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# Kinetics and Mechanism of Oxidation of Some Cycloalcohols by Acidic Solution of Bromamine-T

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Kinetic investigations on Ru(III) catalysed oxidation of methyl cyclohexanol (M-cyhol) and 4-methyl cyclohexanol (4-M-cyhol) by acidic solution of bromamine-T (BAT) have been made in the temperature range 25°–40°C. The reaction shows first order kinetics in BAT, both cyclic alcohols, $H^+$ ions and Ru(III). Insignificant effect of addition of p-toluenesulphonamide (PTS), as one of the reaction products, was observed. The reaction rate decreased on increasing $Cl^-$ while practically no effect of variation of ionic strength of the medium was observed. A suitable mechanism in agreement with observed kinetic data has been proposed.

## INTRODUCTION

Bromamine-T (BAT) has been used as oxidant to study its mode of oxidation for uncatalysed reactions[1–3] and very little attention has been paid to explore the catalytic role of ruthenium(III) chloride with BAT as an oxidant[4–6]. This prompted us to undertake the present investigation in order to reveal a clear picture of mode of Ru(III) catalysis in BAT oxidation of M-cyhol and 4-M-cyhol in acid medium. Aromatic sulphonyl haloamines show diverse chemical behaviour which is generally attributed to their ability to act as halonium cations, hypohalites and N-anions which act as both bases and nucleophiles. The monohaloamines are two electron oxidants and the prominent members of this class are chloramine-T (CAT) and bromanine-T (BAT). The kinetics of reactions of chloramine-T have been reviewed[7] but information about the bromine analogues is scanty. The kinetics of Ru(III) catalysis in BAT oxidations have been recently reported, but so far no one has attempted to probe into the role of ruthenium(III) chloride in oxidation of cyclic alcohols by BAT. In this communication we report here the mechanistic steps in BAT oxidation of methyl cyclohexanol and 4-methyl cyclohexanol in the presence of acidic solution of ruthenium(III) chloride.

## EXPERIMENTAL

Aqueous solution of E. Merck samples of methyl cyclohexanol and 4-methyl cyclohexanol were prepared by dissolving their weighed amounts in double distilled water. BAT solution was prepared and standardised by the method described earlier[1-3]. All other reagents used were of highest purity available. Ruthenium(III) chloride (Johnson and Matthey) solution was prepared by dissolving the sample in hydrochloric acid of known strength.

The reaction was carried out in glass stoppered reaction vessel (Jena glass) which was coated black from outside to eliminate photochemical effects. All the kinetic measurements were made at constant temperature (± 0.1°C). The reaction was initiated by rapid addition of measured volume of BAT to the reaction mixture containing appropriate volumes of all reagents including substrate and mixing them by vigorous shaking. The progress of the reaction was monitored by iodometric estimation of unreacted BAT in a measured aliquot of the reaction mixture at different intervals of time. The course of the reaction was studied for about two half-lives.

Stoichiometric data indicated that 3 moles of BAT were consumed for the oxidation of each mole of cyclic alcohol. The end products corresponding ketones were identified by conventional spot test analysis[8] and also through dinitrophenyl hydrazine (DNP) derivative[9].

## RESULTS AND DISCUSSION

The kinetic results were collected at several initial concentrations of the reactants. First-order kinetics in BAT was established by varying the concentration of BAT at fixed concentrations of all other reactants. Nearly constant values of first order rate constant ($k_1$) at different initial [BAT] indicate first-order dependence on BAT. A linear increase in $k_1$ i.e. first-order rate constant with an increase in [cyclic alcohol] shows first-order kinetics with respect to cyclic alcohol. First order kinetics with respect to $[H^+]$ was obvious from the slope (1.08 in M-cyhol and 1.06 in 4-M-cyhol oxidations) of the curve obtained on plotting log $k_1$ vs log $[H^+]$. First order dependence on [Ru(III)] was evident from the close resemblance between slope value ($0.79 \times 10^2$ for M-cyhol and $0.50 \times 10^2$ for 4-M-cyhol oxidations) of the $k_1$ vs [Ru(III)] and average value of second order rate constant, i.e. $k_2$ or $k_1$/[Ru(III)] ($0.78 \times 10^2$ mol$^{-1}$dm$^3$ s$^{-1}$ for M-cyhol and $0.52 \times 10^2$ mol$^{-1}$ cm$^3$ s$^{-1}$ for 4-M-cyhol oxidations).

Decreasing effect of added $[Cl^-]$ on the rate constant was observed while addition of successive amounts of p-toluenesulphonamide (PTS) did not influence the rate constant. Practically no effect of ionic strength variation (affected by addition of suitable amounts of $NaClO_4$) on rate constant was observed. The energy of activation (ΔE) was calculated from the rate measurements at various temperatures (25–40°C) and its values obtained were 67.62 kJ mol$^{-1}$ and 77.28 kJ mol$^{-1}$ for the oxidation of 2-methyl cyclohexanol and 4-methyl cyclohexanol respectively.

BAT, being a strong electrolyte[5], dissociates as Eq. (1).

$$\underset{\text{(BAT)}}{\text{TsNNaBr}} \rightleftharpoons \underset{\text{(BAT}^-\text{)}}{\text{TsNBr}^-} + \text{Na}^+ \quad (1)$$

where Ts stands for $CH_3C_6H_4SO_2^-$ group.

In acidic medium BAT $^-$ forms *p*-toluenesulphobromamide (BAT′) as given below:

$$\underset{(BAT^-)}{TsNBr^- + H^+} \rightleftharpoons \underset{(BAT')}{TsNHBr} \qquad (2)$$

Dibromo-*p*-toluenesulphobromamide (DBT) is also formed as a result of following reactions:

$$2TsNBr^- + 2H^+ \rightleftharpoons \underset{(DBT)}{TsNBr_2} + TsNH_2 \qquad (3)$$

Thus there are three possible oxidising species of BAT in acidic medium, viz., BAT , BAT$^-$ and DBT. If BAT$^-$ or DBT is assumed to be reactive species of BAT, the rate law derived does not conform to the observed kinetic data. Hence neither of these can be taken as reactive species. Thus under the experimental conditions BAT is the only choice which, when taken as oxidising species, furnishes rate law in agreement with kinetic facts.

The negative effect of addition of chloride ions on the rate constant suggests that the following equilibrium shifts to the right side and thus involvment of $[RuCl_5{\cdot}H_2O]^{2-}$ species in the reaction as catalyst is ensured:

$$[RuCl_6]^{3-} + H_2O \rightleftharpoons [RuCl_5 \cdot H_2O]^{2-} + Cl^- \qquad (4)$$

In the light of the above discussion the following reaction steps are suggested:

$$\underset{(C_1)}{[RuCl_6]^{3-}} + H_2O \overset{K_1}{\rightleftharpoons} \underset{(C_2)}{[RuCl_5H_2O]^{2-}} + Cl^- \qquad (i)$$

$$C_2 + S \overset{K_2}{\rightleftharpoons} \underset{(C_3)}{[RuCl_5S]^{2-}} + H_2O \qquad (ii)$$

where S is 2-methyl cyclohexanol or 3-methyl cyclohexanol.

$$\underset{(BAT^-)}{TsNBr^- + H^+} \underset{K_{-3}}{\overset{K_3}{\rightleftharpoons}} \underset{(BAT')}{TsNHBr} \qquad (iii)$$

$$C_3 + BAT' \xrightarrow[\text{slow and rate determining step}]{kd} [RuCl_5H]^{3-} + Y + H^+ \qquad (iv)$$

where Y is an intermediate.

$$Y + BAT' \xrightarrow[\text{fast}]{K_4} \text{Final products} \qquad (v)$$

$$[RuCl_5H]^{3-} + BAT' + H_2O \xrightarrow{K_5} TsNH_2 + [RuCl_5H_2O]^{2-} + Br^- \qquad (vi)$$

The rate of the reaction in terms of consumption of BAT may be written as Eq. (5):

$$\frac{-d[BAT]}{dt} = n\ kd\ [C_3][BAT'] \qquad (5)$$

where n is number of moles of BAT consumed in oxidation of each mole of cyclic alcohol.

The total concentration of ruthenium (III) chloride i.e. $[Ru(III)]_T$ may be written as Eq. (6):

$$[Ru(III)]_T = [C_1] + [C_2] + [C_3] \qquad (6)$$

The values of $[C_3]$ is obtained by considering steps (i) and (ii) and Eq. (6) and is expressed as Eq. (7):

$$[C_3] = \frac{K_1K_2[S][Ru(III)]_T}{K_1 + [Cl^-] + K_1K_2[S]} \qquad (7)$$

On substituting the value of $[C_3]$ from Eq. (7) in Eq. (5), we have Eq. (8):

$$\frac{-d[BAT]}{dt} = \frac{n\ kd\ K_1K_2[S][Ru(III)]_T[BAT']}{K_1 + [Cl^-] + K_1K_2[S]} \qquad (8)$$

On applying steady state approximation with respect to BAT' and on assuming inequality $K_1K_2[S] << K_1 + [Cl^-]$ the final rate law (9) is obtained:

$$\frac{-d[BAT]}{dt} = \frac{k[BAT][S][H^+][Ru(III)]_T}{K_1 + [Cl^-]} \qquad (9)$$

where $k = n\ kd\ K_1K_2K_3$ and $K_3 = (K_3/K_{-3})$.

The rate Eq. (9) is in complete agreement with all the observed kinetic results. Practically no effect of ionic strength of the madium is also explained clearly by the slow and rate determining Step (iv) which involves a dipole.

## CONCLUSION

It is concluded from the present investigation that in acidic medium BAT' and $[RuCl_5H_2O]^{2-}$ are the reactive species of BAT and ruthenium(III) chloride respectively.

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