The initial rate method was used for kinetic analysis. The reaction rate shows a fractional order in [oxidant] and [substrate] and a first-order dependence on  $[\text{RuCl}_3]$ . The dependence on  $[\text{OH}^-]$  is complicated. A reaction mechanism involving two active catalytic species is proposed. Each one of these species forms an intermediate complex with the substrate. The attack of these complexes by hexacyanoferrate(III) in rate-determining step produces a radical species which is further oxidized in the subsequent step. © 1997 John Wiley & Sons, Ltd.**

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## INTRODUCTION

The oxidation of organic compounds by hexacyanoferrate(III) is generally slow. However, trace amounts of a transition metal such as osmium(VIII),<sup>1</sup> ruthenium(III)<sup>2</sup> or iridium(III)<sup>3</sup> is normally sufficient to catalyze many such oxidations.

In the hexacyanoferrate(III) oxidation of alcohols and diols, different ruthenium catalysts, e.g. Ru(III),<sup>4,5</sup> Ru(VI)<sup>6</sup> and Ru(VIII),<sup>7</sup> have been used. The ruthenium(III)-catalyzed oxidation of some alcohols by alkaline hexacyanoferrate(III)<sup>8–10</sup> generally proceeds via the formation of a complex between the ruthenium(III) species and the substrate and its subsequent disproportionation (slow step) into oxidation products and ruthenium–hydride species. The ruthenium–hydride species are rapidly reconverted to ruthenium(III) by hexacyanoferrate(III). Thus the order with respect to the hexacyanoferrate(III) is zero.

In this paper, we report on the oxidation of propan-1-ol by alkaline hexacyanoferrate(III) using ruthenium(III) as catalyst. We found the oxidation rate varies with the initial hexacyanoferrate(III) concentration. Moreover, the formation of free radicals in the reaction mixture was detected. These results, which have not been reported previously

(although we have described a radical mechanism for the oxidation of butane-2,3-diol<sup>11</sup>), led us to propose a hydrogen-atom transfer mechanism that assumes the attack of hexacyanoferrate(III) on the substrate–catalyst complex in the rate-determining step.

## EXPERIMENTAL

**Materials.** The reagents employed were potassium hexacyanoferrate(III), sodium hydroxide, sodium perchlorate, propan-1-ol (all of A.R. grade, Merck) and ruthenium trichloride (Johnson-Matthey). All the solutions were prepared in water obtained using a Millipore Milli-Q water purification system. A stock solution of ruthenium trichloride ( $2.4 \times 10^{-3}$  M) was prepared by dissolving the sample in very dilute hydrochloric acid ( $16.38 \times 10^{-2}$  M). The ionic strength was kept constant at 0.5 M by adding sodium perchlorate.

**Kinetic measurements.** The temperature of the reaction was kept constant at  $30.0 \pm 0.1$  °C. The reactions were initiated by addition of propan-1-ol to other reagents. The progress of the reaction was followed spectrophotometrically by measuring the optical absorbance of hexacyanoferrate(III) at 420 nm on a Shimadzu UV-160 spectrophotometer. In all the kinetics, an excess of propan-1-ol and sodium hydroxide over the oxidant was used.

The initial rate method<sup>12</sup> was used for kinetic analysis. While such a method is perfectly compatible with the

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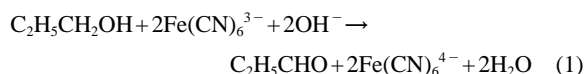
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normal standards of experimental accuracy, in certain circumstances it offers advantages over the integral method (e.g. the presence of competitive reactions is considerably less important when the initial rate method is employed). Although both aldehyde and acid were detected as reaction products, the oxidation of alcohol to aldehyde can be studied by using this method, thus overcoming the over-oxidation problem.

The initial rates were obtained by fitting the absorbance versus time data, for a small percentage of the reaction (5% or less),<sup>12</sup> 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  $\text{M min}^{-1}$ , is given by  $v_0 = -1/\epsilon(dA/dt)_0 = -(d[\text{Fe}(\text{CN})_6^{3-}]/dt)_0$ , where  $\epsilon = 1000 \text{ M}^{-1} \text{ cm}^{-1}$  at 420 nm.

**Products and stoichiometry.** Product analyses were performed on a Hewlett-Packard Model 5890 Series II gas chromatograph equipped with a BP-21 polyethylene glycol column ( $50 \text{ m} \times 0.22 \text{ mm}$  i.d.,  $25 \text{ }\mu\text{m}$  film thickness). The reaction products were determined under the following kinetic conditions:  $[\text{propan-1-ol}] = 0.6 \text{ M}$ ,  $[\text{Fe}(\text{CN})_6^{3-}] = 1.2 \times 10^{-3} \text{ M}$ ,  $[\text{RuCl}_3] = 1.21 \times 10^{-6} \text{ M}$ ,  $[\text{NaOH}] = 0.2 \text{ M}$  and  $I = 0.5 \text{ M}$ . 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 and it was found that propanal (60%) and propionic acid (40%) were the reaction products. We took the ether solution as a reference, obtained from the extraction of an alkaline solution,  $[\text{NaOH}] = 0.2 \text{ M}$ , where  $[\text{propan-1-ol}] = [\text{propanal}] = [\text{propionic acid}] = 0.1 \text{ M}$ .

Moreover, under the conditions  $[\text{Fe}(\text{CN})_6^{3-}] \gg [\text{propan-1-ol}]$  and  $[\text{RuCl}_3] = 1.21 \times 10^{-6} \text{ M}$ ,  $[\text{NaOH}] = 0.2 \text{ M}$  and  $I = 0.5 \text{ M}$ , the reaction was allowed to go to completion and the residual oxidant concentration was determined spectrophotometrically. These measurements indicate that 1 mol of alcohol reacts with 4 mol of oxidant, suggesting that the aldehyde, formed in the first instance, is further oxidized to propionic acid. Therefore, the stoichiometry of the reaction based on propanal as oxidation product is as follows:



## RESULTS

### Effect of $\text{Fe}(\text{CN})_6^{3-}$ concentration

The variation of the initial rate,  $v_0$ , as a function of the oxidant concentration is shown in Figure 1. It is observed that  $v_0$  varies linearly with the hexacyanoferrate(III) concentration at low concentrations (first-order kinetics) and becomes independent of hexacyanoferrate(III) concentration at high concentrations (zero-order kinetics). When  $1/v_0$

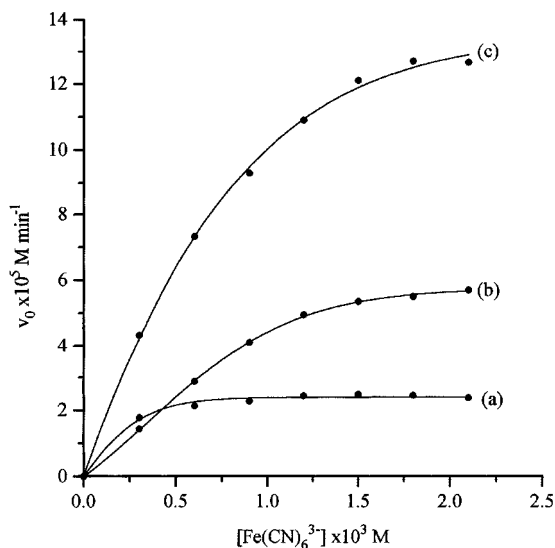


Figure 1. Effect of  $[\text{Fe}(\text{CN})_6^{3-}]$  on the initial rate.  $[\text{RuCl}_3] = 1.21 \times 10^{-6} \text{ M}$ ;  $I = 0.5 \text{ M}$ ;  $T = 30^\circ \text{C}$ . (a)  $[\text{propan-1-ol}] = 0.6 \text{ M}$ ,  $[\text{NaOH}] = 0.1 \text{ M}$ ; (b)  $[\text{propan-1-ol}] = 0.2 \text{ M}$ ,  $[\text{NaOH}] = 0.04 \text{ M}$ ; (c)  $[\text{propan-1-ol}] = 0.2 \text{ M}$ ,  $[\text{NaOH}] = 0.3 \text{ M}$

was plotted versus  $1/[\text{Fe}(\text{CN})_6^{3-}]$ , straight lines with positive slopes and intercepts were obtained.

### Effect of propan-1-ol concentration

It was observed that at low concentrations of propan-1-ol the initial rate is proportional to  $[\text{propan-1-ol}]$  (first-order kinetics); at a higher concentration of propan-1-ol the initial rate becomes independent of that concentration (zero-order kinetics). This variation was studied for different concentrations of hydroxyl ions. The plots of  $1/v_0$  versus  $1/[\text{propan-1-ol}]$  gave straight lines with positive slopes and intercepts (Figure 2), which corresponds to the equation

$$\frac{1}{v_0} = a + \frac{b}{[S]} \quad (2)$$

where  $[S]$  is the propan-1-ol concentration. This result suggests a Michaelis–Menten-type dependence of the initial rate on the concentration of propan-1-ol.

A linear correlation was obtained by plotting  $b$  versus  $1/[\text{Fe}(\text{CN})_6^{3-}]$ , with a positive intercept. The plot of  $a$  versus  $1/[\text{Fe}(\text{CN})_6^{3-}]$  was linear with a zero intercept. Hence the experimental rate equation that shows the dependence of initial rates on oxidant and reductant concentrations can be written as

$$v_0 = \frac{k[\text{Ox}][S]}{k' + k''[S] + k'''[\text{Ox}]} \quad (3)$$

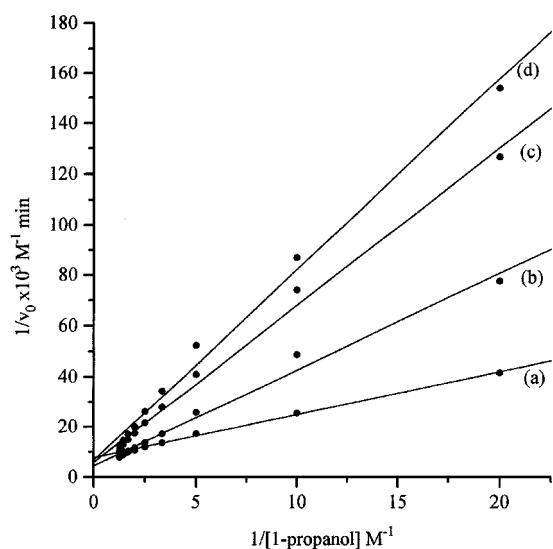


Figure 2. Plot of  $1/v_0$  versus  $1/[\text{propan-1-ol}]$ .  $[\text{Fe}(\text{CN})_6^{3-}] = 1.2 \times 10^{-3} \text{ M}$ ;  $[\text{RuCl}_3] = 1.21 \times 10^{-6} \text{ M}$ ;  $I = 0.5 \text{ M}$ ;  $T = 30^\circ \text{C}$ . (a)  $[\text{NaOH}] = 0.04 \text{ M}$ ; (b)  $[\text{NaOH}] = 0.15 \text{ M}$ ; (c)  $[\text{NaOH}] = 0.3 \text{ M}$ ; (d)  $[\text{NaOH}] = 0.4 \text{ M}$

where  $[\text{Ox}]$  is the potassium hexacyanoferrate(III) concentration.

#### Effect of the basicity of the medium

It was observed (Figure 3) that the initial oxidation rate increases at lower concentration of hydroxide ions, reaching a maximum; further addition of sodium hydroxide decreases the initial rate. It was also observed that when the propan-1-ol concentration increases, the maximum occurs at higher concentration of hydroxide ions.

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

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

where  $A_0 = 0$  since  $v_0$  approaches zero when  $[\text{OH}^-]$  tends towards zero.

Equation (4) was fitted with the help of a non-linear regression program and the best total average error for this equation was found to be 4.5% for grade two. Therefore, equation (4) may be reduced to

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

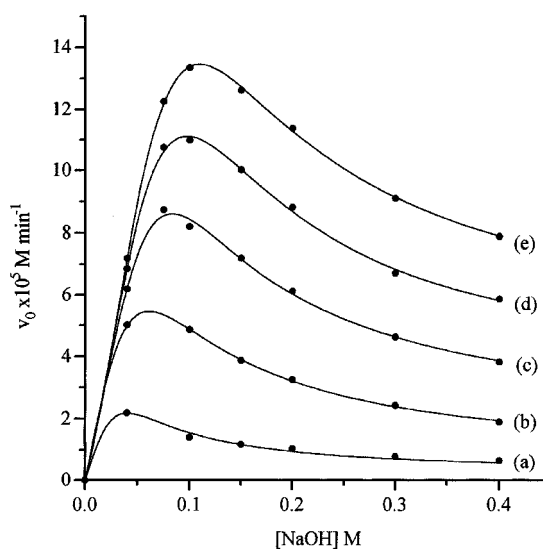


Figure 3. Effect of  $[\text{NaOH}]$  on the initial rate.  $[\text{Fe}(\text{CN})_6^{3-}] = 1.2 \times 10^{-3} \text{ M}$ ;  $[\text{RuCl}_3] = 1.21 \times 10^{-6} \text{ M}$ ;  $I = 0.5 \text{ M}$ ;  $T = 30^\circ \text{C}$ . (a)  $[\text{propan-1-ol}] = 0.05 \text{ M}$ ; (b)  $[\text{propan-1-ol}] = 0.2 \text{ M}$ ; (c)  $[\text{propan-1-ol}] = 0.4 \text{ M}$ ; (d)  $[\text{propan-1-ol}] = 0.6 \text{ M}$ ; (e)  $[\text{propan-1-ol}] = 0.8 \text{ M}$

#### Effect of $\text{RuCl}_3$ concentration

The plots of  $v_0$  versus catalyst concentration were linear with zero intercept (Figure 4). Hence the kinetics are first

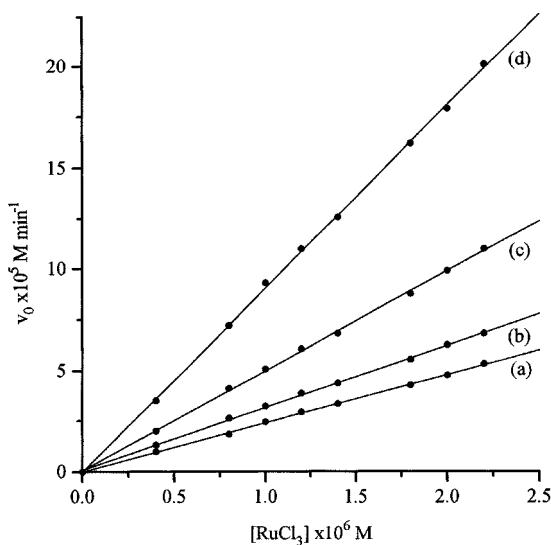


Figure 4. Effect of  $[\text{Ru(III)}]_T$  on the initial rate.  $[\text{Fe}(\text{CN})_6^{3-}] = 1.2 \times 10^{-3} \text{ M}$ ;  $I = 0.5 \text{ M}$ ;  $T = 30^\circ \text{C}$ . (a)  $[\text{propan-1-ol}] = 0.3 \text{ M}$ ,  $[\text{NaOH}] = 0.4 \text{ M}$ ; (b)  $[\text{propan-1-ol}] = 0.2 \text{ M}$ ,  $[\text{NaOH}] = 0.15 \text{ M}$ ; (c)  $[\text{propan-1-ol}] = 0.4 \text{ M}$ ,  $[\text{NaOH}] = 0.2 \text{ M}$ ; (d)  $[\text{propan-1-ol}] = 0.6 \text{ M}$ ,  $[\text{NaOH}] = 0.1 \text{ M}$

order in catalyst concentration and the rate of the uncatalyzed reaction is negligible in comparison with the catalyzed reaction.

#### Absence of polymerization of $\text{RuCl}_3$

No evidence for the existence of oxo-bridged ruthenium(III) complexes was obtained from the following experiment. A  $1 \times 10^{-3} \text{ M}$  solution of 2,2'-bipyridine in toluene was added to a  $5 \times 10^{-5} \text{ M}$  solution of  $\text{Ru(III)}$  in  $0.1 \text{ M}$   $\text{NaOH}$ . The organic ligand was slowly extracted into the aqueous phase. The spectrum of the aqueous phase was then recorded. The absence of an intense band about  $650 \text{ nm}$  indicates that oxo-bridged dimers such as  $[(\text{bipy})_2(\text{H}_2\text{O})\text{RuORu}(\text{H}_2\text{O})(\text{bipy})_2]^{4+}$  are not formed.<sup>13</sup>

The absence of oxo-bridged  $\text{Ru(III)}$  complexes was also confirmed as follows: the evaporation of a  $2.4 \times 10^{-3} \text{ M}$  solution of  $\text{RuCl}_3$  in  $0.04 \text{ M}$   $\text{NaOH}$  to dryness yielded a green solid. The IR spectrum of this solid did not display any absorption bands in the  $800\text{--}900 \text{ cm}^{-1}$  region, where an asymmetric stretch for linear  $\text{M--O--M}$  species<sup>13</sup> is normally located.

#### Substituent effects

Under kinetic conditions, the tertiary alcohol 2-methylbutan-2-ol was unreactive, implying that a hydrogen on the  $\alpha$ -carbon of the alcohol is necessary for the reaction to occur.

#### Reaction with alcohols

It is well known that methanol is more difficult to oxidize than propan-2-ol by a one-electron (hydrogen atom abstraction) path:  $\Delta H^0(\text{R--H}) = 95.9 \text{ kcal mol}^{-1}$  (1 kcal = 4.184 kJ) for  $\text{CH}_3\text{OH}$  and  $90.7 \text{ kcal mol}^{-1}$  for  $(\text{CH}_3)_2\text{CHOH}$  [ $\Delta H^0(\text{R--H})$  is the bond dissociation energy at  $298 \text{ K}$  for the gas-phase reaction  $\text{RH} \rightarrow \text{R}^\bullet + \text{H}^\bullet$ ].<sup>14</sup> Thus, we obtained  $v_0$  (methanol) =  $0.37 \times 10^{-5}$  and  $v_0$  (propan-2-ol) =  $1.26 \times 10^{-5} \text{ M min}^{-1}$  for the conditions [alcohol] =  $0.5 \text{ M}$ ,  $[\text{K}_3\text{Fe}(\text{CN})_6] = 1.2 \times 10^{-3} \text{ M}$ ,  $[\text{NaOH}] = 0.2 \text{ M}$ ,  $[\text{RuCl}_3] = 1.21 \times 10^{-6} \text{ M}$  and  $I = 0.5 \text{ M}$ . This result suggests a hydrogen atom abstraction in the rate-determining step.

#### Detection of free radicals

When acrylonitrile ( $0.01 \text{ M}$ ) was added to the reaction mixture, in a typical kinetic experiment, the initial rate decreased (25%). Also, when acrylonitrile ( $0.7 \text{ M}$ ) was added, large amounts of polymer were formed after a few minutes, indicating the formation of free radicals in the reaction. No polymeric species were formed when acrylonitrile ( $0.7 \text{ M}$ ) was added to the reaction mixture without propan-1-ol.

#### Activation parameters

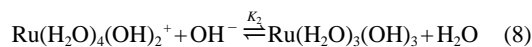
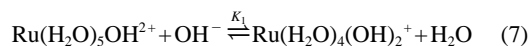
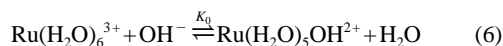
Under the conditions [propan-1-ol] =  $0.5 \text{ M}$ ,  $[\text{Fe}(\text{CN})_6^{3-}] = 1.20 \times 10^{-3} \text{ M}$ ,  $[\text{RuCl}_3] = 1.21 \times 10^{-6} \text{ M}$ ,  $[\text{NaOH}] = 0.3 \text{ M}$  and  $I = 0.5 \text{ M}$ , the experimental activation parameters found were  $\Delta H^\ddagger = 56.07 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -148.38 \text{ J K}^{-1} \text{ mol}^{-1}$ .

#### MECHANISM

Before considering the probable oxidation mechanism, it may be helpful to discuss the species of ruthenium(III) that may act as catalysts in the reaction.

The electronic spectra of  $\text{Ru}(\text{H}_2\text{O})_6\text{OH}^{3+}$  and  $\text{Ru}(\text{H}_2\text{O})_5\text{OH}^{2+}$  show absorption peaks at  $225$  and  $290 \text{ nm}$ , respectively, which are assigned to ligand to metal charge-transfer transitions. Both spectra display a much weaker peak at  $392 \text{ nm}$  assigned to an allowed d-d transition.<sup>15</sup>

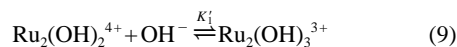
When the pH of a  $4 \times 10^{-5} \text{ M}$  aqueous solution of  $\text{RuCl}_3$  is increased by stepwise addition of  $\text{NaOH}$ , three absorption peaks at  $212$ ,  $280$  and  $390 \text{ nm}$  are observed. First, as  $[\text{OH}^-]$  increases the intensity of the peaks at  $280$  and  $390 \text{ nm}$  increases. In the interval  $[\text{OH}^-] = 10^{-3}\text{--}0.4 \text{ M}$  the intensity of the peaks at  $212$  and  $390 \text{ nm}$  increases while the intensity of the peak at  $280 \text{ nm}$  decreases slightly. Moreover, the absorption peaks are slightly shifted. In the interval of  $[\text{OH}^-]$  used, three unclearly defined isosbestic points located at about  $219$ ,  $357$  and  $429 \text{ nm}$  are observed. This optical behavior could involve the existence of several hydroxo-aquo ruthenium complexes in equilibrium:



where  $\text{p}K_0 = -11.1$ .<sup>16</sup>

Literature data suggest that ruthenium trichloride exists in aqueous alkaline media as  $[\text{Ru}(\text{H}_2\text{O})_{6-x}(\text{OH})_x]^{(3-x)+}$ , where  $x$  is always  $< 6$ .<sup>17-19</sup> Anderson and McConnell<sup>20</sup> observed similar species for hydroxo-aquo ruthenium(IV) complexes.

Given the tendency of  $\text{Ru(III)}$  complexes to form oxo-bridged species, the existence of polynuclear species such as  $(\text{H}_2\text{O})_5\text{Ru}(\text{OH})_2\text{Ru}(\text{H}_2\text{O})_5$  is probable. Thus, an equation similar to equation (7) may be written:



However, the behavior of ruthenium trichloride under the experimental conditions seems to be similar to that of  $\text{Ru(IV)}$ , which has been shown to polymerize slowly.<sup>20</sup> Furthermore, the oxo-bridged dimers have not been detected by using the aforementioned 2,2'-bipyridine test.

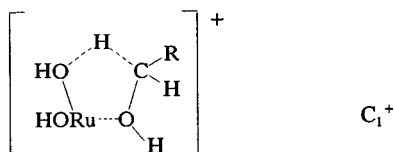
Therefore, we propose a mechanism involving catalytic paths by both the ruthenium complexes  $\text{Ru}(\text{H}_2\text{O})_4(\text{OH})_2^+$  and  $\text{Ru}(\text{H}_2\text{O})_3(\text{OH})_3$ , because equilibrium (6) is largely shifted forwards under the experimental conditions.

The dependence of rates on the concentration of propan-1-ol suggests the formation of an intermediate complex between the alcohol and the active species of the catalyst. Therefore, for the species  $\text{Ru}(\text{H}_2\text{O})_4(\text{OH})_2^+$  the following may be written:



where  $\text{R} = \text{CH}_3\text{CH}_2$ .

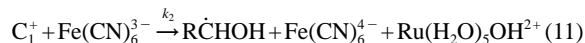
Cundary and Drago<sup>21</sup> have shown that a prior coordination between the substrate and the metal via hydroxylic oxygen, before hydride transfer from methanol to the oxo ligand of  $\text{Ru}(\text{HN}=\text{CHCH}=\text{NH})_2(\text{NH}_3)_2\text{O}^{2+}$ , lowers the activation energy. Such an intermediate complex in the  $\text{Ru}(\text{H}_2\text{O})_4(\text{OH})_2^+$  reaction with propan-1-ol would have the following structure:



The formation of this cyclic intermediate would certainly contribute to the large negative value of entropy observed. A similar intermediate has been proposed in the reaction of  $\text{CrO}^{2+}$  with methanol.<sup>22</sup>

Prior coordination may explain why sterically hindered alcohols react more slowly.<sup>22</sup> We obtained  $v_0 = 6.2 \times 10^{-6} \text{ M min}^{-1}$  for  $(\text{CH}_3)_2\text{CHOH}$  and  $v_0 = 1.0 \times 10^{-5} \text{ M min}^{-1}$  for  $\text{CH}_3\text{CH}_2\text{OH}$  using the following conditions:  $[\text{alcohol}] = 0.1 \text{ M}$ ,  $[\text{K}_3\text{Fe}(\text{CN})_6] = 1.2 \times 10^{-3} \text{ M}$ ,  $[\text{NaOH}] = 0.2 \text{ M}$ ,  $[\text{RuCl}_3] = 2.0 \times 10^{-6} \text{ M}$ ,  $I = 0.5 \text{ M}$  and  $T = 30^\circ\text{C}$ .

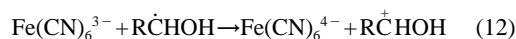
To explain the effect of hexacyanoferrate(III) on the initial reaction rate, we propose the attack of the complex by the oxidant, in a slow step [equation (11)], producing  $\text{Ru}(\text{H}_2\text{O})_5\text{OH}^{2+}$  and a free ketyl radical:



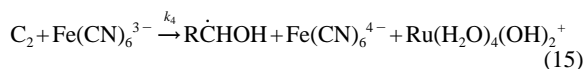
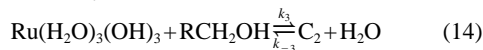
This attack could involve a hydrogen-atom transfer from the  $\alpha\text{-C-H}$  bond to the oxygen of the hydroxo ligand of ruthenium and an outer-sphere one-electron transfer from the ruthenium to the oxidant. This hydrogen atom abstraction is supported by the conventional reactivity order for the aforementioned oxidation of methanol and propan-2-ol. The radical nature of reaction (11) was inferred on the basis of the previously discussed polymerization test.

Awasthi and Upadhyay<sup>2</sup> have also proposed a slow step for the ruthenium(III)-catalyzed oxidation of formaldehyde and acetaldehyde by alkaline hexacyanoferrate(III) which involves the attack of the ruthenium(III)-substrate complex by hexacyanoferrate(III).

Finally, hexacyanoferrate(III) reacts with the ketyl radical to yield the reaction products, i.e. propanal and hexacyanoferrate(II):



We can write the same mechanism for the other active species of the catalyst:



The next steps would be the same as those of reactions (12) and (13). Hence the disappearance rate of hexacyanoferrate(III) is given by

$$-\frac{d[\text{Ox}]}{dt} = 2k_2[\text{C}_1^+][\text{Ox}] + 2k_4[\text{C}_2][\text{Ox}] \quad (16)$$

By applying the steady-state hypothesis to both complexes  $\text{C}_1^+$  and  $\text{C}_2$ , we obtain

$$[\text{C}_1^+] = \frac{k_1[\text{S}][\text{Ru}(\text{H}_2\text{O})_4(\text{OH})_2^+]}{k_{-1} + k_2[\text{Ox}]} \quad (17)$$

$$[\text{C}_2] = \frac{k_3[\text{S}][\text{Ru}(\text{H}_2\text{O})_3(\text{OH})_3]}{k_{-3} + k_4[\text{Ox}]} \quad (18)$$

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

$$[\text{Ru(III)}]_{\text{T}} = [\text{Ru}(\text{H}_2\text{O})_5\text{OH}^{2+}] + [\text{Ru}(\text{H}_2\text{O})_4(\text{OH})_2^+] + [\text{Ru}(\text{H}_2\text{O})_3(\text{OH})_3] + [\text{C}_1^+] + [\text{C}_2] \quad (19)$$

where

$$[\text{Ru}(\text{H}_2\text{O})_4(\text{OH})_2^+] = K_1[\text{Ru}(\text{H}_2\text{O})_5\text{OH}^{2+}][\text{OH}^-] \quad (20)$$

[from equilibrium (7)] and

$$[\text{Ru}(\text{H}_2\text{O})_3(\text{OH})_3] = K_2[\text{Ru}(\text{H}_2\text{O})_4(\text{OH})_2^+][\text{OH}^-] \quad (21)$$

[from equilibrium (8)].

Thus assuming that

$$k_{-1} + k_2[\text{Ox}] \approx k_{-3} + k_4[\text{Ox}] \quad (22)$$

and replacing the expressions for  $[\text{Ru}(\text{H}_2\text{O})_5\text{OH}^{2+}]$ ,  $[\text{Ru}(\text{H}_2\text{O})_4(\text{OH})_2^+]$ ,  $[\text{Ru}(\text{H}_2\text{O})_3(\text{OH})_3]$  and  $[\text{C}_2]$  in terms of  $[\text{C}_1^+]$  into equation (19), solving for  $[\text{C}_1^+]$  gives

$$[\text{C}_1^+] = \frac{k_1 K_1 [\text{OH}^-] [\text{S}] [\text{Ru(III)}]_{\text{T}}}{(1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{OH}^-]^2)(k_{-1} + k_2 [\text{Ox}]) + [\text{S}](k_1 K_1 [\text{OH}^-] + k_3 K_1 K_2 [\text{OH}^-]^2)} \quad (23)$$

It follows from equations (17), (18), (21) and (22) that

$$[C_2] = \frac{k_3}{k_1} K_2 [C_1^+][OH^-] \quad (24)$$

and therefore  $[C_2]$  in terms of the total concentration of ruthenium(III) is

$$[C_2] = \frac{k_3 K_1 K_2 [OH^-]^2 [S][Ru(III)]_T}{(1 + K_1 [OH^-] + K_1 K_2 [OH^-]^2)(k_{-1} + k_2 [Ox]) + [S](k_1 K_1 [OH^-] + k_3 K_1 K_2 [OH^-]^2)} \quad (25)$$

Substitution of the expressions for  $[C_1^+]$  and  $[C_2]$  [equations (23) and (25)] into equation (16) leads to reaction rate:

$$\frac{d[Ox]}{dt} = \frac{2(k_1 k_2 K_1 [OH^-] + k_3 k_4 K_1 K_2 [OH^-]^2)[Ox][S][Ru(III)]_T}{(1 + K_1 [OH^-] + K_1 K_2 [OH^-]^2)(k_{-1} + k_2 [Ox]) + [S](k_1 K_1 [OH^-] + k_3 K_1 K_2 [OH^-]^2)} \quad (26)$$

This equation indicates that at low concentrations of either hexacyanoferrate(III) or substrate the rate is proportional to either  $[Ox]$  or  $[S]$ ; at a higher concentration of either the rate becomes independent of that concentration. Equation (26) shows also a first-order dependence on  $[catalyst]$  and the same complicated dependence on  $[OH^-]$  as observed experimentally. Therefore, all the experimental results are in complete agreement with the rate equation (26). This equation can be expressed as follows:

$$\frac{d[Ox]}{dt} = \frac{2\{P(1)[OH^-] + P(2)[OH^-]^2\}[Ox][S][Ru(III)]_T}{\{1 + P(3)[OH^-] + P(4)[OH^-]^2\}\{P(5) + P(6)[Ox]\} + [S]\{P(7)[OH^-] + P(8)[OH^-]^2\}} \quad (27)$$

The kinetic data were fitted to equation (27) using a non-linear regression program based on the Marquardt algorithm.<sup>23</sup> The values obtained for the parameters of equation (27) were  $P(1)=2.97 \times 10^{11}$ ,  $P(2)=4.22 \times 10^9$ ,  $P(5)=1.00 \times 10^3$ ,  $P(6)=3.42 \times 10^7$ ,  $P(3) \times P(5)=1.00 \times 10^6$ ,  $P(3) \times P(6)=7.45 \times 10^8$ ,  $P(4)=1.64 \times 10^3$ ,  $P(4) \times P(5)=1.63 \times 10^6$ ,  $P(4) \times P(6)=9.57 \times 10^9$ ,  $P(7)=2.07 \times 10^6$  and  $P(8)=1.00 \times 10^5$ . The agreement between  $v_0(\text{calc})$  and  $v_0(\text{exp})$  is satisfactory, as observed in Figure 5. The average error of equation (27) was 5.90%.

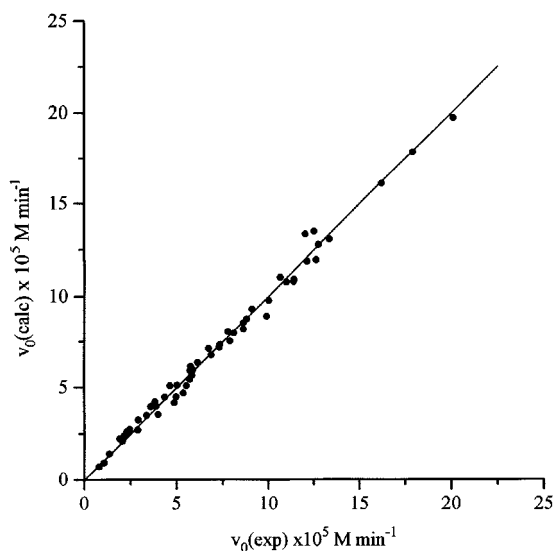


Figure 5. Plot of  $v_0(\text{calc})$  versus  $v_0(\text{exp})$

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