

Comparative study of the catalytic behaviour of Ru(III) and Ru(VI) on the oxidation of alcohols by hexacyanoferrate(III)

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ABSTRACT: The oxidation reactions of 2-methyl-2,4-pentanediol upon treatment with alkaline hexacyanoferrate(III) using Ru(III) or Ru(VI) as catalysts are governed by two quasi-identical experimental rate equations, which show that both catalysts are equally effective for the oxidation of alcohols by $\text{Fe}(\text{CN})_6^{3-}$. The reaction mechanism proposed involves the oxidation of 2-methyl-2,4-pentanediol by the catalyst, a process that occurs through the formation of a substrate–catalyst complex. The decomposition of this complex yields Ru(IV) and a protonated ketone (owing to a hydride transfer from the $\alpha\text{-C—H}$ bond of the alcohol to the oxoligand of ruthenium) in the case of Ru(VI), but a ketyl radical and Ru(II) (hydrogen transfer) for Ru(III). The role of the co-oxidant, $\text{Fe}(\text{CN})_6^{3-}$, is to regenerate the catalyst. For both oxidation reactions, the rate constants of complex decomposition and catalyst regeneration have been determined. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: oxidation; catalysis; hexacyanoferrate(III); ruthenium(III); ruthenium(VI); alcohols; 2-methyl-2,4-pentanediol

INTRODUCTION

The metal-catalysed oxidation of organic substrates is a topic of great interest, especially for reactions in which the substrates are not easily oxidized by common oxidants.^{1–3} One such example is the oxidation in alkaline media of primary and secondary alcohols by hexacyanoferrate(III). The reaction rate is extremely slow, but the presence of ruthenium compounds in catalytic concentrations allows the kinetics to be studied over a reasonable time period.⁴ The most frequently used ruthenium catalysts are Ru(III), Ru(VI) and Ru(VIII) species. Numerous kinetic studies have been undertaken using these catalysts,^{5–8} but the catalytic behaviour has not been systematically compared in any study. The goal of the work described here was to perform a comparative study of the efficiency of Ru(III) and Ru(VI) as catalysts in the oxidation of 2-methyl-2,4-pentanediol with alkaline hexacyanoferrate(III). With this aim in mind, the results found in this work, using Ru(VI) as a catalyst, are compared with those obtained previously for Ru(III).⁹

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EXPERIMENTAL

Reactants. The reagents used, i.e. hexacyanoferrate(III), sodium hydroxide, 2-methyl-2,4-pentanediol and sodium perchlorate, were all of analytical-reagent grade and were purchased from Merck. The solutions were prepared using water obtained from an OSMO BL-6 deionizer from SETA. Sodium ruthenate solution was prepared following the literature procedure.⁶ The purity of stock solutions was assessed by taking into account that the ratio between the absorbance at 465 and 386 nm should equal 2.07 for pure ruthenate.¹⁰

General. The oxidation kinetics of 2-methyl-2,4-pentanediol were followed by measuring the optical absorbance of hexacyanoferrate(III), A , at 420 nm on a Perkin-Elmer Lambda 3B spectrophotometer. The initial rates method was used for kinetic analysis. The initial rates of disappearance of hexacyanoferrate(III) were obtained as described previously,⁹ using the expression $v_0 = -1/\varepsilon(dA/dt)$, where $\varepsilon = 10001 \text{ mol}^{-1} \text{ cm}^{-1}$ at 420 nm. The ionic strength was kept constant at 0.5 M by the addition of sodium perchlorate. The only organic reaction product of the oxidation of 2-methyl-2,4-pentanediol was 4-hydroxy-4-methyl-2-pentanone, which was identified using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a BP-21 polyethylene

glycol column (50 m $\times$ 0.22 μm i.d., 25 μm film thickness). The stoichiometry of the reaction was deduced using an excess concentration of hexacyanoferrate(III) in relation to diol. The residual oxidant concentration was measured spectrophotometrically and this showed that 1 mol of diol consumed 2 mol of hexacyanoferrate(III).

RESULTS

The values of v_0 for five series of kinetic runs at different $[\text{Fe}(\text{CN})_6^{3-}]_0$ are shown in Fig. 1. In each series the value $[\text{diol}]_0$ was varied while the concentrations of ruthenate and hydroxide ions were kept constant. The dependence of v_0 on both $[\text{Fe}(\text{CN})_6^{3-}]_0$ and $[\text{diol}]_0$ was ascertained using a previously described procedure.¹¹ This study led to the following expression:

$$v_0 = \frac{[\text{Fe}(\text{CN})_6^{3-}]_0 [\text{diol}]_0}{k' [\text{diol}]_0 + k'' [\text{Fe}(\text{CN})_6^{3-}]_0 + k''' [\text{diol}]_0 [\text{Fe}(\text{CN})_6^{3-}]_0} \quad (1)$$

where $k' = 3.5 \pm 0.1 \text{ min}$, $k'' = (1.3 \pm 0.1) \times 10^3 \text{ min}$ and $k''' = (1.1 \pm 0.2) \times 10^3 \text{ l mol}^{-1} \text{ min}$. This equation indicates a change of order from one to zero for both hexacyanoferrate(III) and diol species upon increasing their concentrations.

When Ru(III) was used as catalyst, under the same experimental conditions, except that $[\text{Ru(III)}]_0$ was $2.4 \times 10^{-6} \text{ M}$, an equation identical with Eqn (1) was obtained with the parameters now being $k' = 1.3 \pm 0.1 \text{ min}$, $k'' = (1.3 \pm 0.4) \times 10^3 \text{ min}$ and $k''' = (1.4 \pm 0.2) \times 10^3 \text{ l mol}^{-1} \text{ min}$.

The variation of v_0 with $[\text{catalyst}]_0$ is shown in Fig. 2 for the oxidation of 2-methyl-2,4-pentanediol by hexacyanoferrate(III) using Ru(VI) and Ru(III) as catalysts.

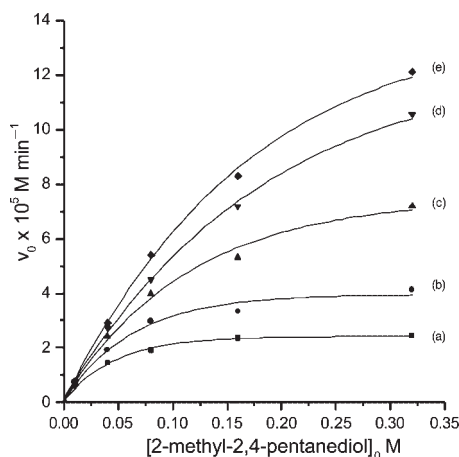


Figure 1. Plot of v_0 vs $[\text{2-methyl-2,4-pentanediol}]_0$. $[\text{RuO}_4^{2-}]_0 = 2.0 \times 10^{-6} \text{ M}$, $[\text{NaOH}] = 0.1 \text{ M}$, $I = 0.5 \text{ M}$ and $T = 30^\circ\text{C}$; $[\text{Fe}(\text{CN})_6^{3-}]_0 =$ (a) 1.0×10^{-4} ; (b) 2.0×10^{-4} ; (c) 4.0×10^{-4} ; (d) 8.0×10^{-4} ; (e) $1.2 \times 10^{-3} \text{ M}$

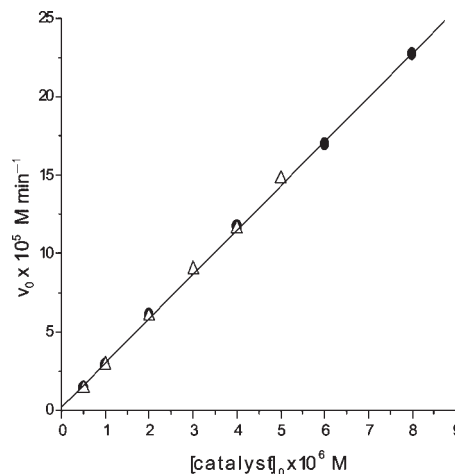


Figure 2. Effect of $[\text{catalyst}]_0$ on the initial rate. $[\text{2-Methyl-2,4-pentanediol}]_0 = 0.08 \text{ M}$, $[\text{Fe}(\text{CN})_6^{3-}]_0 = 1.2 \times 10^{-3} \text{ M}$, $[\text{OH}^-] = 0.1 \text{ M}$, $T = 30^\circ\text{C}$, $I = 0.5 \text{ M}$. Δ , Ru(VI); $\bullet$, Ru(III)

The v_0 - $[\text{catalyst}]_0$ data were fitted to a linear regression, which gave the following expression:

$$v_0 = v_{\text{unc}} + k_c [\text{catalyst}]_0 \quad (2)$$

where the respective values of v_{unc} and k_c are $(3.0 \pm 0.1) \times 10^{-7} \text{ mol l}^{-1} \text{ min}^{-1}$ and $29.53 \pm 0.04 \text{ min}^{-1}$ for Ru(VI) and $(2.2 \pm 0.2) \times 10^{-6} \text{ mol l}^{-1} \text{ min}^{-1}$ and $28.16 \pm 0.03 \text{ min}^{-1}$ for Ru(III). These results indicate that the kinetics are first order with respect to catalyst and that the rate of the uncatalysed reaction, v_{unc} , is negligible compared with that of the catalysed reaction.

For both catalysts the initial rate passes through a maximum as $[\text{OH}^-]$ is varied, as shown in Fig. 3. In the case of Ru(VI), v_0 does not tend to zero at very low $[\text{OH}^-]$, whereas it does for Ru(III). The variation of v_0 with the basicity of the medium is complicated and obeys the following equation:

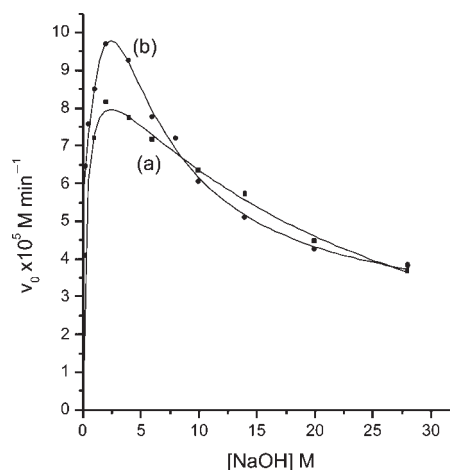


Figure 3. Variation of v_0 with respect to $[\text{NaOH}]$. $[\text{Fe}(\text{CN})_6^{3-}]_0 = 1.2 \times 10^{-3} \text{ M}$, $I = 0.5 \text{ M}$ and $T = 30^\circ\text{C}$. $[\text{2-Methyl-2,4-pentanediol}]_0 = 0.08 \text{ M}$. (a) $[\text{Ru(III)}]_0 = 2.4 \times 10^{-6} \text{ M}$; (b) $[\text{Ru(VI)}]_0 = 2.0 \times 10^{-6} \text{ M}$

$$v_0 = \frac{A_0 + A_1[\text{OH}^-] + A_2[\text{OH}^-]^2}{1 + B_1[\text{OH}^-] + B_2[\text{OH}^-]^2} \quad (3)$$

The v_0 -[OH⁻] data were fitted to Eqn (3) by means of a non-linear regression program. The best average error was obtained for Ru(VI) when $A_2 = 0$ and for Ru(III) when $A_0 = 0$.

The possible formation of free radicals as intermediates was investigated by adding radical scavengers to the reaction mixture. The addition of either 0.01 M acrylonitrile or 1.6×10^{-4} M 2,4,6-tri-*tert*-butylphenol (a stronger radical scavenger) did not have any effect on the reaction rate when Ru(VI) was used as catalyst. For Ru(III), however, the presence of 0.01 M acrylonitrile reduced v_0 by 15% and the addition of 1.6×10^{-4} M 2,4,6-tri-*tert*-butylphenol decreased v_0 by 40%. Moreover, when 0.7 M acrylonitrile was added to the reaction mixture, polymeric species were observed after a few minutes.

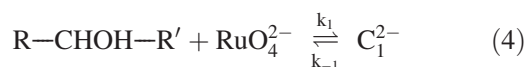
The oxidation of cyclobutanol was carried out because the nature of its oxidation products depends on the reaction mechanism. One-electron oxidation produces acyclic four-carbon compounds, which appear to be derived from the primary free radical $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$, whereas two-electron oxidation produces cyclobutanone directly.^{12,13} The following kinetic conditions were employed in this experiment: [OH⁻] = 0.1 M, $I = 0.5$ M and $T = 30^\circ\text{C}$. Under these conditions the oxidation of 0.08 M cyclobutanol by 2.0×10^{-3} M hexacyanoferrate(III) using 2.5×10^{-6} M catalyst produced butanal as the major product in the case of Ru(III) and cyclobutanone in the case of Ru(VI).

Although the organic substrate is a diol, only the 2-hydroxy group will be oxidized, as observed experimentally, because tertiary alcohols (0.1 M *tert*-butanol) were found not to react under kinetic conditions.¹¹ The presence of a hydrogen on the α -carbon of the alcohol is therefore necessary for the reaction to progress.¹⁴

The observed oxidation rate of $\text{CD}_3\text{-CDOD-CD}_3$ was compared with that of $\text{CH}_3\text{-CHOH-CH}_3$ in order to verify the existence of a kinetic isotope effect. A substantial primary kinetic isotope effect was indeed observed [$(v_{0,\text{H}}/v_{0,\text{D}}) = 5.9$] for both catalysts under the following kinetic conditions: [catalysts] = 2.0×10^{-6} M, $[\text{Fe}(\text{CN})_6^{3-}] = 1.2 \times 10^{-3}$ M, [diol] = 0.5 M, [OH⁻] = 0.2 M, $I = 0.5$ M and $T = 30^\circ\text{C}$.

DISCUSSION

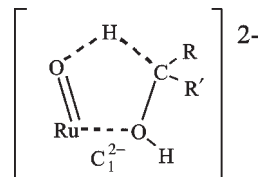
For Ru(VI) the dependence of the initial rate on $[\text{R-CHOH-R'}]_0$ [where $\text{R} = (\text{CH}_3)_2\text{COHCH}_2$ and $\text{R}' = \text{CH}_3$] suggests the formation of an intermediate complex, C_1^{2-} , between RuO_4^{2-} and the organic substrate:



which then decomposes slowly to produce a reduced form of catalyst, $\text{RuO}_3(\text{OH})^{3-}$, and a protonated ketone as follows:

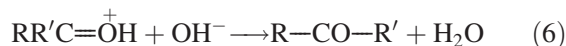


Such an intermediate would have the following structure:

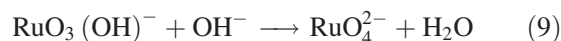
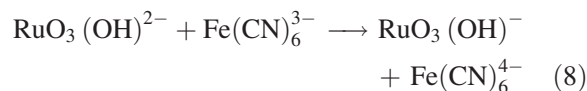
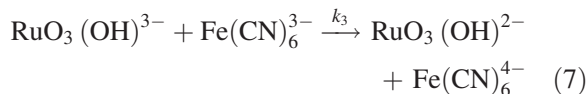


Step 5 involves a hydride transfer from the α -C-H bond of the alcohol to the oxo ligand of ruthenium, a process that is favoured by the prior coordination of the organic substrate to the metal through the oxygen of the hydroxy group.¹⁵ The occurrence of this hydride transfer is supported by the following experimental results: (a) a moderate kinetic isotope effect, which indicates cleavage of a C-H bond, and the absence of free radicals in the reaction mixture, (b) oxidation of cyclobutanol produces cyclobutanone as the sole product and (c) the negative value of the Hammett reaction constant found for the oxidation of benzyl alcohol.¹⁶

The following rapid reaction would yield the corresponding ketone:



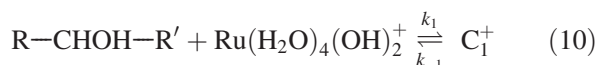
The dependence of v_0 on $[\text{Fe}(\text{CN})_6^{3-}]_0$ can be explained if it is accepted that the oxidation of the reduced form of catalyst occurs. In this way, the role of the co-oxidant, $\text{Fe}(\text{CN})_6^{3-}$, is solely the regeneration of the catalyst through steps (7) and (8):



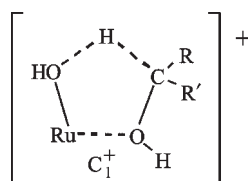
Step (7) is supported by the previously discovered fact that the oxidation of alcohols by catalytic quantities of ruthenate proceeds at a similar rate to the reoxidation of the reduced form of the catalyst by $\text{Fe}(\text{CN})_6^{3-}$.¹¹ Step (7) is fast relative to oxidation of the substrate at high $[\text{Fe}(\text{CN})_6^{3-}]_0$ and, under these circumstances, v_0 does

not depend on $[\text{Fe}(\text{CN})_6^{3-}]_0$. At low $[\text{Fe}(\text{CN})_6^{3-}]_0$, however, both reactions have a comparable rate and v_0 is dependent on $[\text{Fe}(\text{CN})_6^{3-}]_0$.

For Ru(III),⁹ we obtained the same variation of v_0 with $[\text{R}-\text{CHOH}-\text{R}']_0$ and $[\text{Fe}(\text{CN})_6^{3-}]_0$ as in the case of Ru(VI). For this reason we propose an analogous scheme to that outlined in steps (4)–(9) (a slightly different scheme was reported in our previous paper). Given that the active catalytic species of Ru(III) is $\text{Ru}(\text{H}_2\text{O})_4(\text{OH})_2^+$,⁹ the following equations can be proposed:



The intermediate C_1^+ would have the following structure:



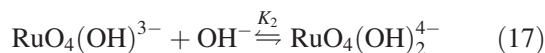
The decomposition of C_1^+ yields a ketyl radical and Ru(II). Step (11) involves a hydrogen atom transfer from the $\alpha\text{-C}-\text{H}$ bond of the alcohol to the oxygen of the hydroxo ligand of ruthenium. Evidence for this transfer is provided by the presence of free radicals in the reaction mixture and by the fact that the oxidation of cyclobutanol yields butanal as the major product.

In the absence of scavengers, the rate of disappearance of hexacyanoferrate(III) is determined by steps (11) and (14) as follows:

$$-\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = k_2[\text{C}_1^+] + k_3[\text{Fe}(\text{CN})_6^{3-}] \times [\text{Ru}(\text{H}_2\text{O})_5(\text{OH})^+]$$

If the added scavengers compete with hexacyanoferrate for the ketyl radical, the disappearance rate of hexacyanoferrate(III) would be expected to decrease, as observed experimentally.

The dependence of v_0 on $[\text{OH}^-]$ in the case of ruthenate may be explained by assuming the existence of two active species of catalyst, RuO_4^{2-} and $\text{RuO}_4(\text{OH})^{3-}$, which are in equilibrium as follows:¹⁶

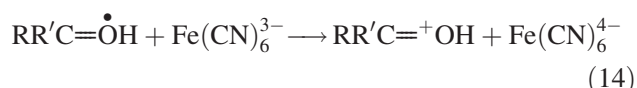
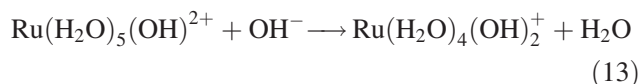
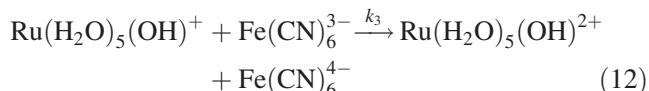


The existence of these hydroxy-oxy complexes of ruthenium was suggested by Luoma and Brubaker, who studied the reaction between perruthenate and manganate ions in aqueous alkaline media.¹⁷

Application of the steady-state conditions with respect to $\text{RuO}_3(\text{OH})^{3-}$ and C_1^{2-} , and on the assumption that the reactivities of RuO_4^{2-} and $\text{RuO}_4(\text{OH})^{3-}$ are equal (for simplicity), gives the following theoretical rate equation for the disappearance of hexacyanoferrate(III):

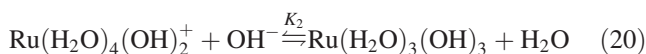
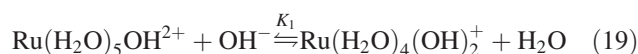
$$-\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{2k_1k_2k_3k_A[\text{Fe}(\text{CN})_6^{3-}][\text{diol}][\text{Ru(VI)}]_T}{k_1k_2k_A[\text{diol}] + k_3(k_{-1} + k_2)k_B[\text{Fe}(\text{CN})_6^{3-}] + k_1k_3k_A[\text{Fe}(\text{CN})_6^{3-}][\text{diol}]} \quad (18)$$

Regeneration of the catalyst occurs through steps (12) and (13), whereas the fast step (14) and a step as (6) would yield 4-hydroxy-4-methyl-2-pentanone:



where $[\text{Ru(VI)}]_T$ is the sum of the concentrations of Ru(VI) and Ru(IV); the concentration of Ru(V) would be negligible at any time because such species are involved in fast steps. Moreover, $k_A = 1 + K_1[\text{OH}^-]$ and $k_B = 1 + K_1[\text{OH}^-] + K_1K_2[\text{OH}^-]^2$. Equation (18) explains the dependence of v_0 on $[\text{OH}^-]$, $[\text{Fe}(\text{CN})_6^{3-}]$, $[\text{diol}]$ and $[\text{catalyst}]$.

In the case of Ru(III), the dependence of v_0 on $[\text{OH}^-]$ can be justified, as reported previously,⁵ by accepting that the catalytic reactive species are $\text{Ru}(\text{H}_2\text{O})_4(\text{OH})_2^+$ and $\text{Ru}(\text{H}_2\text{O})_3(\text{OH})_3$, which are involved in the following equilibria:



Application of the steady-state conditions with respect to $\text{Ru}(\text{H}_2\text{O})_5(\text{OH})^+$ and C_1^{2-} , and on the assumption that the reactivities of $\text{Ru}(\text{H}_2\text{O})_4(\text{OH})_2^+$ and $\text{Ru}(\text{H}_2\text{O})_3(\text{OH})_3$ are equal (for the sake of simplicity), provides the following equation:

$$-\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{2k_1k_2k_3k_A[\text{Fe}(\text{CN})_6^{3-}][\text{diol}][\text{Ru(III)}]_T}{k_1k_2k_A[\text{diol}] + k_3(k_{-1} + k_2)k_B[\text{Fe}(\text{CN})_6^{3-}] + k_1k_3k_A[\text{Fe}(\text{CN})_6^{3-}][\text{diol}]} \quad (21)$$

In this case $[\text{Ru(III)}]_T$ is the sum of the concentrations of Ru(III) and Ru(II) ; $k_A = K_1[\text{OH}^-] + K_1K_2[\text{OH}^-]^2$ and $k_B = 1 + K_1[\text{OH}^-] + K_1K_2[\text{OH}^-]^2$. This equation is consistent with all of the results obtained.

Equations (18) and (21) are very similar because they contain the same dependence of v_0 on the concentration of catalyst, substrate and hexacyanoferrate(III). However, the dependence of v_0 on $[\text{OH}^-]$ is slightly different in the two equations. Comparison of these equations with the experimental equation that combines Eqns (1) and (2) provides the rate constants for intermediate complex decomposition, k_2 , and catalyst regeneration, k_3 . The respective values of k_2 and k_3 were found to be $(2.7 \pm 0.5) \times 10^2 \text{ min}^{-1}$ and $(8.2 \pm 0.5) \times 10^4 \text{ l mol}^{-1} \text{ min}^{-1}$ for Ru(VI) and $(1.9 \pm 0.3) \times 10^2 \text{ min}^{-1}$ and $(2.0 \pm 0.2) \times 10^5 \text{ l mol}^{-1} \text{ min}^{-1}$ for Ru(III) .

CONCLUSION

The kinetics for the oxidation of 2-methyl-2,4-pentane-diol by $\text{Fe}(\text{CN})_6^{3-}$, using Ru(VI) or Ru(III) as catalysts, are governed by very similar experimental rate equations. These equations show a change of order from one to zero for both hexacyanoferrate(III) and diol species upon increasing their concentrations and are first order with respect to the catalyst. The reaction mechanism proposed involves oxidation of 2-methyl-2,4-pentane-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) . Intermediate complex

decomposition involves a hydride transfer from the α -C—H bond of the alcohol to the oxo ligand of ruthenium in the case of Ru(VI) , but a hydrogen transfer for Ru(III) . Reduced catalyst species are later oxidized by $\text{Fe}(\text{CN})_6^{3-}$ to regenerate the catalyst. For both oxidations the rate

constants of complex decomposition and catalyst regeneration have been obtained.

Acknowledgement

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