Alcohol oxidation catalysed by Ru(VI) in the presence of alkaline hexacyanoferrate(III)[†]

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The oxidation of sodium lactate, 2-methyl-2,4-pentanediol, 2,4-butanediol, 2-butanol and 2-propanol upon treatment with alkaline hexacyanoferrate(III) using a Ru(VI) catalyst is highly effective for the oxidation of alcohols by $Fe(CN)_6^{3-}$. The reaction mechanism proposed involves the oxidation of the alcohol 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 carbocation (owing to a hydride transfer from the α-C—H bond of the alcohol to the oxoligand of ruthenium). The role of the co-oxidant, hexacyanoferrate(III), is to regenerate the catalyst. In the oxidation reactions, the rate constants for complex decomposition and catalyst regeneration have been determined and a comparative study of the structure versus reactivity has been carried out. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: alcohol oxidation; hexacyanoferrate(III); ruthenium(VI)

INTRODUCTION

The metal-catalysed oxidation of organic substrates is a topic of major 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 study of the kinetics in a reasonable time period.[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 characteristics justify the use of ruthenium complexes in homogeneous alcohol oxidations. Moreover, the use of a catalyst is compatible with the existence of sensitive linkages in the alcohol molecule.[6] The most frequently used ruthenium catalysts are Ru(III), Ru(VI) and Ru(VIII) species and numerous kinetic studies have been undertaken using these catalysts.[7–18] The goal of the work described here was to gain an understanding of the decomposition process of the catalyst-substrate complex with Ru(VI) as catalysts in conjunction with alkaline hexacyanoferrate(III). With this aim in mind, the results found in this work for different alcohol oxidation reactions, using Ru(VI) as catalyst, are compared with the Taft steric effects and the pK_a values of each alcohol in order to predict the reactivity the alcohols.

EXPERIMENTAL

Reactants

The reagents used, i.e. hexacyanoferrate(III), sodium hydroxide, sodium lactate, 2-methyl-2,4-pentanediol, 2,3-butanediol, 2-butanol, 2-propanol and sodium perchlorate were all A.R. grade and were purchased from Merck. The solutions were prepared using deionized water from an OSMO BL-6 deionizer from SETA. Sodium ruthenate solution was prepared according to a literature procedure.[8] The purity of stock solutions was assessed by measuring the ratio between the absorbance at 465 and 386 nm, which should equal 2.07 for pure ruthenate.[19]

General

The oxidation kinetics for the alcohols 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 the kinetic analysis. The initial rates of disappearance of hexacyanoferrate(III) were obtained as described previously[20] using the expression $v_0 = -1/\varepsilon(dA/dt)$, where $\varepsilon = 1000 M^{-1} cm^{-1}$ 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 the alcohols was the corresponding ketone, which was identified using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a BP-21 polyethylene glycol column (50 m length $\times$ 0.22 μm i.d., 25 μm film thickness). The stoichiometry of the reaction was obtained using a concentration excess of hexacyanoferrate(III) in relation to the alcohols. The residual oxidant concentration was measured spectrophotometrically and showed that 1 mol of alcohol consumed 2 mol of hexacyanoferrate(III).

RESULTS

The v_0 values for five series of kinetic runs at different $[Fe(CN)_6^{3-}]_0$ are shown in Fig. 1. In each series the concentration values of alcohol, ruthenate, hydroxide ions, temperature and ionic strength were kept constant ($[alcohol] = 0.05$ M, $[NaOH] = 0.15$ M, $[Ru(VI)] = 6 \times 10^{-6}$ M, $T = 30\,^\circ$C and $I = 0.5$ M). Analysis of the

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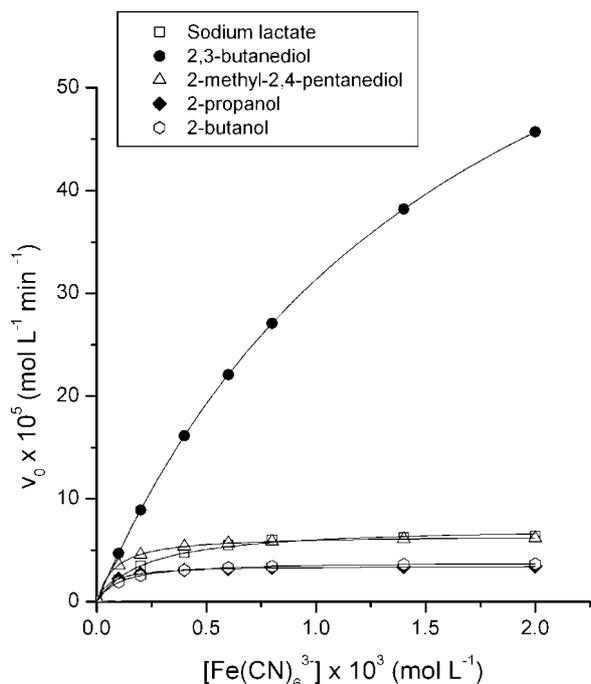
Figure 1. Plot of v_0 vs. $[Fe(CN)_6^{3-}]_0$;$[alcohol] = 0.05\,M$, $[NaOH] = 0.15\,M$, $[Ru(VI)] = 6 \times 10^{-6}\,M$, $T = 30\,°C$ and $I = 0.5\,M$

Figure 2. Plot of v_0 vs. $[S]_0$, where $[S] = [alcohol]_0$; $[Fe(CN)_6^{3-}]_0 = 8 \times 10^{-4}\,M$, $[NaOH] = 0.15\,M$, $[Ru(VI)] = 3 \times 10^{-6}\,M$, $T = 30\,°C$ and $I = 0.5\,M$

data obtained shows a good correlation with the expression:

$$v_0 = \frac{k_1' \left[Fe(CN)_6^{3-}\right]_0}{k_2' + k_3' \left[Fe(CN)_6^{3-}\right]_0} \qquad (1)$$

The dependence of v_0 on $[alcohol]_0$, while the other parameters are kept constant ($[Fe(CN)_6^{3-}]_0 = 8 \times 10^{-4}\,M$, $[NaOH] = 0.15\,M$, $[Ru(VI)] = 3 \times 10^{-6}\,M$, $T = 30\,°C$ and $I = 0.5\,M$), is shown in Fig. 2. The dependence of v_0 on $[alcohol]_0$ shows a Michaelis–Menten behaviour, as described previously.[21] This study led to the following expression:

$$v_0 = \frac{k_1'' [alcohol]_0}{k_2'' + k_3'' [alcohol]_0} \qquad (2)$$

Thus, the dependence of v_0 on both $[Fe(CN)_6^{3-}]_0$ and $[alcohol]_0$ can be described by the fitted expression:

$$v_0 = \frac{A [alcohol]_0 \left[Fe(CN)_6^{3-}\right]_0}{B + C [alcohol]_0 + D \left[Fe(CN)_6^{3-}\right]_0 + E [alcohol]_0 \left[Fe(CN)_6^{3-}\right]_0} \qquad (3)$$

A plot of the experimental data shows that the parameter B is negligible in comparison to the other factors (by almost three orders of magnitude), so the equation can be rearranged to

$$v_0 = \frac{A [alcohol]_0 \left[Fe(CN)_6^{3-}\right]_0}{C [alcohol]_0 + D \left[Fe(CN)_6^{3-}\right]_0 + E [alcohol]_0 \left[Fe(CN)_6^{3-}\right]_0} \qquad (4)$$

Equations (1) and (2) indicate a change of order from one to zero for both hexacyanoferrate(III) and alcohol species upon increasing their concentrations.

The variation of v_0 with $[catalyst]_0$ is shown in Fig. 3 for the oxidation of the different alcohols by hexacyanoferrate(III) using Ru(VI) as a catalyst. The v_0 $[catalyst]_0$ data were fitted to a linear regression and this gave the following expression:

$$v_0 = v_{unc} + k_c [catalyst]_0 \qquad (5)$$

These results indicate that the kinetics are first order with respect to catalyst concentration and the rate of the unanalysed reaction, v_{unc}, is negligible compared to that of the catalysed reaction.

For the studied alcohols, the initial rate passes through a maximum as $[OH^-]$ is varied, as shown in Fig. 4 for the case of sodium lactate. In this figure, it can be observed that v_0 does not tend to zero at very low $[OH^-]$. The variation of v_0 with the basicity of the medium is complicated and can obey to the following equation:

$$v_0 = \frac{A_0 + A_1 [OH^-] + A_2 [OH^-]^2}{1 + B_1 [OH^-] + B_2 [OH^-]^2} \qquad (6)$$

The v_0 versus $[OH^-]$ data were fitted to Eqn (6) by means of a nonlinear regression program, in order to obtain the parameters A and B. The best average error was obtained when $A_2 = 0$.

The possible formation of free radicals as intermediates was investigated by the addition of radical scavengers to the reaction mixture. The addition of either $0.01\,M$ acrylonitrile or $1.6 \times 10^{-4}\,M$ 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 the catalyst.

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 pro-
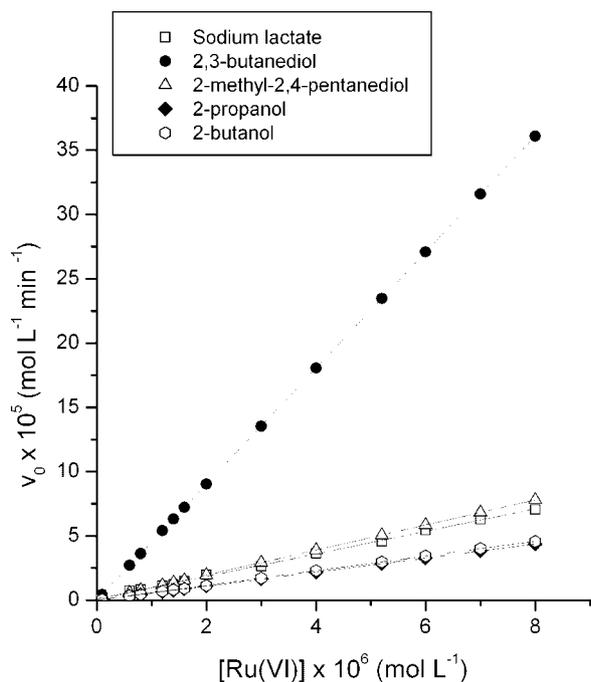
Figure 3. Effect of [catalyst]$_0$ on the initial rate; [Fe(CN)$_6^{3-}$]$_0$ = 8×10^{-4} M, [alcohol]$_0$ = 0.05 M, [NaOH] = 0.15 M, T = 30 °C and I = 0.5 M

duces cyclobutanone directly.[22,23] The following kinetic conditions were employed in this experiment: [OH$^-$] = 0.1 M, I = 0.5 M and T = 30 °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 cyclobutanone as the major product.

Although the organic substrates encompass a wide variety of alcohols, including diols, only the 2-hydroxyl group will be oxidized, as observed experimentally, because tertiary alcohols
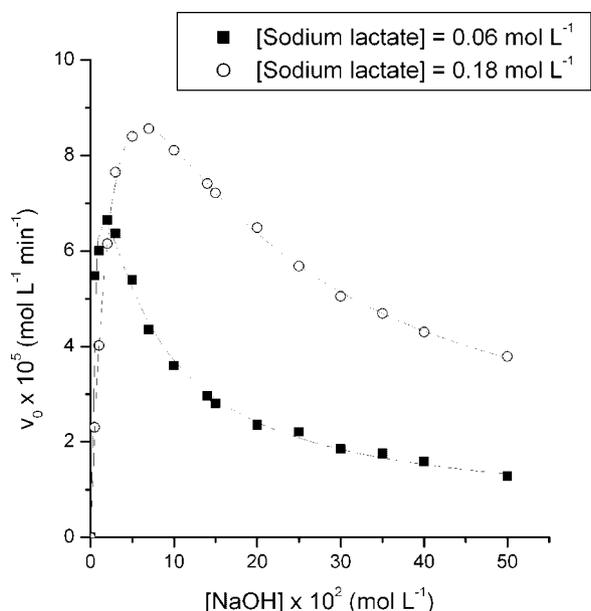
Figure 4. Variation of v_0 with respect to [NaOH]. [Fe(CN)$_6^{3-}$]$_0$ = 1.2×10^{-3} M, I = 0.5 M and T = 30 °C

(0.1 M *tert*-butanol) were found to be unreactive under kinetic conditions.[21] The presence of a hydrogen on the α-carbon of the alcohol is, therefore, necessary for the reaction to progress[24] due to the fact that tertiary alcohols do not react under the experimental conditions employed.

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

The relative rates of oxidation of meso- and DL-hydrobenzoin were measured in order to determine if the oxidation proceeds through either an intermediate chelate complex or a complex in which only one hydroxyl group is coordinated with the ruthenium(VI).[25] The experimental data obtained indicate that both isomers were oxidized at comparables rates, so we can conclude that the oxidation of the alcohols involves the coordination of only one hydroxyl group to ruthenium(VI).

DISCUSSION

As previously discussed[7,20,21,26] for Ru(VI), the dependence of the initial rate on [CH$_3$ − CHOH − R]$_0$ suggests the formation of an intermediate complex, C$_1^{2-}$, between RuO$_4^{2-}$ and the organic substrate:

$$CH_3 - CHOH - R + RuO_4^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_1^{2-} \qquad (7)$$
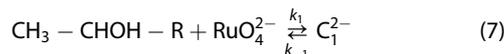
where C$_1^{2-}$ has the following structure:
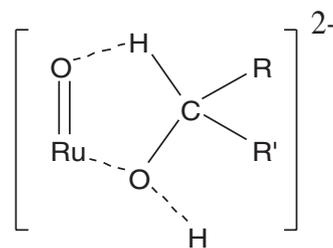
which decomposes slowly to produce a reduced form of catalyst, RuO$_3$(OH)$^{3-}$, and a carbocation as follows:

$$C_1^{2-} \xrightarrow{k_2} CH_3 - \overset{+}{C}OH - R + RuO_3(OH)^{3-} \qquad (8)$$

Step 7 involves a hydride transfer from the α-C—H bond of the alcohol to the oxoligand 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.[26] The occurrence of this hydride transfer is supported by the following experimental results: (a) a moderate kinetic isotopic 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.[27]

The following fast reaction would yield the corresponding ketone:

$$CH_3 - \overset{+}{C}OH - R + OH^- \rightarrow CH_3 - CO - R + H_2O \qquad (9)$$
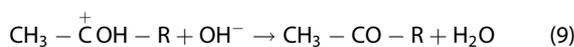
The dependence of v_0 on $[Fe(CN)_6^{3-}]_0$ can be explained if one accepts that the oxidation of the reduced form of catalyst occurs. In this way, the role of the co-oxidant, $Fe(CN)_6^{3-}$, is solely the regeneration of the catalyst through steps 10 and 11.

$$RuO_3(OH)^{3-} + Fe(CN)_6^{3-} \xrightarrow{k_3} RuO_3(OH)^{2-} + Fe(CN)_6^{4-} \quad (10)$$

$$RuO_3(OH)^{2-} + Fe(CN)_6^{3-} \rightarrow RuO_3(OH)^- + Fe(CN)_6^{4-} \quad (11)$$

$$RuO_3(OH)^- + OH^- \rightarrow RuO_4^{2-} + H_2O \quad (12)$$

Step 9 is supported by the previously described fact that the oxidation of alcohols by small quantities of ruthenate proceeds at a similar rate to the reoxidation of the reduced form of the catalyst by $Fe(CN)_6^{3-}$.[21] Step 9 is fast relative to oxidation of the substrate at high $[Fe(CN)_6^{3-}]_0$ and, under these circumstances, v_0 does not depend on $[Fe(CN)_6^{3-}]_0$. At low $[Fe(CN)_6^{3-}]_0$, however, both reactions a have comparable rate and v_0 is dependent on $[Fe(CN)_6^{3-}]_0$.

The dependence of v_0 on $[OH^-]$ may be explained by assuming the existence of two active species of catalyst, RuO_4^{2-} and $RuO_4(OH)^{3-}$, which are in equilibrium as follows:[26]

$$RuO_4^{2-} + OH^- \overset{k_1}{\underset{}{\rightleftharpoons}} RuO_4(OH)^{3-} \quad (13)$$

$$RuO_4(OH)^{3-} + OH^- \overset{k_2}{\underset{}{\rightleftharpoons}} RuO_4(OH)_2^{4-} \quad (14)$$
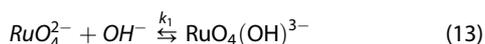
The existence of these hydroxy-oxy complexes of ruthenium was suggested by Luoma and Brubaker, who studied the reaction between perruthenate and manganate ions in an aqueous alkaline medium.[28]

Application of the steady state conditions with respect to $RuO_3(OH)^{3-}$ and C_1^{2-}, and on the assumption that the reactivity of RuO_4^{2-} and $RuO_4(OH)^{3-}$ are equal (for simplicity) gives the following theoretical rate equation for the disappearance of hexacyanoferrate(III):

Figure 5. Influence of the steric hindrance on the complex decomposition rate (k_2)

On considering the values in Table 1, it can be seen that k_3, the regeneration of the catalyst, is a constant value that is independent of the nature of the substrate. However, the value of k_2, the intermediate complex decomposition, varies as a function of the substrate. Considering these facts, a correlation between the structure of a given substrate and oxidation rate can be obtained using the Taft equation.[29]

$$E_S = \ln \frac{k_X}{k_H^l} \quad (16)$$

$$-\frac{d\left[Fe(CN)_6^{3-}\right]}{dt} = \frac{2k_1 k_2 k_3 k_A \left[Fe(CN)_6^{3-}\right][\text{diol}][Ru(VI)]_T}{k_1 k_2 k_A [\text{diol}] + k_3(k_{-1} + k_2)k_B \left[Fe(CN)_6^{3-}\right] + k_1 k_3 k_A \left[Fe(CN)_6^{3-}\right][\text{ol}]} \quad (15)$$

where $k_A = 1 + K_1 [OH^-]$ and $k_B = 1 + K_1 [OH^-] + K_1 K_2 [OH^-]^2$ and $[Ru(VI)]_T$ 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. Equation (15) explains the dependence of v_0 on $[OH^-]$, $[Fe(CN)_6^{3-}]$, [alcohol] and [catalyst].

Comparison of Eqn (15) with the experimental rate Eqn (4) provides the rate constants for intermediate complex decomposition, k_2, and catalyst regeneration, k_3. The respective values of k_2 and k_3 for each alcohol are summarized in Table 1.

Taft steric parameters were obtained by the addition of the different molecular fragments in each alcohol[30] and their values are shown in Table 1. A linear correlation is obtained when $\ln k_2$ versus Taft steric parameters is represented, as shown in Fig. 5.

The pK_a values give a relatively good measure of the nucleophilic nature of molecules. A plot of pK_a values and σ_{steric} data is shown in Fig. 6 and a good linear correlation is observed. This linear correlation indicates that the higher the pK_a value of the alcohol the more nucleophilic it is. If the alcohol is more

Table 1. Complex decomposition rate (k_2) and catalyst regeneration (k_3) obtained when experimental data were fitted to expression (15) and values of σ_{steric} and pK_a for each alcohol studied

Substrate	k_2 (min^{-1})	k_3 (M^{-1} min^{-1})	pK_a	σ_{steric}
Sodium lactate	253.81 ± 11.4	$(7.08 \pm 0.9) \times 10^4$	—	2.62
2,3-butanediol	291.12 ± 9.2	$(7.10 \pm 0.8) \times 10^4$	14.85	2.1
2-methyl-2,4-pentanediol	267.23 ± 7.7	$(7.13 \pm 0.7) \times 10^4$	14.2	2.5
2-propanol	58.48 ± 3.6	$(7.76 \pm 0.4) \times 10^4$	15.7	1.57
2-butanol	40.31 ± 2.9	$(7.63 \pm 0.5) \times 10^4$	14.93	1.61

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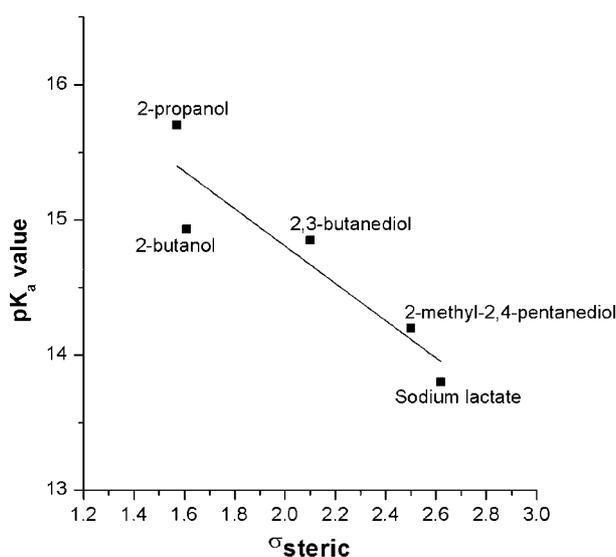
Figure 6. Relationship between the pK_a of the alcohol and its σ_{steric}

nucleophilic, the intermediate C_1^{2-} is more stable and, as a result, the complex decomposition rate constant is lower.

CONCLUSION

The kinetics for the oxidation of alcohols by $Fe(CN)_6^{3-}$, using Ru(VI) as a catalyst, are governed by very similar experimental rate equations. These equations show a change in order from one to zero for both hexacyanoferrate(III) and alcohol upon increasing their concentrations and are first order with respect to the catalyst concentration. The reaction mechanism proposed involves alcohol oxidation by Ru(VI) through the formation of a substrate-catalyst complex, which subsequently decomposes to yield Ru(IV). Decomposition of the intermediate complex involves a hydride transfer from the α-C—H bond of the alcohol to the oxoligand of ruthenium and depends on the structure of the substrate (alcohol). The reduced catalyst species are subsequently oxidized by $Fe(CN)_6^{3-}$ to regenerate the catalyst. This rate constant for each alcohol studied does not depend on the nature of the alcohol. For the overall alcohol oxidation, the rate constants for complex decomposition and catalyst regeneration have been obtained. Finally, a correlation between the reaction rate of complex decomposition and the inductive and conjugative effects has been established. On considering Figs 5 and 6, one can conclude that alcohols with more than one functional group have a higher rate constant. When the alcohol is

more nucleophilic, the intermediate C_1^{2-} is more stable and the complex decomposition rate constant is lower. This finding confirms that if the alcohol molecule contains more than one functional group, the intermediate complex decomposition process becomes faster than in single linear alcohols. This effect can be attributed to the inductive and conjugative effect of the 'extra' functional groups present in these molecules.

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