Ru(III) CATALYSIS IN OXIDATION OF n-PROPANOL AND n-BUTANOL BY ACIDIC SOLUTIONS OF BROMAMINE-T

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Abstract—Kinetics of Ru(III) catalysed oxidation of n-propanol and n-butanol by acidic solutions of bromamine-T have been investigated. The results show that oxidation of both alcohols follows first-order kinetics in bromamine-T, both alcohols, hydrogen ion concentration and Ru(III). Decreasing effect of [chloride ion] variation on reaction rate was observed. No effect of p-toluenesulphonamide and ionic strength of the medium was observed. Activation parameters have been calculated and recorded. A suitable mechanism in conformity with the above observations has been proposed.

Earlier, no attempt had been made to investigate the kinetic studies of oxidation of substrates by bromamine-T (BAT) although it has been used, recently, for the direct and indirect determination of a variety of substances.¹ It has been observed for the first time that the reaction between bromamine-T and these alcohols proceeds with measurable velocity in the presence of catalytic amount of Ru(III) chloride in acidic media. The present communication reports the kinetics and mechanism of Ru(III) catalysed oxidation of n-propanol and n-butanol in perchloric acid solutions.

EXPERIMENTAL

Bromamine-T soln was prepared by the method of Nair et al.¹ and was standardised iodometrically. E. Merck p.a. sample of chloramine-T, Koch-Light (England) sample of *p*-toluenesulphonamide and Ru(III) chloride (Johnson, Mathey Chemical Ltd.) sample were used. All the chemicals used were of analytical reagent grade. Doubly distilled water was used throughout the course of investigations. Calculated amount of bromamine-T soln was added to the already equilibrated mixture containing substrate, perchloric acid, Ru(III) chloride and KCI solns to initiate the reaction. The kinetics of the reactions were followed by examining aliquot portions of the mixture at different intervals of time for bromamine-T iodometrically.

RESULTS

The values of first-order rate constants recorded in Table 1 at several initial concentrations of bromamine-T and both the substrates indicate first-order dependence of the reactions on bromamine-T as well as on n-propanol and nbutanol. The average values of second-order rate constants ($k_2 = k_1$ /[Substrate]) have been calculated as 5.28 ± 0.03 and $5.85 \pm 0.07 \times 10^{-1} 1 \text{ mol}^{-1} \text{ min}^{-1}$ for the oxidation of n-propanol and n-butanol, respectively under the conditions of Table 1.

The effect of hydrogen ion concentration on the

rate of oxidation of the substrates was studied under the conditions of Fig. 1. The plots of log k_1 against log [H⁺] produced straight lines with slopes 1.04 and 1.07 for n-propanol and n-butanol, respectively, establishing first-order kinetics with respect to hydrogen ion concentration. First-order dependence of the reactions on Ru(III) was obvious from the slopes (1.02 for n-propanol and 1.00 for n-butanol) of the straight lines (Fig. 2) obtained from the plots of log k_1 vs log [Ru(III)].

Insignificant effect of *p*-tolucnesulphonamide (one of the reaction products), negligible effect of ionic strength of the medium (affected by addition of various amounts of NaClO₄) and marked effect due to chloride ions variation were observed (Table 2). The kinetic data obtained at 30, 35, 40 and 45° were given in Table 2. The values of energy of activation (ΔE) and entropy of activation (ΔS) were calculated and were found as 12.81 K cal/mole and - 19.48 e.u. respectively (n-propanol) and 11.76 K cal/mole and - 22.74 e.u. respectively (n-butanol).

Stoichiometry and product analysis. Various sets of experiments were carried out with varying bromamine-T alcohol ratios. The excess of bromamine-T left in each set was estimated. These studies showed that one mole of alcohol consumed two moles of bromamine-T and accordingly, the following stoichiometric equation could be formulated, where R represents $CH_3C_4H_4SO_2$ - and R' represents $-C_2H_5$ (in n-propanol) or $-C_3H_7$ (in n-butanol).

$$2RN.NaBr + R'CH_2OH + H_2O$$

$$\rightarrow 2RNH_2 + 2NaBr + R'COOH. (1)$$

Propionic acid and butyric acid were identified as end products in oxidation of n-propanol and nbutanol, respectively by spectrophotometric and chromatographic techniques.

10 ³ [Bromamine-T]/	10 ² [Alcohol]/	10 ³ k ₁ /min ⁻¹	
М	<u>M</u>	n-Propanol	n-Butanol
1.00	2.00	10.80	11.80
1.25	2.00	10.79	11.82
1.67	2.00	10.77	11.77
2.00	2.00	10.80	11.79
2.50	2.00	10.80	11.80
4.00	2.00	10.80	11.78
2.00	1.00	5.41	5.86
2.00	1.30	6.88	7.45
2.00	1.70	9.19	9.82
2.00	2.00	10.80	11.79
2.00	2.50	13.43	14.85
2.00	5.00	26.80	29,49

Table 1. Effect of concentration of reactants at 35°. [HClO_J = 2.00×10^{-2} M, [Ru(III) chloride] = 0.88×10^{-6} M, [Cl⁻] = 5.00×10^{-2} M

DISCUSSION

Ru(III) chloride in hydrochloric acid forms $[RuCl_6]^{3-}$ which is in equilibrium with $[RuCl_5(H_2O)]^{2-}$ as given below.²⁻⁴

$$[RuCl_{d}]^{3-} + H_2O \rightleftharpoons [RuCl_{5}(H_2O)]^{2-} + Cl^{-}.$$
 (2)

In acidic medium equilibrium (2) in right direction would be highly favoured, suggesting $[RuCl_5(H_2O)]^{2-}$ as the real reactive species^{5,6} of Ru(III) chloride in our present studies. In acidic medium bromamine-T would give⁷ p-toluenesulphobromamide (BAT') in eqn (3).

$$CH_{3}C_{6}H_{4}SO_{2}NBr^{-} + H^{+} \rightleftharpoons CH_{3}C_{6}H_{4}SO_{2}NHBr \quad (3)$$
(BAT)
(BAT')

BAT would also produce dibromo p-toluenesulphonamide (DBT) and free sulphonamide according to eqn (4).⁷

$$2CH_{3}C_{6}H_{4}SO_{2}NBr^{-} + 2H^{+}$$

$$\Rightarrow CH_{3}C_{6}H_{4}SO_{2}NBr_{2} + CH_{3}C_{6}H_{4}SO_{2}NH_{2}.$$
 (4)
(DBT)

Thus we have three oxidising species of bromamine-T, viz. BAT, BAT' and DBT. When either



Fig. 1. Plot of log k, against log[H⁺]. A → [n-Propanol], B → [n-Butanol], [Bromamine-T] = 2.00×10^{-3} M, [Ru(III) chloride] = 0.88×10^{-6} M, [n-Propanol] = [n-Butanol] = 2.00×10^{-2} M, [Cl⁻] = 5.00×10^{-2} M.

BAT or DBT is assumed as actual oxidising species, the rate law deduced does not explain our observed kinetics and hence either of them cannot be assumed as real oxidising species. Hence, BAT' is the only choice which can be assumed as actual oxidising species in our case. Similar species of chloramine-T have also been reported in acidic medium where H⁺ ions have been observed to show an accelerating effect on the rate of oxidation of hexacyanoferrate(II),⁸ p-cresol⁹ and methyl aryl sulphides.¹⁰

Considering the reactive species of bromamine-T and Ru(III) chloride as described above and all other kinetic observations, the reaction mechanism for the oxidation of n-propanol and n-butanol showing identical kinetics may be described as given below where S stands for the alcohols.

$$CH_3C_6H_4SO_2NBr^- + H^+ \rightleftharpoons CH_3C_6H_4SO_2NHBr$$
 (i)
BAT BAT'

$$[Ru^{III}Cl_{d}]^{3-} + H_{2}O = [Ru^{III}Cl_{5}(H_{2}O)]^{2-} + Cl^{-} \quad (ii)$$

(C₁) (C₂)

$$C_2 + CH_3C_6H_4SO_2NHBr = Complex(X)$$
 (iii)



Fig. 2. Plot of log k₁ against log [Ru(III) chloride]. [HClO₄] = 2.00×10^{-2} M, [Bromamine-T] = 2.00×10^{-3} M, A \rightarrow [n-Propanol] = B \rightarrow [n-Butanol] = 2.00×10^{-2} M, [Cl⁻] = 5.00×10^{-2} M.

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Temp./°C	Ionic	{[CI⁻]/M	10 ³ k ₁ /min ⁻¹	
	strength $(\mu)/M$		n-Propanol	n-Butanol
30	0.08	0.05	7.77	8.63
35	0.08	0.05	10.80	11.79
40	0.08	0.05	14.10	16.11
45	0.08	0.05	21.56	22.39
35	0.09	0.05	10.82	11.80
35	0.10	0.05	10.81	11.82
35	0.12	0.05	10.80	11.78
35	0.15	0.05	10.78	11.77
35	0.20	0.05	10.79	11.79
35	0.25	0.05	10.80	11.80
35	0.30	0.05	10.81	11.80
35	0.50	0.05	10.80	11.81
35	0.58	0.05"	32.41	39.36
35	0.58	0.08"	20.82	26.45
35	0.58	0.10"	17.05	22.26
35	0.58	0.20"	10.80	12.73
35	0.58	0.30"	8.57	9.80
35	0.58	0.50"	7.13	8.08
35°	0.08	0.05	10.78	11.82
35°	0.08	0.05	10.80	11.79
		0.05	10.81	11.80
35 ^d	0.08	0.05		

Table 2. [Bromamine-T] = 2.00×10^{-3} M, [HClO₄] = 2.00×10^{-2} M [Ru-(III) chloride] = 0.88×10^{-6} M, [n-Propanol] = [n-Butanol] = 2.00×10^{-2} M

 $d \rightarrow [CH_3C_4H_4SO_2NH_2] = 1.50 \times 10^{-3} M$ $e \rightarrow [CH_3C_4H_4SO_2NH_2] = 2.00 \times 10^{-3} M$ $(X) + R'CH_2OH \xrightarrow{k_2} - \frac{d}{Slowest}$

(S)
$$\frac{Stowest}{4}$$

rate determining step
[Ru^{III}Cl₅(H₂O)]²⁻ + R'CHO + H⁺ + Br⁻
+ CH₃C₆H₄SO₂NH₂ (iv)

$$\begin{array}{c} R'CHO \xrightarrow{R_3} R'COOH + Other products. (v) \\ Ru(III) ppecies + BAT \\ (fast) \end{array}$$

Where R' is $-C_2H_5$ (in n-propanol) and $-C_3H_7$ (in n-butanol). The total [Ru(III)] may be written as eqn (5).

$$[Ru(III)]_{T} = [C_1] + [C_2] + [X].$$
(5)

The value of [X] may be determined on solving eqn (5) in terms of [X] with the help of steps (II) and (III) and may be written as eqn (6) with reasonable assumption $1 \ge K_3[BAT']$

$$[X] = \frac{K_2 K_3 [Ru(III)]_{H} [BAT] [H_2 O]}{[CI^-] + K_2 [H_2 O]}.$$
 (6)

Considering stoichiometric data, the rate of the reaction as measured by the consumption of bromamine-T, is given by eqn (7).

$$\frac{-\mathrm{d}[\mathrm{BAT}]}{\mathrm{dt}} = 2k_2[\mathrm{X}][\mathrm{R'CH}_2\mathrm{OH}]. \tag{7}$$

The final rate law (8) may be written by considering step (i) and eqns (6) and (7).

$$-\frac{\mathrm{d}[\mathbf{B}\mathbf{A}^{T}]}{\mathrm{d}t} = \frac{2\mathbf{k}[\mathbf{B}\mathbf{A}^{T}][\mathbf{A}[\mathrm{cohol}][\mathbf{R}\mathbf{u}(\mathbf{I}\mathbf{I})]_{T}[\mathbf{H}^{+}]}{\mathbf{K}_{2}[\mathbf{H}_{2}\mathbf{O}] + [\mathbf{C}\mathbf{I}^{-}]}$$
(8)

where $\mathbf{k} = \mathbf{k}_2 \mathbf{K}_1 \mathbf{K}_2 \mathbf{K}_3 [\mathbf{H}_2 \mathbf{O}]$

The formation of corresponding aldehydes (R'CHO) in step (IV) was proved experimentally when in a separate experiment the corresponding aldehydes were observed to be rapidly oxidised under the same experimental conditions. The rate law (8) is in complete agreement with our kinetic observations and accords well with stoichiometry, negligible effect of ionic strength of the medium, insignificant effect of p-toluenesulphonamide and values of the activation parameters.

Structure of the complex formed in step (III) is not known but, in order to account for its hydride ion abstracting capacity, a cyclic structure (I) can be assigned:



It is clear from structure (I) that the electron density around the nitrogen atom in Nbromotoluene-p-sulphonamide is decreased and N-Br bond becomes weaker. Subsequently the electrophilic character and, therefore, the hydride ion abstracting capacity of N-bromotoluene-*p*sulphonamide is increased after complexation resulting in an interaction with the alcohol. Freeman and Scott¹¹ have also suggested that the oxidation of mandelic acid by alkaline permanganate proceeds either by a hydride ion transfer or a hydrogen atom abstraction from the mandelate dianion by permanganate and thus support the above mechanism.

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