Asian Journal of Chemistry Vol. 17, No. 3 (2005), 1415–1422

Kinetics and Mechanism of Ru(III) Catalyzed Oxidation of Cyclopentanol and Cyclohexanol by Chloramine-T in Perchloric Acid Medium

S.P. MISHRA, ANJU SINGH, JYOTI VERMA, V.K. SRIVASTAVA and R.A. SINGH*
Chemical Kinetics Research Laboratory
Department of Chemistry, T.D.P.G. College, Jaunpur-222 002, India
E-mail: rasinghtdc@rediffmail.com

The kinetics of Ru(III) chloride catalysed oxidation of cyclopentanol and cyclohexanol by acidic solution of chloramine-T (CAT) has been investigated. The result indicates first order kinetics with respect to each of CAT, cycloalcohols, Ru(III) and (H^+). Negligible effect of [Cl^-] and ionic strength variations on reaction rate was observed. Insignificant effect of addition of *p*-toluene sulphonamide, a reduction product of CAT, was observed. A suitable mechanism consistent with kinetic results has been proposed.

Key Words: Kinetics, Ru(III), Oxidation, Cyclopentanol, Cyclohexanol, Chloramine-T, Perchloric acid.

INTRODUCTION

The sodium salt of *p*-toluene sulphochloramide, commonly known as chloramine-T acts both as an oxidizing and chlorinating agent[1–5]. The potential applications of this compound remain largely unrealized as not much information is available in literature[6–7]. The reaction between cycloalcohol and chloramine-T (CAT) in acidic medium was observed to be very slow. However, in the presence of ruthenium(III) chloride reaction between cycloalcohol (*viz*., cyclopentanol and cyclohexanol) and CAT in acidic medium proceed with a measurable rate.

Therefore, it was imperative to study the kinetics of oxidation of cyclopentanol and cyclohexanol by CAT in the presence of acidic solution of ruthenium(III) chloride. In the present communication we report the results of oxidation of cyclopentanol and cyclohexanol by chloramine-T in perchloric acid medium with ruthenium(III) as catalyst.

EXPERIMENTAL

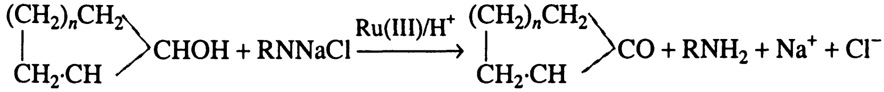
The reagents employed were cyclopentanol and cyclohexanol [E. Merck], ruthenium trichloride (Johnson-Matthey), chloramine-T (E. Merck) and perchloric acid (E. Merck). All other reagents used were of AR grade. All the solutions were prepared in doubly distilled water.

The solution of chloramine-T (CAT) was prepared by direct weighing and was standardized iodometrically. The solution of ruthenium trichloride was prepared by dissolving the sample in very dilute HCl. The final strengths of ruthenium(III) chloride and HCl were kept at 1.92×10^{-2} and 1.64×10^{-1} mol dm^{-3}, respectively. The stock solution of ruthenium(III) chloride and chloramine-T were stored in black coated bottles to prevent photochemical decomposition. The reaction vessels were also coated black. A thermostatic water bath was used to maintain the desired temperature within ±0.1°C. The reactions were initiated by the addition of chloramine-T solution to other reagents.

Although the order of addition had no effect on the rate, the progress of the reaction was followed by determining chloramine-T iodometrically in aliquots withdrawn after suitable time intervals.

Stoichiometry and product analysis

The reaction mixtures containing a known excess of [chloramine-T] over [cycloalcohol] were kept in the presence of $HClO_4$ and ruthenium(III) at 35°C for 72 h. Estimation of the unreacted chloramine-T showed that one mole of each of cyclopentanol and cyclohexanol consumes one mole of chloramine-T. The presence of corresponding cycloketones was confirmed by spot tests and also through dinitrophenylhydrazine derivatives[8].



$$\begin{matrix}(CH_2)_nCH_2 \\ | \\ CH_2{\cdot}CH\end{matrix}\!\!>\!CHOH + RNNaCl \xrightarrow{Ru(III)/H^+} \begin{matrix}(CH_2)_nCH_2 \\ | \\ CH_2{\cdot}CH\end{matrix}\!\!>\!CO + RNH_2 + Na^+ + Cl^-$$

where n = 1 in cyclopentanol, n = 2 in cyclohexanol and R = p-$CH_3C_6H_4SO_2$-group.

RESULTS AND DISCUSSION

The kinetic investigations were carried out at several initial concentrations of reactants. The reactions followed first order kinetics with respect to chloramine-T (CAT). The pseudo first-order rate constants in CAT ($k_{obs.}$) were evaluated from (–dc/dt) values. The observed rate constant ($k_{obs.}$) remained nearly constant at several initial concentrations of CAT in the presence of ruthenium(III) (Table-1) which further confirmed first-order dependence of rate with respect to CAT in oxidation of both cyclopentanol and cyclohexanol. The results of effect of change of concentration of each cycloalcohol and $[H^+]$ are summarized in Tables 2A and 2B.

The results indicate that $k_{obs.}$, *i.e.*, first-order rate constant increases linearly on increasing the concentration of each of cyclopentanol and cyclohexanol, showing first-order dependence of reactions on each cycloalcohol concentration. The first-order in cycloalcohol is further confirmed by nearly unity slope (1.08 and 1.02 in case of cyclopentanol and cyclohexanol, respectively) obtained from

$k_{obs.}$ *vs.* [cycloalcohol] plots (Fig. 1). The direct proportionality of $k_{obs.}$ with $[H^+]$ shows that the reaction follows first order kinetics in $[H^+]$ (Tables 2A and 2B). Addition of acetic acid (v/v %) to the reaction mixture decreases the rate constant in oxidation of both cycloalcohols.

TABLE-1

EFFECT OF VARYING CONCENTRATION OF [CAT] ON THE RATE CONSTANT IN OXIDATION OF CYCLOPENTANOL AND CYCLOHEXANOL AT 35°C

[Cycloalcohol] = 5.00×10^{-2} mol dm^{-3},
[KCl] = 5.00×10^{-2} mol dm^{-3}, $\mu = 7.50 \times 10^{-2}$ mol dm^{-3}

[CAT] × 10^3 (mol dm^{-3})	$k_{obs.} \times 10^4$ (s^{-1})	
	Cyclopentanol (a)	Cyclohexanol (b)
0.80	3.64	3.10
1.00	3.70	3.10
1.32	3.67	3.10
1.60	3.67	3.11
2.00	3.64	3.07
2.60	—	2.96
2.80	3.67	—
3.20	—	2.98
4.00	3.62	3.02
2.00 (c)	2.46	1.94
2.00 (d)	5.20	4.36
2.00 (e)	7.86	7.06
2.00 (f)	1.48 (j)	3.76
2.00 (g)	1.18 (j)	3.42
2.00 (h)	0.84 (j)	2.92
2.00 (i)	0.46 (j)	2.48

(a) $[HClO_4] = 1.25 \times 10^{-2}$ mol dm^{-3}, [Ru(III)] = 2.64×10^{-6} mol dm^{-3},
(b) $[HClO_4] = 1.00 \times 10^{-2}$ mol dm^{-3}, [Ru(III)] = 4.00×10^{-6} mol dm^{-3}
(c) 30°C, (d) 40°C,
(e) 45°C, (f) (Acetic acid) % (v/v) = 5
(g) (Acetic acid) % (v/v) = 15 (h) (Acetic acid) % (v/v) = 30
(i) (Acetic acid) % (v/v) = 50 (j) [cyclopentanol] = 2.00×10^{-2} mol dm^{-3}

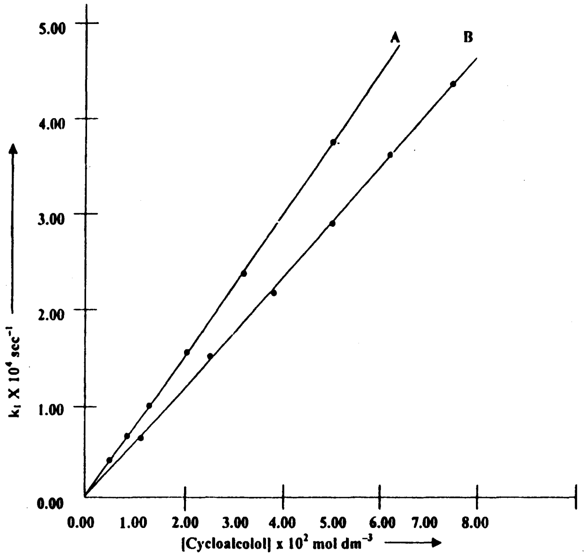


Fig. 1. A—Cyclopentanol (Under the condition of Table-2A)
B—Cyclohexanol (Under the condition of Table-2B)

TABLE-2A
EFFECT OF VARYING CONCENTRATION OF REACTANTS AT 35°C ON RATE CONSTANT

[CAT] = 1.00×10^{-3} mol dm^{-3}
[KCl] = 5.00×10^{-2} mol dm^{-3}, $\mu = 1.00 \times 10^{-2}$ mol dm^{-3}

[Cyclopentanol] × 10^2 (mol dm^{-3})	[$HClO_4$] × 10^2 (mol dm^{-3})	Ru(III) × 10^6 (mol dm^{-3})	$k_{obs.} \times 10^4$ (s^{-1})
0.50	1.25	2.64	0.41
1.00	1.25	2.64	0.77
1.50	1.25	2.64	1.12
2.00	1.25	2.64	1.60
3.30	1.25	2.64	2.56
5.00	1.25	2.64	3.70
5.00	1.00	2.64	2.95
5.00	1.60	2.64	4.74
5.00	2.00	2.64	5.91
5.00	3.00	2.64	8.82
5.00	4.50	2.64	13.26
5.00	1.00	0.66	0.92
5.00	1.00	1.32	1.78
5.00	1.00	1.98	2.68
5.00	1.00	3.30	4.56
5.00	1.00	3.96	5.42

TABLE 2B
EFFECT OF VARYING CONCENTRATION OF REACTANTS AT 35°C ON RATE CONSTANT

[CAT] = 2.00×10^{-3} mol dm^{-3}
[KCl] = 5.00×10^{-2} mol dm^{-3}, $\mu = 8.50 \times 10^{-2}$ mol dm^{-3}

[Cyclohexanol] $\times 10^2$ (mol dm^{-3})	[HClO$_4$] $\times 10^2$ (mol dm^{-3})	Ru(III) $\times 10^6$ (mol dm^{-3})	k$_{obs.}$ $\times 10^4$ (s^{-1})
1.25	1.00	4.00	0.72
2.50	1.00	4.00	1.52
3.75	1.00	4.00	2.21
5.00	1.00	4.00	2.96
6.25	1.00	4.00	3.71
7.50	1.00	4.00	4.32
5.00	0.50	4.00	1.48
5.00	1.50	4.00	4.56
5.00	2.00	4.00	6.00
5.00	2.50	4.00	7.64
5.00	3.00	4.00	9.08
5.00	1.00	1.00	0.78
5.00	1.00	2.00	1.60
5.00	1.00	3.00	2.30
5.00	1.00	5.00	3.98
5.00	1.00	6.00	4.71

The plots of k$_{obs.}$ *vs.* [Ru(III)] were linear (figure not shown) with slopes nearly unity (1.08 in cyclopentanol and 0.96 in cyclohexanol) showing first-order dependence in [Ru(III)] (Tables 2A and 2B). The results of variation of ionic strength (μ) of the medium (affected by addition of suitable amounts of NaClO$_4$), addition of KCl and *p*-toluene sulphonamide (PTS) indicate that there is almost negligible effect of μ, [Cl$^-$] and [PTS] on k$_{obs.}$ (Table-3). The reactions were carried out at 30°, 35°, 40° and 45°C and results at these temperatures led to compute energy of activation (E$_a$), entropy of activation ($\Delta S^{\#}$) and free energy of activation ($\Delta G^{\#}$) for the title reactions. The values of E$_a$, $\Delta S^{\#}$ and $\Delta G^{\#}$ are 15.38 kcal mol^{-1}, 14.67 e.u. and 11.48 kcal mol^{-1} respectively for the oxidation of cyclopentanol while for the oxidation of cyclohexanol these values are 16.42 kcal mol^{-1}, 17.34 e.u. and 11.70 kcal mol^{-1} respectively.

In acidic medium, chloramine-T exists in many forms. The protonation of anion of strong electrolyte[9] chloramine-T has thoroughly been investigated. The anion of chloramine-T gets protonated[10] in acidic solution as follows:

TABLE-3

EFFECT OF VARIATION OF IONIC STRENGTH (μ), [Cl⁻] AND ADDITION OF *p*-TOLUENE SULPHONAMIDE (PTS) ON THE RATE CONSTANT AT 35°C

[Cycloalcohol] = 5.00×10^{-2} mol dm^{-3} [CAT] = 2.00×10^{-3} mol dm^{-3}

[KCl] × 10^2 (mol dm^{-3})	[PTS] × 10^3 (mol dm^{-3})	$\mu \times 10^2$ (mol dm^{-3})	$k_{obs.} \times 10^4$ s^{-1}	
			Cyclopentanol	Cyclohexanol
1.00	—	11.50	3.70 (a)	3.02 (b)
2.00	—	11.50	3.64 (a)	3.05 (b)
4.00	—	11.50	3.72 (a)	3.10 (b)
6.00	—	11.50	3.63 (a)	3.08 (b)
8.00	—	11.50	3.62 (a)	3.03 (b)
10.00	—	11.50	3.65 (a)	3.07 (b)
5.00	1.00	11.50	2.95 (b)	7.64 (c)
5.00	2.00	11.50	3.00 (b)	7.82 (c)
5.00	3.00	11.50	3.12 (b)	7.71 (c)
5.00	4.00	11.50	3.08 (b)	7.60 (c)
5.00	5.00	11.50	2.92 (b)	7.72 (c)
5.00	—	6.25	3.67 (a)	2.96 (b)
5.00	—	8.25	3.48 (a)	3.08 (b)
5.00	—	11.50	3.65 (a)	3.00 (b)
5.00	—	20.25	3.68 (a)	2.97 (b)
5.00	—	30.50	3.58 (a)	3.06 (b)

[Ru(III)] = 2.64×10^{-6} mol dm^{-3} (cyclopentanol); 4.00×10^{-6} mol dm^{-3} (cyclohexanol); [$HClO_4$] = 1.25×10^{-2} mol dm^{-3} (a); 1.00×10^{-2} mol dm^{-3} (b) and 2.50×10^{-2} mol dm^{-3} (c)

$$\underset{(CAT^-)}{RNCl^-} + H^+ \overset{K'}{\rightleftharpoons} RNHCl \quad (K' = 3.8 \times 10^4 \text{ at } 25°C)$$

$$RNHCl + H^+ \overset{K''}{\rightleftharpoons} RN^+H_2Cl \quad (K'' = 1.02 \times 10^2 \text{ at } 25°C)$$

The following equilibria[11, 12] may also exist in acidic media.

$$2RNCl^- + 2H^+ \rightleftharpoons RNCl_2 + RNH_2$$

$$RNCl_2 + H_2O \rightleftharpoons RNHCl + HOCl$$

$$RNHCl + H_2O \rightleftharpoons RNH_2 + HOCl$$

Thus in acidified solution of chloramine-T, the possible oxidizing species are RNHCl, RN^+H_2Cl, $RNCl_2$, HOCl and CAT itself. If $RNCl_2$ were to be reactive species, the rate law would require second order dependence on CAT, which is contrary to the observed first-order in CAT. If RN^+H_2Cl or HOCl or RNHCl were to be reactive species of chloramine-T, then the reaction would require second-order in [H^+], inverse first-order in PTS and fractional order in PTS respectively contrary to first order in [H^+] and zero effect of PTS on reaction rate. Therefore, the only choice left is CAT itself existing as anion (CAT^-) which can be assumed to be effective oxidizing species of CAT.

In acidic solution ruthenium(III) chloride exists as $[RuCl_6]^{3-}$, which is involved in the following equilibrium[13] as Ru(III) chloride forms $[RuCl_6]^{3-}$ in HCl solution.

$$[RuCl_6]^{3-} + H_2O \rightleftharpoons [RuCl_5{\cdot}H_2O]^{2-} + Cl^-$$

In view of insignificant effect of successive addition of $[Cl^-]$ on the reaction rate, it is safe to assume $[RuCl_6]^{3-}$ as reactive species of ruthenium(III) chloride in acidic solution.

Consider reactive species of chloramine-T and ruthenium(III) chloride in acidic medium as (CAT^-) and $[RuCl_6]^{3-}$ respectively.

The following scheme is proposed where S is either cyclopentanol or cyclohexanol. CAT exists in solution as (CAT^-).

$$S + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ \tag{i}$$

$$[RuCl_6]^{3-} + SH^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{Complex (A)} \tag{ii}$$

$$[CAT^-] + A \xrightarrow{k} [RuCl_6H]^{4-} + \text{Products} \tag{iii}$$

$$[RuCl_6H]^{4-} + CAT^- \xrightarrow{\text{Fast}} [RuCl_6]^{3-} + PTS + HOCl \tag{iv}$$

The rate of reaction may be expressed in terms of loss of [CAT] as given below where $[CAT^-]$ is equivalent to [CAT].

$$-\frac{d[CAT]}{dt} = k[CAT][A] \tag{1}$$

On applying steady state approximation to [A] from steps (ii) and (iii), we have

$$[A] = \frac{k_2[RuCl_6]^{3-}[SH^+]}{k_{-2} + k[CAT]} \tag{2}$$

Again on applying steady state approximation to $[SH^+]$ and considering steps (i) and (ii), we have

$$[SH^+] = \frac{k_1[S][H^+]}{k_{-1} + k_2[RuCl_6]^{3-}} \tag{3}$$

Considering equations (1), (2) and (3) together, we have

$$-\frac{d[CAT]}{dt} = \frac{kk_1k_2[CAT][S][H^+][RuCl_6]^{3-}}{(k_{-1} + k_2[RuCl_6]^{3-})(k_{-2} + k[CAT])} \tag{4}$$

On assuming the inequalities $k_{-2} \gg k[CAT]$ and $k_{-1} \gg k_2[RuCl_6]^{3-}$, we have equation (5) from (4).

$$-\frac{d[CAT]}{dt} = kK_1K_2[CAT][S][H^+][RuCl_6]^{3-} \tag{5}$$

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

The rate law (5) explains the first-order kinetics with respect to each of chloramine-T, cycloalcohol, $[H^+]$ and ruthenium trichloride. Positive effect of dielectric constant of the medium on the rate of the reaction indicates that the rate increases with polarity of the medium showing possible formation of charge activated complex in the transition state which is more hydrated than reactants. The rate expression (5) also explains negligible effect of addition of *p*-toluene sulphonamide (PTS) on the rate constant.

REFERENCES

1. A. Berka, J. Vulterin and J. Zyka, Newer Redox Titrants, Pergamon Press, Oxford, p. 37 (1965).
2. M.M. Campbell and G. Johnson, *Chem. Rev.*, **78**, 65 (1978).
3. M.C. Agarwal and S.K. Upadhyay, *J. Sci. Ind. Res.*, **42**, 508 (1983).
4. V.M. Sadagopa, Ramanujan and N.M. Trieff, *J. Chem. Soc. (Perkin Trans. II)*, 1275 (1977).
5. P.S. Radhakrishnamurthi and B.M. Sosmel, *Indian J. Chem.*, **16A**, 598 (1978).
6. K.V. Uma and S.M. Mayanna, *J. Indian Chem. Soc.*, **62**, 426 (1985).
7. P.S. Radhakrishnamurthi and M.D. Prasad, *J. Indian Chem. Soc.*, **55**, 456 (1978).
8. I. Vogel, Elementary Practical Organic Chemistry, Part 3, Longmans Green, London (1958).
9. E. Bishop and V.J. Jennings, *Talanta*, **1**, 197 (1958).
10. T. Higuchi, K. Ikeda and A. Hussain, *J. Chem. Soc. B*, 546 (1967).
11. S.S. Narayanana and V.R.S. Rao, *Radiochim. Acta*, **32**, 211 (1983).
12. B. Singh and R. Chand, *Tetrahedron*, **41**, 2871 (1985).
13. H.H. Cady and R.F. Connich, *J. Am. Chem. Soc.*, **80**, 2646 (1950).

(*Received*: 15 April 2004; *Accepted*: 1 March 2005) AJC-4116