Mechanism of Ru(III) Catalysis in Chloramine-T Oxidation of Some Unsaturated Acids

RASHMI SAXENA

Department of Chemistry
Harcourt Butler Technological Institute
Kanpur 208 002, India

Kinetics of ruthenium(III) catalysed oxidation of maleic and acrylic acids by chloramine-T in presence of alkali have been studied. The results showed first order dependence of rate with respect to oxidant and the catalyst. The effect of [substrate] on the rate was positive only at low substrate concentrations. The variation of [OH⁻] resulted in a negligible effect on the rate. Sodium perchlorate has a negative effect on the reaction rate. A suitable mechanism in conformity with the kinetic data has been proposed.

INTRODUCTION

Chloramine-T (CAT) has widely been used as an oxidant in acidic as well as in alkaline medium[1,2]. The use of ruthenium(III) as catalyst during chloramine-T oxidation has also been made[3,4]. The oxidation of unsaturated acids *viz.* maleic acid, acrylic acid by chloramine-T does not proceed in absence of the catalyst. However, in presence of ruthenium(III), the oxidation proceeds with a measurable rate. It was, therefore, imperative to study the title investigations in detail.

EXPERIMENTAL

The reagents *viz.* maleic acid, acrylic acid, ruthenium trichloride (Johnson–Matthey), chloramine-T, sodium hydroxide (BDH) were of AR grade.
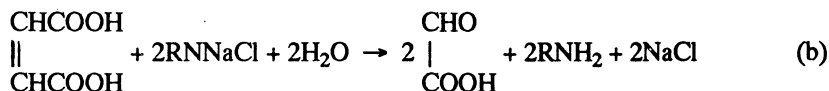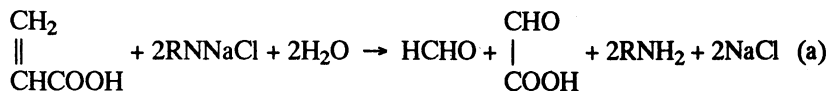
Ruthenium(III) chloride solution was prepared by dissolving the sample in hydrochloric acid of known strength. The final strengths of $RuCl_3$ and HCl were kept at 19.2×10^{-3} mol dm⁻³ and 1.0×10^{-3} mol dm⁻³ respectively. The stock solution of $RuCl_3$ was stored in a black coated bottle to prevent photochemical decomposition. Doubly distilled water was used throughout the investigations.

A thermostatic water bath was used to maintain the desired temperature within ± 0.1°C. The reactions were initiated by addition of chloramine-T solution to reaction mixture although the order of addition had no effect on the rate. The progress of reaction was followed by determining chloramine-T iodometrically in aliquots withdrawn after a suitable time interval. The iodine liberated by ruthenium(III) was taken into account.

Stoichiometry and Product Analysis

Various sets of the reaction mixtures containing a known excess of [chloramine-T] over [substrate] were kept in presence of NaOH and ruthenium(III) at 40°C for 72 hrs. Estimation of unreacted chloramine-T showed that one mole of each

substrate consumes two moles of chloramine-T. The results may be represented with the help of the following stoichiometric equations:

$$
\begin{matrix} CH_2 \\ \| \\ CHCOOH \end{matrix} + 2RNNaCl + 2H_2O \rightarrow HCHO + \begin{matrix} CHO \\ | \\ COOH \end{matrix} + 2RNH_2 + 2NaCl \quad (a)
$$

$$
\begin{matrix} CHCOOH \\ \| \\ CHCOOH \end{matrix} + 2RNNaCl + 2H_2O \rightarrow 2 \begin{matrix} CHO \\ | \\ COOH \end{matrix} + 2RNH_2 + 2NaCl \quad (b)
$$

The end products formaldehyde and glyoxalic acid were detected by spot tests[5] and confirmed by TLC and dinitrophenylhydrazine (DNP) derivative.

RESULTS AND DISCUSSION

The reactions were studied at various initial concentrations of the reactants. The log [chloramine-T] *versus* time plots were linear upto 85% of the reactions and, therefore, pseudo-first order rate constants in chloramine-T (k_{obs}) were evaluated from the slopes of these plots. The same values of rate constants (k_{obs}) at different initial chloramine-T concentrations (Table 1) also confirmed the first order dependence of rate with respect to oxidant.

TABLE 1
RATE CONSTANTS AT VARIOUS INITIAL [REACTANTS] AT 40°C

[CAT] × 10^3 (mol dm^{-3})	[S] × 10^2 (mol dm^{-3})	[OH$^-$] × 10^3 (mol dm^{-3})	k_{obs} × 10^4 (sec^{-1})	
			A Maleic acid	B Acrylic acid
1.5	2.0	1.0	0.40	0.40
2.0	2.0	1.0	0.40	0.38
3.0	2.0	1.0	0.38	0.35
3.5	2.0	1.0	0.40	0.40
4.0	2.0	1.0	0.38	0.38
2.0	0.5	1.0	0.24	0.20
2.0	1.0	1.0	0.32	0.30
2.0	3.0	1.0	0.45	0.43
2.0	4.0	1.0	0.53	046
2.0	6.0	1.0	0.55	0.48
2.0	2.0	0.2	0.38	0.40
2.0	2.0	0.6	0.38	0.43
2.0	2.0	1.0	0.40	0.43
2.0	2.0	1.5	0.38	0.47
2.0	2.0	2.0	0.36	0.47
2.0	2.0	3.0	0.38	0.43

[Ru(III)] = 9.6×10^{-5} mol dm^{-3} and 19.2×10^{-5} mol dm^{-3} for maleic acid and acrylic acid respectively. Effect of [OH$^-$] was studied at a fixed ionic strength (0.003 mol dm^{-3} maintained by NaClO$_4$).

A change in the initial concentration of substrate resulted in an increase in the

observed rate constant at lower concentrations of the substrate. At higher concentrations of the substrate the effect was negligible (Table 1).

The effect of [OH⁻] was studied at a fixed ionic strength ($\mu = 0.003$ mol dm⁻³ maintained by NaClO₄). The amount of acid present in the catalyst was taken into account. It is clear from the data in Table 1 that the effect of varying [NaOH] on the rate is negligible in each case.

The plots of k_{obs} versus [Ruthenium(III)] (Fig. 1) was linear passing through the origin suggesting first order dependence of rate in catalyst and also the rate of uncatalysed path is negligible.

The effect of change in ionic strength was studied by carrying out investigations
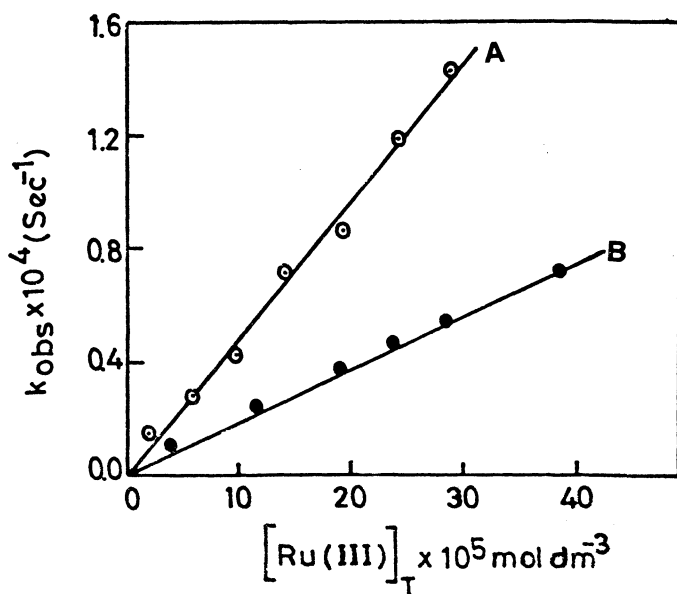

Fig. 1.   Plots of (k_{obs}) versus [Ru(III)]$_T$ at 40°C
[CAT] = 2.0×10^{-3} mol dm⁻³, [Substrate] = 2.0×10^{-2} mol dm⁻³, and
[NaOH] = 1.0×10^{-3} mol dm⁻³ (A. Meleic acid; B. Acrylic acid).

in the presence of different amount of sodium perchlorate (upto 0.20 mol dm⁻³) which resulted in a negative effect on the reaction rate. For example in case of maleic acid the values of k_{obs} were 0.40, 0.35, 0.30 and 0.28 × 10⁻⁴ sec⁻¹ on addition of nil, 5.0, 10.0 and 15.0 × 10⁻² mol dm⁻³ NaClO₄ in presence of 2.0×10^{-3} mol dm⁻³ chloramine-T, 2.0×10^{-2} mol dm⁻³ maleic acid, 1.0×10^{-3} mol dm⁻³ NaOH and 9.6×10^{-5} mol dm⁻³ ruthenium(III) at 40°C. Addition of p-toluene sulphonamide (reaction product of chloramine-T) also resulted in a retarding effect on the observed rate constant.

The rates were also studied at different temperatures viz. 40, 45, 50, 55°C and the energies of activation obtained from Arrhenius plots were 35.0 and 40.0 (±0.5) kJ mol⁻¹ for maleic and acrylic acid respectively.

Ruthenium(III) chloride exists in the hydrated[6] form as [Ru(H₂O)₆]³⁺. Metal

ions of the form $[Ru(H_2O)_6]^{3+}$ are also known to exist as $[Ru(H_2O)_5 (OH^-)]^{2+}$ in presence of alkali[7]. In the present investigations, the rate of oxidation is independent of OH^- concentrations, therefore, the $[Ru(H_2O)_5 (OH^-)]^{2+}$ species may be considered as the main reactive species of the catalyst.

The studies on ruthenium(III) catalysed oxidation of organic compounds have shown that the oxidation proceeds by the abstraction of H^- by a Ru(III) species from α-carbon atom of the substrate[8,9].

In an alkaline solution, chloramine-T hydrolyses[2] according to the following equations:

$$RNNaCl + H_2O \rightleftharpoons RNHCl + NaOH \tag{1}$$

$$RNHCl + NaOH \rightleftharpoons RNH_2 + NaClO \tag{2}$$
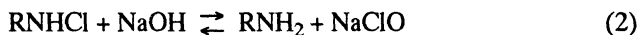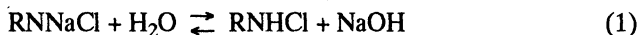
(where $R = CH_3C_6H_4SO_2$)

Thus various oxidising species[2] in an alkaline solution are CAT itself, N-chlorotoluene-*p*-sulphonamide (RNHCl) and hypochlorite ion (ClO^-). An independent nature of rate with respect to $[OH^-]$ (experimental observations) ruled out the possibility of RNHCl as the reactive species. The main oxidising species under the present experimental conditions, are therefore CAT and OCl^- which would be in equilibrium as represented by equation (3)

$$RNNaCl + H_2O \rightleftharpoons RNH_2 + NaClO \tag{3}$$
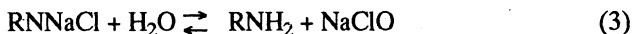
First order dependence of rate with respect to chloramine-T, a negative salt effect (reaction between two oppositely charged ions) and a retarding effect of *p*-toluene sulphonamide (RNH_2) on the rate clearly indicate ClO^- as the reactive species of chloramine-T.

Considering the above facts and experimental results, the mechanism for the oxidation process may be proposed as given in Scheme I. The fast conversion of $[Ru(III)H]^{2+}$ back into the catalyst in presence of various oxidant is also reported in the literature.

On the basis of above mechanism, the rate of disappearance of chloramine-T may be represented as,

$$-\frac{d[CAT]}{dt} = k_2[X][CAT] \tag{4}$$

where $[X] = k_1[S][C_1]$ from step (i)

Again considering total concentration of catalyst at any time as

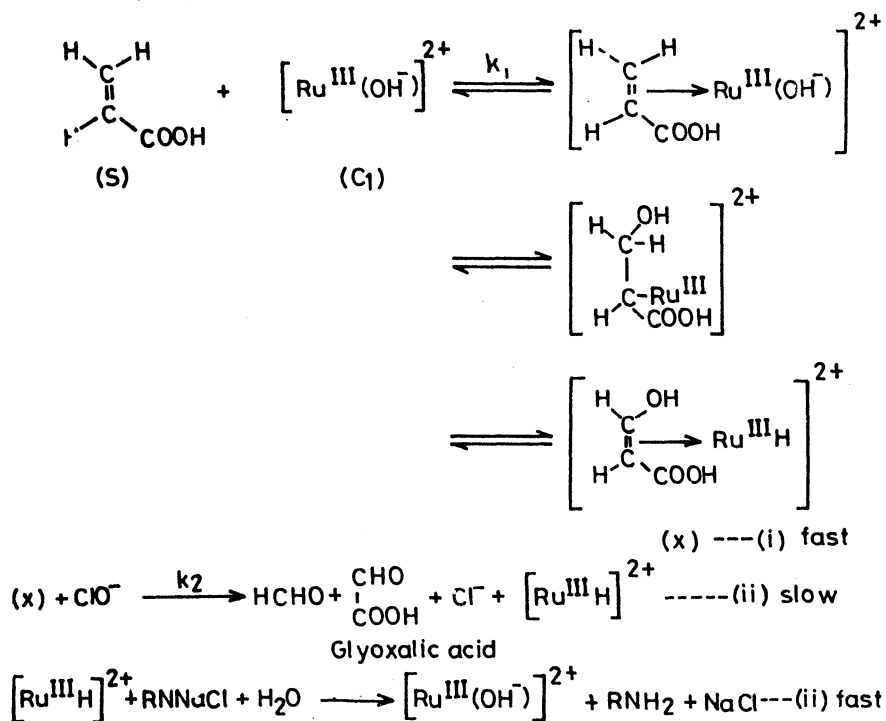$$[Ru^{III}]_T = [C_1] + [X] \tag{5}$$

The value of $[X]$ in terms of $[Ru^{III}]_T$ may be given as

$$[X] = \frac{K_1[S][Ru^{III}]_T}{1 + K_1[S]} \tag{6}$$

and, therefore, the rate law equation has been obtained as

$$-\frac{d[CAT]}{dt} = \frac{k_2K_1[S][Ru^{III}]_T[CAT]}{1 + K_1[S]} \tag{7}$$

(S)   (C₁)

(x) ---(i) fast

$(x) + ClO^- \xrightarrow{k_2} HCHO +$ CHO / COOH $+ Cl^- + \left[Ru^{III}H\right]^{2+}$ -----(ii) slow

Glyoxalic acid

$\left[Ru^{III}H\right]^{2+} + RNNaCl + H_2O \longrightarrow \left[Ru^{III}(OH^-)\right]^{2+} + RNH_2 + NaCl$ ---(ii) fast

In case of Maleic acid

(x) --- (i) fast
----(ii) slow

$(x) + ClO^- \xrightarrow{k_3} 2$ CHO / COOH $+ Cl^- + \left[Ru^{III}H\right]^{2+}$
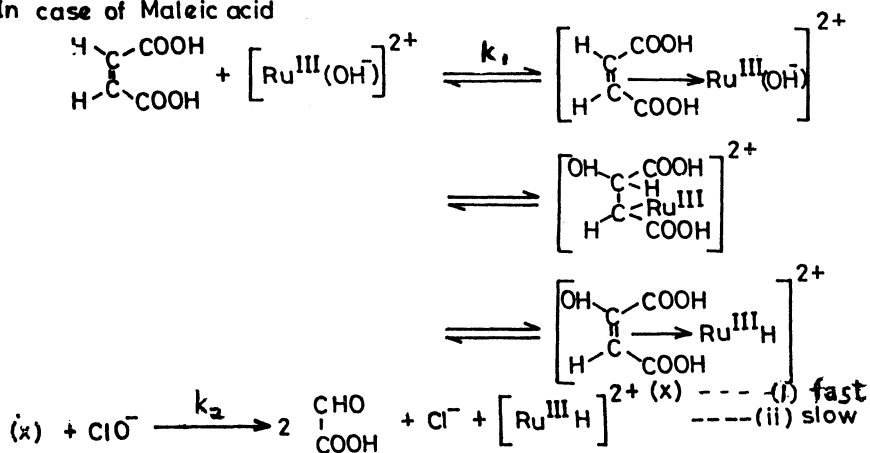
Scheme 1

Since the step (i) (Scheme I) is fast, $K_1[S] \gg 1$ may be taken as a suitable approximation at higher substrate concentrations. The rate law (7) thus reduced to equation (8).

$$-\frac{d[CAT]}{dt} = K_2[Ru^{III}]_T[CAT]$$

which is in agreement with the experimental results.

ACKNOWLEDGEMENTS

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