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Kinetics of Ru(III) Catalysed Oxidation of Cyclohexanol by Bromamine-T in Hydrochloric Acid

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The kinetics of Ru(III) catalysed oxidation of cyclohexanol by acidic solution of bromamine-T (BAT) have been reported. The reaction shows first-order kinetics in each of bromamine-T, cyclohexanol, H^+ ions and Ru(III). Decreasing effect of chloride ions was observed. Ionic strength variation did not influence the reaction rate. Negligible effect of addition of *p*-toluene sulphonamide (one of the reaction products) was observed. A suitable mechanism consistent with observed kinetic results has been proposed.

INTRODUCTION

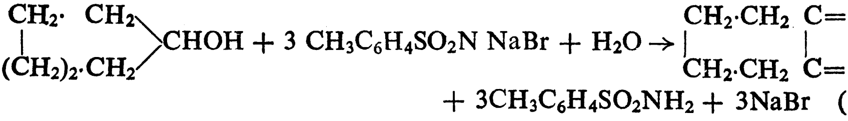
N-haloamides, imides and halogens belong to the group of versatile agents used for the oxidation of organic compounds[1–3]. Bromamine-T belongs to this group and has been used in the oxidation of several organic compounds[4]. Although some attempts have been made earlier[5,6] to study the mode of oxidation by bromamine-T (BAT) in uncatalysed reactions, but scant reports are available for Ru(III) catalysed oxidation[7] by bromamine-T. The present paper reports the kinetics and mechanism of bromamine-T oxidation of cyclohexanol in the presence of Ru(III) as catalyst in hydrochloric acid medium.

EXPERIMENTAL

All the reagents used were of highest purity available. BAT solution was prepared and standardised by the method described earlier[5]. Cyclohexanol was E. Merck grade. Hydrochloric acid was used as a source of hydrogen ions. All solutions were prepared in double distilled water. The reaction was followed upto two half-lives by the iodometric estimation of the unreacted BAT at various time intervals.

Stoichiometry and Product Analysis

Different sets of experiments were carried out with varying BAT–Cyclohexanol ratios. Estimation of excess of BAT left in each set showed that three moles of BAT were consumed for the oxidation of each mole of cyclohexanol and accordingly, following stoichiometric equation(1) could be formulated.



$$\begin{matrix}CH_2\cdot\ CH_2\\ | \\ (CH_2)_2\cdot CH_2\end{matrix}\!\!>\!CHOH + 3\,CH_3C_6H_4SO_2N\,NaBr + H_2O \rightarrow \begin{matrix}CH_2\cdot CH_2 & C{=}O\\ | & |\\ CH_2\cdot CH_2 & C{=}O\end{matrix} + 3CH_3C_6H_4SO_2NH_2 + 3NaBr \quad (1)$$

The end product corresponding 1, 2-diketone was identified by conventional spct test analysis[8] and also through dinitrophenylhydrazine (DNP) derivative[9].

RESULTS AND DISCUSSION

The results of oxidation of cyclohexanol by BAT in acidic solution of Ru (III) have been recorded in Table 1. First-order dependence of the reaction on cyclohexanol, H+ ions and Ru(III) is evident from the linear relationship between first-order rate constant i.e. k_1 and each of cyclohexanol, H+ ions and Ru(III). First order kinetics in BAT is obvious from the nearly constant values of k_1. Table 2 contains effect of variation

TABLE 1

a

$[BAT] \times 10^3$ M	0.80	1.00	1.32	2.00	2.80	4.00
$k_1 \times 10^4$ S^{-1}	3.64	3.70	3.68	3.64	3.67	3.63

a → [Cyclohexanol] = 5.00×10^{-2}M, [HCl] = 1.25×10^{-2} M, [Ru (III)] = 2.64×10^{-6} M, [KCl] = 5.00×10^{-2} M and Temp. 30°C

b

[Cyclohexanol]$\times 10^2$ M	0.50	1.00	1.50	2.00	3.30	5.00
$k_1 \times 10^4$ S^{-1}	0.41	0.77	1.12	1.60	2.56	3.70
$k_2 \times 10^2$ M^{-1} L S^{-1}	0.82	0.77	0.75	0.80	0.79	0.74

b → [BAT] = 1.00×10^{-3} M, [Ru (III)] = 2.64×10^{-6} M, [HCl] = 1.25×10^{-2} M, [KCl] = 5.00×10^{-2} M and Temp. 30°C

c

$[HCl] \times 10^2$ M	1.00	1.25	1.60	2.00	3.00	4.50
$k_1 \times 10^4$ S^{-1}	2.95	3.70	4.72	5.91	8.82	13.26
$k_2 \times 10^2$ M^{-1} L S^{-1}	2.95	2.96	2.95	2.96	2.94	2.94

c → [BAT] = 1.00×10^{-3} M, [Cylclohexanol] = 5.00×10^{-2} M, [Ru(III)] = 2.64×10^{-6} M, Temp. 30°C, Total [Cl^-] = 6.25×10^{-2} M

d

[Ru (III)]$\times 10^6$ M	0.66	1.32	1.98	2.64	3.30	3.96
$k_1 \times 10^4$ S^{-1}	0.92	1.78	2.67	3.70	4.56	5.42
$k_2 \times 10 M^{-1}$ LS^{-1}	1.39	1.35	1.33	1.40	1.38	1.35

d → [BAT] = 1.00×10^{-3} M, [Cyclohexanol] = 5.00×10^{-2} M, [HC] = 1.25×10^{-2} M, [KCl] = 5.00×10^{-2} M and Temp. 30°C of [Cl⁻], *p*-toluenesulphonamide and temperature. Negligible effect of ionic strength of the medium is also obvious from the kinetic data of Table 2. Variation of *p*-toluenesulphonamide (*p*-TS) concentration did not influence the reaction rate, but decreasing effect of added chloride ions was observed. The energy of activation was calculated from the rate measurements at 25, 30, 35 and 40°C and was found to be 14.72 kcal/mol.

TABLE 2

a

$[KCl]\times10^{2}$ M	... 1.00	2.00	2.50	3.00	4.00	5.00
$k_1\times10^{4}$ S^{-1}	... 13.50	10.60	8.80	6.50	4.80	3.70

a → $[BAT] = 1.00\times10^{-3}$ M, $[HCl] = 1.25\times10^{-2}$ M, $[Cyclohexanol] = 5.00\times10^{-2}$ M, $[Ru(III)] = 4.00\times10^{-6}$ M and Temp. 30°C

b

$[p\text{-TS}]\times10^{3}$ M	... 0.25	0.50	1.00	2.00	2.50	4.00
$k\times10^{4}$ S^{-1}	... 3.76	3.78	3.69	3.70	3.78	3.76

b → $[BAT] = 1.00\times^{-3}$ M, $[Cyclohexanol] = 5.00\times10^{-2}$ M, $[HCl] = 1.25\times10^{-2}$ M $[Ru(III)] = 2.64\times10^{-6}$ M and Temp. 30°C

c

$\mu\times10^{2}$ M	... 6.25	7.00	8.25	10.25	16.25
$k_1\times10^{4}$ S^{-1}	... 3.70	3.69	3.80	3.71	3.73

c → $[BAT] = 1{\cdot}00\times10^{-3}$ M, $[Cyclohexanol] = 5{\cdot}00\times10^{-2}$ M, $[HCl] = 1{\cdot}25\times10^{-2}$ M, $[Ru(III)] = 5.64\times10^{-6}$ M, $[KCl] = 5.00\times10^{-2}$ M and Temp. 30°C

d

Temp. °C	... 25	30	35	40
$k_1\times10^{4}$ S^{-1}	... 2.46	3.64	5.20	7.86

d → $[BAT] = 2.00\times10^{-3}$ M, $[Cyclohexanol] = 5.00\times10^{-2}$ M, $[HCl] = 1.25\times10^{-2}$ M, $[Ru(III)] = 2.64\times10^{-6}$ M, $[KCl] = 5.00\times10^{-2}$ M

It has been earlier reported[7] that BAT is a strong electrolyte and dissociates as given below.

$$\underset{(BAT)}{TsNNaBr} \rightleftharpoons \underset{(BAT^-)}{TsNBr^-} + Na^+ \qquad (2)$$

where Ts stands for $CH_3C_6H_4SO_2$.

In acidid medium BAT⁻ would take up proton to form *p*-toluenesulphobromamide (BAT′) as given below.

$$\underset{(BAT^-)}{TsNBr^-} + H^+ \rightleftharpoons \underset{(BAT')}{TsNHBr} \qquad (3)$$

A part of BAT^- is also likely to be converted into dibromo *p*-toluene sulphonamide (DBT) as in eqn. (4).

$$2TsNBr^- + 2H^+ \rightleftharpoons TsNBr_2 + TsNH_2 \tag{4}$$

Thus either of the three species BAT^-, BAT' and DBT may be involved in the oxidation process in acidic medium. If either (BAT^-) or DBT is taken as reactive species of bromamine-T, the rate law obtained on this assumption does not explain the kinetic results. Hence none of these can be taken as reactive species of BAT. Thus under the circumstances, BAT' is the only choice which can be assumed as oxidising species. The rate law, obtained on taking BAT' as real oxidising species, fully explains all the results.

The negative effect of Cl^- suggests that the following equilibrium favours the right direction and thus

$$[RuCl_6]^{3-} + H_2O \rightleftharpoons [RuCl_5H_2O]^{2-} + Cl^- \tag{5}$$

$[RuCl_5H_2O]^{2-}$ is the real catalytic species of ruthenium(III) chloride in the present case.

The following steps are proposed on the basis of kinetic results taking BAT' and $[RuCl_5H_2O]^{2-}$ as the oxidising and catalytic species of BAT and Ru (III) chloride respectively.

$$\underset{(C_1)}{[RuCl_6]^{3-}} + H_2O \overset{k_1}{\rightleftharpoons} \underset{(C_2)}{[RuCl_5H_2O]^{2-}} + Cl^- \tag{I}$$

$$C_2 + S \overset{k_2}{\rightleftharpoons} \underset{(C_3)}{[RuCl_5S]^{2-}} + H_2O \tag{II}$$

$$\underset{(BAT)}{TsNBr^- + H^+} \underset{k_1'}{\overset{k_1'}{\rightleftharpoons}} \underset{(BAT')}{TsNHBr} \tag{III}$$

$$C_3 + BAT' \xrightarrow{k_2'} [RuCl_5H]^{3-} + Y + H^+ \tag{IV}$$

Slow and rate determining step

where S is cyclohexanol, Y is an intermediate.

$$[RuCl_5H]^{3-} + BAT' + H_2O \xrightarrow[\text{fast}]{k_3} TsNH_2 + [RuCl_5H_2O]^{2-} + Br^- \tag{V}$$

$$Y + BAT' \xrightarrow[\text{fast}]{k_4} \text{Final product} \tag{VI}$$

The rate of the reaction in terms of loss of concentration of BAT may be written as eqn. (6).

$$\frac{-d[BAT]}{dt} = nk_2'[C_2][BAT'] \tag{6}$$

where n is the number of moles of BAT required to oxidise each mole of cyclohexanol.

Considering steps (I-V) the value of $[C_3]$ is obtained as given in eqn (7).

$$[C_3] = \frac{k_1k_2[S][Ru(III)]_T}{k_l + [Cl^-] + k_1k_2[S]} \tag{7}$$

On substituting the value of $[C_3]$ from eqn. (7) in eqn. (6) we have eqn. (8)

$$\frac{-d[BAT]}{dt} = \frac{n\,k'_2\,k_1\,k_2[S][BAT'][Ru(III)_T}{k_l + [Cl^-] + k_1k_2[S]} \tag{8}$$

On applying steady state treatment to [BAT′] and considering eqn. (8) with the assumption $k_1\,k_2[S] \ll (k_l + [Cl^-])$ we have final rate law (9).

$$\frac{-d\,[BAT]}{dt} = \frac{k[BAT][S][H^+][Ru(III)]_T}{k_l + [Cl^-]} \tag{9}$$

where $k = n\,k'_2\,k_1\,k_2\,k_3$ and $k_3 = k_1/k'_{-1}$

The rate eqn (9) fully explains all the observed kinetic results. It also explains negligible effect of ionic strength variation, suggesting involvement of atleast a dipole in the slow and rate determining step (step (IV)).

REFERENCES

1. R. Filler, *Chem. Rev.*, **63**, 21 (1963).
2. M. M. Campbell and G. Johnson, *Chem. Rev.*, **78**, 65 (1978).
3. L. Horner, E. H. Winkelmann, Newer Methods of Preparative Organic Chemistry (Ed. W. Forest), Academic Press, New York (1964).
4. C. G. R. Nair and P. Indrasenan, *Talanta*, **23**, 239 (1976).
5. S. Gunsekaran and N. Venkatasubramanian, *Indian J. Chem.*, **22**, 774 (1983).
6. B. Singh and R. Chand, *Tetrahedron*, **41**, 2871 (1985).
7. B. Singh, N. B. Singh and B. B. L. Saxena, *Indian J. Chem.*, **61**, 319 (1984).
8. F. Feigl, Spot Tests in Organic Analysis, Elsevier, Amsterdam, p. 325 (1966).
9. I. Vogel, Elementary Practical Organic Chemistry, Part III, Longmans Green, London, p. 73 (1958).

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