Kinetics and mechanism of ruthenium (III) chloride catalysed oxidation of propanol by N-chloro-*p*-toluene sulfonamide (chloramine-T) in aqueous acid medium

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Kinetics of ruthenium (III) chloride catalysed oxidation of propanal has been studied.

Keywords: ruthenium (III) chloride, propanol

Chloramine-T (CAT), the sodium salt of N-chloro-*p*-toluene sulfonamide is a source of chloronium ion, hypochlorite and N-anions. This is the reason that this reagent acts both as a base and a nucleophile.[1] The reagent exhibits wider applications[1] and is considered to be a disinfectant and antiseptic.[2] The reagent has frequently been employed as a redox titrant in analytical chemistry[5,6] and as a chlorinating agent in organic syntheses. A little known reducing properties of alcohols towards non-metallic oxidants in solution prompted us to undertake a kinetic study of this reaction.

The kinetics were studied by undertaking the reactions in glass stoppered Erlenmeyer flasks painted black on the outside to avoid photo light effects which were suspended in a water-bath thermostated at ±0.1°C unless stated otherwise. The reaction progress was monitored by withdrawing aliquots of the reaction mixture, periodically assaying chloramine-T iodometrically.[7,8] Triplicate rate measurements were reproducible to within ±4%. Pseudo first-order rate constants were calculated wherever reaction conditions permitted.

The stoichiometry corresponds to the reaction as represented by equation (1)

$$RNHCl + CH_3CH_2CH_2OH \xrightarrow{Ru^{III}} CH_3CH_2CHO + RNH_2 + HCl \quad (1)$$

where R = CH_3–$C_6H_4SO_2$

The NMR spectral analysis of 2,4-dinitrophenyl hydrazone derivative of the oxidation product of propanol confirms the product to be propanal.

The kinetic order with respect to chloramine-T is one, whereas the order with respect to propanol and hydrogen ion concentrations, respectively, is complex. The species of chloramine-T in aqueous acid medium are governed by the following equilibria (2)–(7).

$$RNClNa \rightleftharpoons RNCl^- + Na^+ \quad (2)$$

$$RNCl^- + H^+ \rightleftharpoons RNHCl \quad (3)$$

$$2\ RNHCl \rightleftharpoons RNCl_2 + RNH_2 \quad (4)$$

$$RNHCl + H_2O \rightleftharpoons HOCl + RNH_2 \quad (5)$$

$$RNCl_2 + H_2O \rightleftharpoons RNHCl + HOCl \quad (6)$$

$$HOCl \rightleftharpoons H^+ + OCl^- \quad (7)$$

The disproportionation and hydrolysis of RNHCl in steps (4) and (5) respectively are ruled out on the premise that the order with respect to chloramine-T is one. However, *p*-toluene sulfonamide does not affect the rate. Therefore, neither hydrolysis nor disproportionation of the oxidant and the species obtained thereupon have any role in the mechanism of the reaction.

Considering the experimental observations and the arguments as advanced above, the following mechanism consisting of steps (8)–(9) accounts for the results.

$$RNHCl + H^+ \overset{K_1}{\rightleftharpoons} RNH_2^+Cl \quad (8)$$

$$RuCl_3 + R'CH_2OH \overset{K_2}{\rightleftharpoons} [Cl_3Ru\ldots R'CH_2OH] \quad (9)$$

$$[Cl_3Ru\ldots R'CH_2OH] + RNH_2^+Cl \xrightarrow{k} RuCl_3 + RNH_3^+ + HCl \quad (10)$$

where R′ = CH_3–CH_2–.

The complexation in step (10) is not unique in the light of earlier reported[16(d)] ruthenium (III) chloride complexes of a binary as well as a ternary nature with ascorbic acid.

Such a mechanism leads to the rate law (11) or (12)

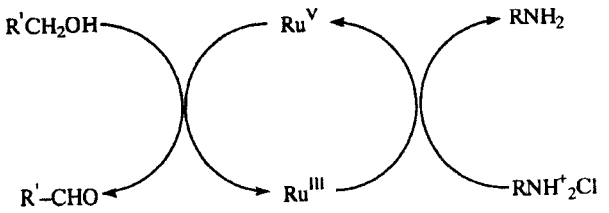
$$\frac{-d\,[CAT]}{dt} = \frac{k\,K_1K_2[RNHCl]\,[Ru^{III}]\,[R'CH_2OH]\,[H^+]}{(1 + K_2\,[R'CH_2OH])\,(1 + K_1\,[H^+])} \quad (11)$$

$$k'_1 = \frac{k\,K_1K_2[R'CH_2OH]\,[H^+]\,[Ru^{III}]}{(1 + K_2\,[R'CH_2OH])\,(1 + K_1\,[H^+])} \quad (12)$$

where k'_1 is an observed pseudo first order rate constant.

k_1, K_1 and K_2 have been evaluated graphically. The rate is drastically affected by ionic strength.

The role of the catalyst has been assigned to the operation of the catalyst redox cycle as in Scheme 1.



Scheme 1

However, a preferable portrait of the reaction events has been suggested as in Scheme 2 through hydride ion transfer.

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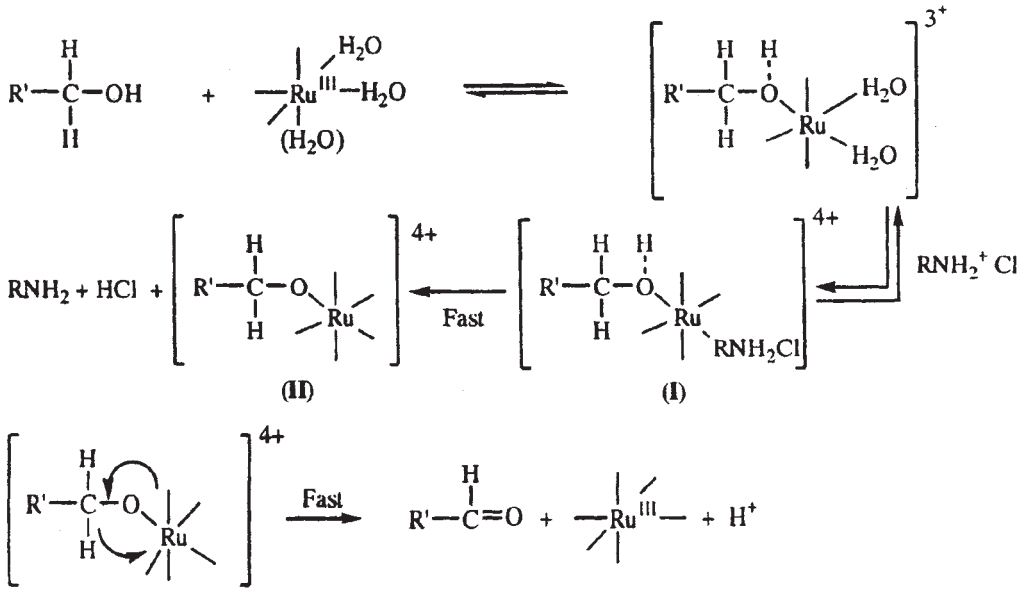

Scheme 2

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