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Kinetics and Mechanism of Ruthenium(III) Chloride Catalyzed Oxidation of Propane-1,3-diol by Thallium(III) in Acid Perchlorate Medium

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The mode of electron transfer in ruthenium(III) chloride catalyzed oxidation of propane-1,3-diol by thallium(III) is explained by hydride ion abstraction.

Kinetics of ruthenium(III) chloride catalyzed oxidation of propane-1,3-diol with thallium(III) in acid perchlorate medium have been studied. The observed stoichiometry of the reaction corresponds to the reaction as represented by eqn. (1)

$$\mathrm{CH_2(OH)CH_2CH_2OH + Tl^{III}} \longrightarrow \mathrm{CH_2(OH)CH_2CHO + Tl^{I} + 2H^{+}} \qquad (1)$$

The product 3-hydroxypropanal was confirmed spectrally as its hydrazone derivative. The kinetics were monitored estimating thallium(III) iodometrically[3] without any interference from the substrate or its oxidation product. The only precaution in iodometry was vigorous stirring of the liberated iodine on each addition of thiosulfate solution as titrant. The kinetic measurements in triplicate were reproducible to within ±5%.

The kinetic orders with respect to the catalyst and oxidant are each unity and products do not affect the rate of the reaction. Thallium(III) is known to undergo hydrolysis in aqueous acid solution [eqn. (2)]

$$\mathrm{Tl^{3+} + H_2O} \overset{K_h}{\rightleftharpoons} \mathrm{Tl(OH)^{2+} + H^{+}} \qquad (2)$$

The value of K_h was estimated to be 0.088 at 30 °C employing the enthalpy change of hydrolysis (69.4 kJ mol^{-1}). Since the rate of the reaction decreases with increasing hydrogen ion concentration, the hydrolysed species $\mathrm{Tl(OH)^{2+}}$ is more reactive than the aqua ion ($\mathrm{Tl^{3+}}$). Despite the fact that little has conclusively been established about speciation of $\mathrm{RuCl_3}$ species in solution, labile anionic species are discounted. It is very likely, as in other systems,[12] that $\mathrm{RuCl_3}$ as such is the reactive form of the catalyst. Thus a mechanism of the reaction events can be envisaged as follows:

$$\mathrm{Tl^{3+} + H_2O} \overset{K_h}{\rightleftharpoons} \mathrm{Tl(OH)^{2+} + H^{+}} \qquad (2)$$

$$\mathrm{Cl_3Ru^{III} + Tl(OH)^{2+}} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{[TlOH{-}Ru^{V}Cl_3]} \qquad (3)$$

$$\mathrm{[TlOH{-}Ru^{V}Cl_3] + Diol} \xrightarrow{k_3} \mathrm{Cl_3Ru^{III} + Tl^{+} + H_3O^{+} + CHOCH_2CH_2OH} \qquad (4)$$

The loss of thallium(III) can be described by the rate law (5)

$$-\frac{\mathrm{d[Tl^{III}]}}{\mathrm{d}t} = \frac{k_1 k_3 K_h \mathrm{[Ru^{III}][Tl^{III}][Diol]}}{(k_2 + k_3\mathrm{[Diol]})(K_h + [\mathrm{H^+}])} \qquad (5)$$

Since the rate is independent of the diol concentration, the relation $k_3[\mathrm{Diol}] \gg k_2$ is valid which reduces the rate law (5) to (6) or (7)

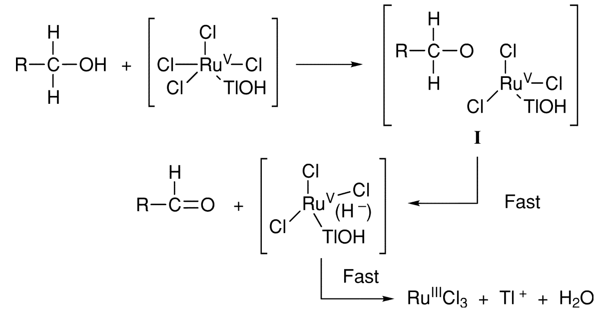
$$\frac{-\mathrm{d[Tl^{III}]}}{\mathrm{d}t} = \frac{k_1 K_h \mathrm{[Ru^{III}][Tl^{III}]}}{(K_h + [\mathrm{H^+}])} \qquad (6)$$

or

$$k = \frac{k_1 K_h}{(K_h + [\mathrm{H^+}])} \qquad (7)$$

The value of k_h has been determined from plots of k^{-1} *vs.* $[\mathrm{H^+}]$ and is in agreement with earlier reported values.

The mode of electron transfer from the substrate to the oxidant is indicated in Scheme 1 which accounts for the experimental characteristics of the reaction.



Scheme 1

Adduct (**I**) as indicated in Scheme 1 intramolecularly undergoes electron transfer yielding another $\mathrm{Ru^{V}{-}Tl^{I}}$ adduct. Since ruthenium(V) is highly reactive and $\mathrm{Tl^{I}}$ is weakly coordinating, ruthenium(V) attacks the α-carbon of the diol after release of thallium(I). Such an attack through hydride ion transfer from the α-carbon of the diol is facilitated to accomplish electron transfer. The pattern of reactivity of $\mathrm{Pb^{IV}}$, $\mathrm{Tl^{III}}$ and $\mathrm{Hg^{II}}$ towards diols has been compared since the chemistry of thallium(III) is considered to be intermediate between that of $\mathrm{Pb^{IV}}$ and $\mathrm{Hg^{II}}$ which it neighbours in the Periodic Table.

Techniques used: IR, ^{1}H NMR

References: 17

Figs: 2

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