

## Mechanistic Aspects of Ru(III) Catalyzed Oxidation of Cyclopentanol by Chloramine-T in Acidic Medium

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The kinetics of Ru(III) catalyzed oxidation of cyclopentanol by chloramine-T has been investigated in acidic medium. The reaction shows first order kinetics with respect to cyclopentanol, chloramine-T,  $H^+$  and Ru(III). There is insignificant effect of ionic strength, PTS and KCl on the reaction rate. The dielectric constant of the medium has positive effect. Elevation of temperature increases the rate of reaction in oxidation of cyclopentanol. A mechanism consistent with the above kinetic results has been suggested.

**Key Words:** Kinetics, Ru(III), Oxidation, Cyclopentanol, Chloramine-T.

### INTRODUCTION

Less widely used but potent oxidant chloramine-T with high redox potential ( $E_{red} = 1.138$  V at pH 0.65) has been used in kinetic studies involving it as an oxidant both in acidic as well as in alkaline media<sup>1-3</sup>. Catalyzed oxidation of cycloalcohols is reported in a few papers<sup>4,5</sup> but Ru(III) catalyzed oxidation of cyclopentanol by chloramine-T has not been reported till today. Thus the use of catalytic amount of ruthenium(III) chloride<sup>6,7</sup> prompted us to investigate the kinetics and mechanism of ruthenium(III) catalyzed oxidation of cyclopentanol by chloramine-T.

### EXPERIMENTAL

All chemicals were of AR grade and doubly distilled water was used throughout. The stock solution of chloramine-T (CAT) (E. Merk) was prepared by dissolving its weighed amount in doubly distilled water and its strength was checked by estimating it iodometrically using starch as indicator. Ruthenium(III) chloride (Johnson Matthey) solution was prepared by dissolving the sample in hydrochloric acid of known strength<sup>8</sup>.

All the kinetic measurements were carried out at constant temperature ( $\pm 0.1^\circ C$ ). The reaction was initiated by rapid addition of chloramine-T (CAT) to the reaction mixture, containing appropriate quantities of cyclopentanol, perchlo-

ric acid, Ru(III) chloride and water and mixing them by vigorous shaking. The progress of the reaction was monitored by estimating the amount of unconsumed CAT at regular time intervals iodometrically.

## RESULTS AND DISCUSSION

The kinetics of cyclopentanol was investigated at several initial concentrations of the reactants (Table-1). First order dependence in CAT was followed at all initial concentrations of CAT. The order in substrate (cyclopentanol) computed from the slope of  $\log k_1$  *vs.*  $\log$  [substrate] (Fig. 1) was found to be approximately one. This established that the reaction follows first order kinetics with respect to cyclopentanol. The rate of reaction was found to be highly influenced by [Ru(III)]. It was observed that with increasing [Ru(III)] the first order rate constant increased linearly (Table-1) which proves first order dependence on [Ru(III)]. From the plot of  $-dc/dt$  *vs.*  $[H^+]$  it is clear that the reaction is also first order with respect to  $[H^+]$ .

TABLE-1  
EFFECT OF VARIATION OF  $[H^+]$ , [CAT], CYCLOPENTANOL  
AND CATALYST ON REACTION RATE CONSTANT, AT

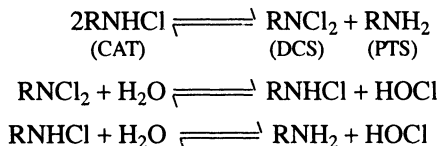
$T = 35^\circ\text{C}$ ,  $KCl = 5.00 \times 10^{-2} \text{ mol dm}^{-3}$

[Cyclopentanol] $\times 10^2$ ( $\text{mol dm}^{-3}$ )	[CAT] $\times 10^3$ ( $\text{mol dm}^{-3}$ )	$[HClO_4] \times 10^2$ ( $\text{mol dm}^{-3}$ )	[Ru(III)] $\times 10^6$ ( $\text{mol dm}^{-3}$ )	$[-dc/dt] \times 10^7$ ( $\text{mol dm}^{-3}$ )	$k_1 \times 10^4$ ( $\text{s}^{-1}$ )
5.00	0.80	1.25	2.64	2.40	3.64
5.00	1.00	1.25	2.64	2.90	3.70
5.00	1.32	1.25	2.64	4.15	3.67
5.00	2.00	1.25	2.64	6.40	3.64
5.00	2.80	1.25	2.64	9.18	3.67
5.00	4.00	1.25	2.64	13.50	3.62
3.30	1.00	1.25	2.64	2.00	2.56
2.00	1.00	1.25	2.64	1.25	1.60
1.50	1.00	1.25	2.64	0.88	1.12
1.00	1.00	1.25	2.64	0.60	0.77
0.50	1.00	1.25	2.64	0.32	0.41
5.00	1.00	1.25	0.66	0.72	0.92
5.00	1.00	1.25	1.32	1.40	1.78
5.00	1.00	1.25	1.98	2.10	2.68
5.00	1.00	1.25	3.30	3.58	4.56
5.00	1.00	1.00	3.96	4.26	5.42
5.00	1.00	1.00	2.64	2.32	2.95
5.00	1.00	1.60	2.64	3.72	4.74
5.00	1.00	2.00	2.64	4.64	5.91
5.00	1.00	3.00	2.64	6.92	8.82
5.00	1.00	4.50	2.64	10.41	13.26



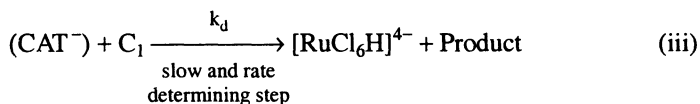
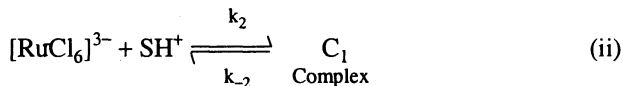


Following equilibrium may also exit in acidic media.



Thus in the acidified solution of chloramine-T, the possible oxidizing species are RNHCl, RNCl<sub>2</sub>, HOCl and CAT as such. If RNCl<sub>2</sub> were to be reactive species, the rate law would require second order dependence on CAT, which is contrary to the experimental observation. If HOCl were to be reactive species, a first order retardation of the rate by added PTS would be expected which is again contrary to the observed zero effect. Further if RNHCl were to be reactive species then fractional order with respect to PTS would be required which is also contrary to observed zero effect of PTS. Hence in view of above description CAT itself may be taken as real reactive species of chloramine-T. Sometimes CAT<sup>-</sup> is also taken as reactive species with CAT.

The following steps are suggested for the oxidation of cyclopentanol under the experimental conditions. Here S stands for cyclopentanol and (CAT<sup>-</sup>) has been used for CAT as CAT exists in solution as (CAT<sup>-</sup>).



where (CAT<sup>-</sup>) represents CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NCI<sup>-</sup>. The rate of the reaction may be determined in term of rate of loss of [CAT] as given below:

$$-\frac{d[\text{CAT}]}{dt} = k_d [\text{CAT}^-] [\text{C}_1] \tag{1}$$

On applying steady state approximation to [C<sub>1</sub>] we have from steps (ii) and (iii),

$$-\frac{d[\text{C}_1]}{dt} = 0 = k_2 [\text{RuCl}_6]^{3-} [\text{SH}^+] - k_{-2} [\text{C}_1] - k_d [\text{CAT}^-] [\text{C}_1]$$

or

$$[\text{C}_1](k_{-2} + k_d[\text{CAT}^-]) = k_2[\text{RuCl}_6]^{3-} [\text{SH}^+]$$

$$[\text{C}_1] = \frac{k_2[\text{RuCl}_6]^{3-} [\text{SH}^+]}{k_{-2} + k_d[\text{CAT}^-]} \tag{2}$$

On comparing equations (1) and (2), we have

$$-\frac{d[\text{CAT}]}{dt} = \frac{k_2 k_d [\text{RuCl}_6]^{3-} [\text{SH}^+] [\text{CAT}^-]}{k_{-2} + k_d [\text{CAT}^-]} \quad (3)$$

Again applying steady state approximation to  $[\text{SH}^+]$  we have from steps (i) and (ii) as given below:

$$-\frac{d[\text{SH}^+]}{dt} = 0 = k_1 [\text{S}] [\text{H}^+] - k_{-1} [\text{SH}^+] - k_2 [\text{SH}^+] [\text{RuCl}_6]^{3-}$$

or

$$[\text{SH}^+] = \frac{k_1 [\text{S}] [\text{H}^+]}{k_{-1} + k_2 [\text{RuCl}_6]^{3-}} \quad (4)$$

By comparing eqns. (3) and (4), we have

$$-\frac{d[\text{CAT}]}{dt} = \frac{k_1 k_2 k_d [\text{S}] [\text{CAT}^-] [\text{RuCl}_6]^{3-} [\text{H}^+]}{(k_{-1} + k_2 [\text{RuCl}_6]^{3-})(k_{-2} + k_d [\text{CAT}^-])} \quad (5)$$

On assuming  $k_{-2} \gg k_d [\text{CAT}^-]$  and  $k_{-1} \gg k_2 [\text{RuCl}_6]^{3-}$  we have

$$-\frac{d[\text{CAT}]}{dt} = \frac{k_1 k_2 k_d [\text{CAT}^-] [\text{S}] [\text{H}^+] [\text{RuCl}_6]^{3-}}{(k_{-1})(k_{-2})} \quad (6)$$

Since,  $[\text{CAT}^-] = [\text{CAT}]$ ,

$$-\frac{d[\text{CAT}]}{dt} = K_1 K_2 k_d [\text{CAT}] [\text{S}] [\text{H}^+] [\text{RuCl}_6]^{3-} \quad (7)$$

where  $K_1 = \frac{k_1}{k_{-1}}$  and  $K_2 = \frac{k_2}{k_{-2}}$ .

The rate law (7) explains first order dependence on chloramine-T, cyclopentanol, medium ( $\text{H}^+$ ) and Ru(III). From the above rate law, it is also clear that there is no effect of *p*-toluene sulphonamide (PTS) and KCl.

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