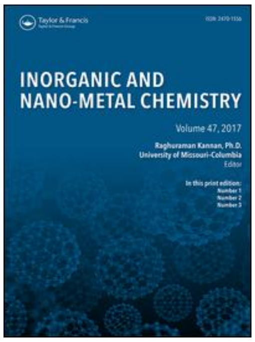

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Catalysis and mechanistic study of Ru(III) and Os(VIII) on the oxidation of taurine by BAT in acid and alkaline media: a kinetic modeling

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ABSTRACT

The study of oxidation kinetics of drug molecules is of much noteworthy in order to understand their mechanistic chemistry in redox systems. Taurine, being a potent drug molecule, has a wide range of activities in biological system. Therefore, the kinetics of oxidation of taurine (TAU) by bromamine-T (BAT) in HCl medium, catalyzed by Ru(III) and in NaOH medium, catalyzed by Os(VIII) has been investigated at 313 K. The rate law in acidic medium is: $\text{rate} = k[\text{BAT}]_t[\text{TAU}]^0[\text{Ru(III)}]^{0.95}[\text{H}^+]^{-0.67}$. But, it takes the form, $\text{rate} = k[\text{BAT}]_t[\text{TAU}]^{0.46}[\text{Os(VIII)}]^{0.89}[\text{OH}^-]^{-0.53}$ in basic medium. Addition of halide ions and p-toluenesulfonamide had no significant effect on the rate in both the cases. Decrease in dielectric constant of medium decreases the reaction rate in both the media. The conjugate acid, $CH_3C_6H_4SO_2NHBr$ (TsNHBr), is assumed to be the oxidizing species in both the media. Equilibrium and decomposition constants have been evaluated in each case.

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Oxidation kinetics; taurine; bromamine-T; Ru(III); Os(VIII)

Introduction

Haloamines gained importance as both bases and nucleophiles.[1] They can interact with wide range of functional groups. Bromamine-T (BAT) is a mild oxidant and one of the important members of organic haloamines group. Literature survey has confirmed many of its reactions with variety of substrates.[2–7] BAT, the bromamine analogue of chloramine-T, is known to be a better oxidizing agent than chloro compounds in acidic and alkaline media with two electron change per mole giving p-toluenesulfonamide or PTS ($CH_3C_6H_4SO_2NH_2$) and sodium bromide. According to the literature survey, less information is available on kinetics and mechanistic investigations of oxidation of biologically important compounds with BAT.

Taurine (2-aminoethenesulfonic acid) is an amino acid used as antihypertensive, hypoglycemic, and cardiac drug in pharmaceuticals. Therapeutically[8] also it finds applications for the treatment of variety of conditions which include cardiovascular diseases, epilepsy, seizure disorders, and muscular degeneration. Though it finds large number of applications in biological systems,[9–11] literature survey reveals no reports on the catalysis and mechanism of oxidation of this substrate by any of the oxidants viewed from the kinetic and mechanistic points. So, there was a need for understanding the oxidation and mechanism of this substrate in the presence of catalyst so that the study would give useful information on the kinetic and mechanistic chemistry of this drug in biological systems.

In recent years, Ru(III) and Os(VIII) have been extensively used as catalysts in several redox reactions,[12–18] particularly in acidic and alkaline media, respectively. Preliminary experiments revealed that the reactions between TAU and BAT were found to be ‘very slow’ to be measured in HCl and NaOH media. Alternatively, it was found that Ru(III) and Os(VIII) are excellent catalysts for the facile oxidation of TAU by BAT in acidic and alkaline media, respectively.

In the light of these viewed observations, the present investigations were undertaken. In this research, we report the detailed kinetics of TAU oxidation by BAT with Ru(III) and Os(VIII) catalysis in HCl and NaOH medium, respectively, in order to elucidate the plausible mechanism, to procure appropriate rate law, and also to appraise the reactivity of the catalysts.

Experimental

Materials

Bromamine-T was prepared as reported in the literature.[19] Its purity was checked by iodometry, UV and IR spectra. An aqueous solution of BAT was standardized iodometrically and was preserved in brown bottle to prevent any of its photochemical deterioration. Taurine (s.d.fine) was used as received and aqueous solutions of desired strength were prepared whenever required. $RuCl_3$ (Arora-Mathey) and OsO_4 (Johnson-Mathey) solutions were prepared in 0.05 mol/dm^3 HCl and 0.05 mol/dm^3 NaOH, respectively. Allowance for the amount of acid/alkali present in the catalyst solution was made, while preparing the reaction mixtures for kinetic runs. Heavy water (D_2O, 99.4%) was

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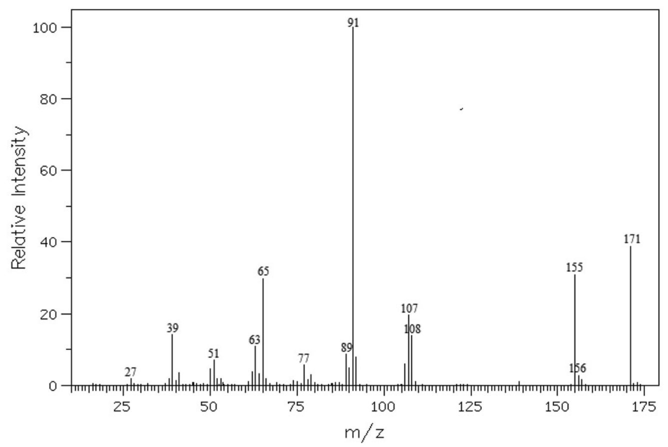


Figure 1. GC-mass spectra of p-toluenesulfonamide with its molecular ion peak at 171 amu.

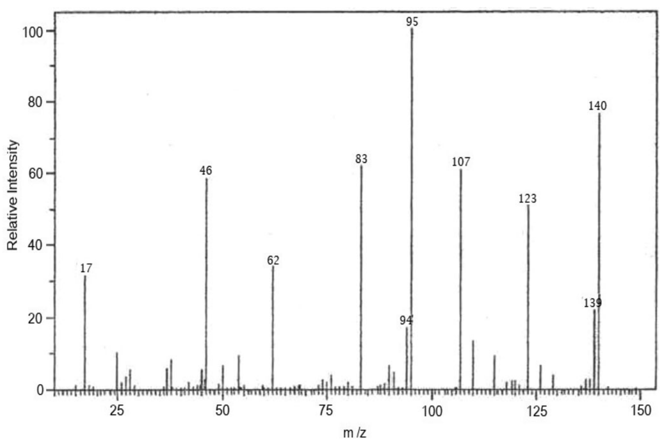


Figure 2. GC-mass spectrum of sulfoacetic acid with its molecular ion peak at 140 amu.

obtained from Bhabha Atomic Research Center, Mumbai, for studying the solvent isotope effect. The dielectric constant (D)[20] of the reaction mixture was altered by the addition of methanol in varying proportions (v/v). All the other reagents were of analytical grades of purity. The solutions of all reagents used in this work were freshly prepared with doubly distilled water before use.

Kinetic procedure

All kinetic runs were performed under pseudo-first order conditions of $[\mathrm{TAU}]_0 \gg [\mathrm{BAT}]_0$, at 313 ± 0.1 K. The reactions were carried out in glass-stoppered Pyrex boiling tubes whose outer surfaces were covered black to eliminate the photochemical effects. For each run, the requisite amount of substrate, HCl and Ru(III) (in acid medium), substrate, NaOH and Os(VIII) (in basic medium), and water (to maintain total volume constant for all runs) were introduced into the tube and thermostatted at 313 ± 0.1K for thermal equilibrium. A measured amount of oxidant (BAT) also thermostatted at the same temperature was added rapidly to the above mixture to initiate the reaction. The mixture was sporadically shaken to attain uniform concentration. The progress of the reaction was monitored by pipetting 5 ml of aliquot into ice cold water (containing known amount of KI and H_2SO_4 solutions) at regular intervals of time and titrating against standard sodium thiosulfate solution using starch indicator near the end point to determine unreacted BAT. The reaction was followed for more than two half-lives. The pseudo-first order rate constants (k' s^{-1}) calculated from the linear plots of log[BAT] verses time were reproducible to ±5%. The regression analysis of experimental data was carried out using scientific calculator, from which the regression coefficient 'r' was calculated.

Stoichiometry and product analysis

Reaction mixtures containing varying proportions of BAT to substrate in the presence of HCl/NaOH (0.6×10^{-2} mol/dm^3) and Ru(III)/Os(VIII) (1.93×10^{-5} mol/dm^3) were equilibrated at 313 K for 48 h. Determination of unreacted BAT revealed that one mole of TAU consumed two moles of BAT in both the media and confirmed by the following stoichiometric equation:

$$\begin{aligned} &\mathrm{NH_2{-}CH_2{-}CH_2{-}SO_3H} + \mathrm{2TsNBrNa} + \mathrm{2H_2O} \\ &\quad \rightarrow \mathrm{HOOC{-}CH_2{-}SO_3H} + \mathrm{2TsNH_2} + \mathrm{2Na^+} + \mathrm{2Br^-} \\ &\qquad + \mathrm{NH_3} \end{aligned} \tag{1}$$

where, Ts = p-$CH_3C_6H_4SO_2$–.

The reaction mixture was stirred for 24 h at 313 K. After the completion of reaction (monitored by TLC), the reaction products were neutralized by NaOH/HCl and extracted with ether. The products were separated by column chromatography on silica gel (60–200 mesh) using gradient elution (from dichloro methane to chloroform) and were detected as follows. The p-toluenesulfonamide (PTS: $TsNH_2$), reduction product of BAT, was detected by paper chromatography.[21] Benzyl alcohol saturated with water was used as the solvent with 0.5% vanillin in 1% HCl solution as spray reagent ($R_f = 0.905$). It was confirmed by its melting point 137–138 °C (lit. m.p. 137–140 °C) and GC-mass spectrum. The GC–MS data were obtained on 17A Shimadzu Gas Chromatography with a QP-5050 mass spectrometer using electron input ionizer technique. The mass spectrum showing a molecular ion peak at 171 amu (Figure 1) clearly confirms PTS. The oxidation product of taurine was found to be the sulfoacetic acid in both the media and was confirmed by GC–MS analysis. The mass spectrum showing a molecular ion peak at 140 amu (Figure 2) clearly confirms sulfoacetic acid.

Results and discussion

In order to find out the effect of concentration of oxidant on reaction rate, the oxidant concentration was varied at constant concentration of other ingredients. The plots of log[BAT] (0.2×10^{-3}–2.0×10^{-3} mol/dm^3) versus time were linear ($r > 0.9928$) depicting a first-order dependence of reaction rate on $[\mathrm{BAT}]_o$ for both Ru(III) and Os(VIII) catalyzed reactions. The pseudo-first order rate constants, k', are listed in Table 1. Further, the values of k' are remain

Table 1. Effect of the concentration of TAU, BAT, H^+/OH^-, and catalyst on the rate of reaction at 313 K.

$10^3[BAT]_o$ (mol/dm^3)	$10^2[TAU]_o$ (mol/dm^3)	$10^2[H^+/OH^-]$ (mol/dm^3)	10^5[Catalyst] (mol/dm^3)	10^4 k' (s^{-1}) Ru(III)	Os(VIII)
0.2	1.0	0.6	1.93	3.72	5.45
0.5	1.0	0.6	1.93	3.99	5.21
1.0	1.0	0.6	1.93	3.84	5.37
1.5	1.0	0.6	1.93	3.81	5.51
2.0	1.0	0.6	1.93	3.69	5.45
1.0	**0.2**	0.6	1.93	3.73	2.58
1.0	**0.5**	0.6	1.93	3.61	3.89
1.0	**1.0**	0.6	1.93	3.84	5.37
1.0	**2.0**	0.6	1.93	3.78	7.21
1.0	**3.0**	0.6	1.93	3.69	8.91
1.0	1.0	**0.2**	1.93	7.89	9.51
1.0	1.0	**0.4**	1.93	4.98	6.60
1.0	1.0	**0.6**	1.93	3.84	5.37
1.0	1.0	**0.8**	1.93	3.05	4.65
1.0	1.0	**1.0**	1.93	2.68	4.02
1.0	1.0	0.6	**0.48**	0.79	1.45
1.0	1.0	0.6	**0.96**	1.58	2.85
1.0	1.0	0.6	**1.93**	3.84	5.37
1.0	1.0	0.6	**3.86**	6.81	9.87
1.0	1.0	0 6	**5.78**	10.02	14.3

Values in bold letters indicate the variation of concentration of that particular reactant while the concentration of other reactants kept constant.

constant with the variation in $[BAT]_o$, confirming the first-order dependence of rate on $[BAT]_o$ in both the cases. Under similar experimental conditions, an increase in $[TAU]_o$ did not alter the k' values, indicating that the rate was independent of $[TAU]_o$ (Table 1) in acidic medium catalyzed by Ru(III). But the values of k' found to be increased with an increase in $[TAU]_o$ in basic medium catalyzed by Os(VIII). The plot of $\log k'$ versus $\log[TAU]$ (0.2×10^{-2}–3.0×10^{-2} mol/dm^3) was linear ($r = 0.9998$) with a slope of 0.46 indicating a fractional order dependence of rate on $[TAU]_o$ (Table 1).

The rate was found to be decreased on the variation of concentration of medium (H^+/OH^-) (Table 1) keeping other experimental conditions constant. The plots of $\log k'$ versus $\log[H^+/OH^-]$ (0.2×10^{-2}–1.0×10^{-2} mol/dm^3) were linear ($r > 0.9995$) with the slopes of -0.67 and -0.53 in acid and alkaline medium, respectively, indicating a fractional inverse dependence of rate in both the media. An increase in [catalyst] (Table 1) led to increase the reaction rate in both the cases and the plots of $\log k'$ versus log[catalyst] (0.48×10^{-5}–5.78×10^{-5} mol/dm^3) were linear ($r > 0.9986$) with the slopes of 0.95 and 0.89, respectively, for Ru(III) and Os(VIII) catalysts indicating first-order dependence of rate on [catalyst].

The reaction rate was not affected by Cl^- or Br^- ions (0.4×10^{-2}–3.0×10^{-2} mol/dm^3) showed that no inter halogen is formed in the reaction in both the cases.

The effect of ionic strength on reaction rate of both Ru(III) and Os(VIII) catalysis was studied by varying the concentration of $NaClO_4$ (0.1–0.5 mol/dm^3) at constant concentration of all other reactants. The added $NaClO_4$ did not affect the reaction rate significantly, indicating the non-ionic species involvement in the rate-limiting step of both Ru(III) catalyzed and Os(VIII) catalyzed reactions. Hence, no attempt was made to keep the ionic strength of the medium constant for kinetic runs in both the cases.

Table 2. Effect of varying dielectric constant of the medium on reaction rate at 313 K.

%MeOH (v/v)	D	10^4 k' (s^{-1}) Ru(III)^a	Os(VIII)^b
0	76.73	3.84	5.37
10	72.37	3.16	4.37
20	67.48	2.56	3.51
30	62.71	2.06	2.69

^{a}Experimental conditions: $[BAT]_o = 1.0 \times 10^{-3}$ mol/dm^3; $[TAU]_o = 1.0 \times 10^{-2}$ mol/dm^3; $[HCl] = 0.6 \times 10^{-2}$ mol/dm^3; $[Ru(III)] = 1.93 \times 10^{-5}$ mol/dm^3; $T = 313$ K.

^{b}Experimental conditions: $[BAT]_o = 1.0 \times 10^{-3}$ mol/dm^3; $[TAU]_o = 1.0 \times 10^{-2}$ mol/dm^3; $[NaOH] = 0.6 \times 10^{-2}$ mol/dm^3; $[Os(VIII)] = 1.93 \times 10^{-5}$ mol/dm^3; $T = 313$ K.

The effect of dielectric constant 'D' of the medium on reaction rate was studied by adding MeOH (0–30%, v/v) to the reaction mixture. A decrease in the rate (Table 2) was observed with an increase in the MeOH content in both the cases and the plots of $\log k'$ versus $1/D$ were linear ($r > 0.9996$) with negative slopes indicating the negative ion–dipole interaction in the rate determining step of Ru(III) catalyzed reactions and dipole–dipole interaction in the rate-limiting step of Os(VIII) catalyzed reactions. The dielectric constant values for MeOH–H_2O mixtures were taken from the literature.[22]

As the rate was dependent both on $[H^+]$ and $[OH^-]$, solvent isotope studies were made in both the media using D_2O. The solvent isotope effect $k'(H_2O)/k'(D_2O)$ was found to be 1.10 and 1.16 for Ru(III) and Os(VIII) catalyzed reactions, respectively.

The effect of temperature on the rate of reaction for both Ru(III) and Os(VIII) catalyzed reactions was studied at different temperatures (303 - 323 K) keeping other experimental conditions constant. The values of activation parameters were computed from Arrhenius plots of $\log k'$ versus $1/T$ ($r > 0.9987$) for the overall reaction in each case and the results are presented in Table 3.

Mechanism and rate law for Ru(III) catalyzed reactions in acidic medium

According to the electronic spectral studies,[23,24] the different octahedral forms of Ru(III) chloride *viz.* $[RuCl_5(H_2O)]^{2-}$, $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$, and $[RuCl(H_2O)_5]^{+2}$ do not exist in aqueous solutions. Although, the following equilibrium exist for Ru(III) in acidic solutions:[25–27]

$$RuCl_3 \cdot nH_2O + 3HCl \rightarrow [RuCl_6]^{3-} + nH_2O + 3H^+ \tag{2}$$

$$[RuCl_6]^{3-} + H_2O \leftrightarrow [RuCl_5(H_2O)]^{2-} + Cl^- \tag{3}$$

The above equilibrium has been employed in many redox reactions catalyzed by Ru(III) in acid medium.[28,29] Since no effect of chloride ion on reaction rate is observed in the present study, equilibrium (3) does not play any role in the reaction. Hence, the complex ion, $[RuCl_5(H_2O)]^{2-}$ is assumed to be the most likely catalyzing species which reacts

Table 3. Temperature dependence and activation parameters for Ru(III) and Os(VIII) catalyzed and uncatalyzed oxidation of taurine by BAT in acidic and basic media, respectively.

Temperature (K)	$k' \times 10^4$ (s^{-1})		Activation parameters	Values	
	Ru(III)[a]	Os(VIII)[b]		Ru(III)[a]	Os(VIII)[b]
303	1.41 (0.08)	2.27 (0.07)	E_a (kJ mol^{-1})	73.8 (82.8)	65.6 (85.9)
308	2.23 (0.13)	3.36 (0.11)	$\Delta H^{\#}$ (kJ mol^{-1})	71.4 (80.2)	62.9 (83.3)
313	3.84 (0.24)	5.37 (0.19)	$\Delta S^{\#}$ (J K^{-1} mol^{-1})	−83.2 (−78.2)	−107 (−70.0)
318	5.84 (0.40)	7.90 (0.32)	$\Delta G^{\#}$ (kJ mol^{-1})	97.4 (106)	96.5 (105)
323	9.26 (0.64)	12.21 (0.55)	–	–	–

Values in parenthesis refer to uncatalyzed reactions. Similar experimental conditions as above were employed for uncatalyzed reactions except catalyst.

[a] Experimental conditions for catalyzed reactions: $[BAT]_o = 1.0 \times 10^{-3}$ mol/dm^3; $[TAU]_o = 1.0 \times 10^{-2}$ mol/dm^3; $[HCl] = 0.6 \times 10^{-2}$ mol/dm^3; $[Ru(III)] = 1.93 \times 10^{-5}$ mol/dm^3.

[b] Experimental conditions for catalyzed reactions: $[BAT]_o = 1.0 \times 10^{-3}$ mol/dm^3; $[TAU]_o = 1.0 \times 10^{-2}$ mol/dm^3; $[NaOH] = 0.6 \times 10^{-2}$ mol/dm^3; $[Os(VIII)] = 1.93 \times 10^{-5}$ mol/dm^3.

$$\mathrm{TsNH_2Br^+} \xrightleftharpoons{K_1} \mathrm{TsNHBr + H^+} \qquad \text{(i) fast}$$

$$\mathrm{TsNHBr + Ru(III)} \xrightarrow{k_2} \mathrm{(X)} \qquad \text{(ii) slow and r.d.s}$$

$$\mathrm{(X) + TAU} \xrightarrow{k_3} \mathrm{(X')} \qquad \text{(iii) fast}$$

$$\mathrm{(X') + TsNHBr} \xrightarrow{k_4} \mathrm{Products} \qquad \text{(iv) fast}$$

Scheme 1. General mechanism in acid medium.

with the oxidant species to form a complex intermediate (X).

The oxidizing species of acidified BAT solutions[30,31] are TsNHBr, $TsNBr_2$, HOBr, and H_2OBr^+. Since second-order dependence of rate on $[BAT]_o$ was not noticed in the present case, the involvement of $TsNBr_2$ as oxidizing species can be ruled out. On the other hand, since the added p-toluenesulfonamide ($TsNH_2$) did not alter the reaction rate, HOBr can also be ruled out as oxidizing species. Based on these kinetic results, TsNHBr is assumed to be the oxidizing species in the present study and in the presence of acid, TsNHBr further protonates to $TsNH_2Br^+$. But an inverse fractional order on $[H^+]$ suggested the deprotonation of $TsNH_2Br^+$ to regenerate TsNHBr, which is most likely the active oxidant species involved in the oxidation of taurine. Based on these facts, a general mechanism (Scheme 1) can be proposed for the Ru(III) catalyzed oxidation of taurine by BAT in acid medium to account the observed kinetics.

In Scheme 1, X and X′ represent complex intermediate species whose structures are shown in Scheme 2, where a detailed mechanistic interpretation of Ru(III) catalyzed TAU—BAT reaction in acidic medium has shown. In the initial fast equilibrium, the cation $TsNH_2Br^+$ is deprotonated to form TsNHBr. In the next rate-limiting step, TsNHBr reacts with the catalyst to form intermediate complex X. In the next fast step, the catalyst in complex X facilitates the nucleophilic attack of TAU on bromine of oxidant and undergoes subsequent hydrolysis to form intermediate complex X′ with the elimination of NH_3 and regenerating the catalyst. In the next fast step, complex X′ reacts with another mole of oxidant to yield the final product sulfoacetic acid.

Scheme 1 leads to the following rate law:

The total effective concentration of BAT is

$$[\mathrm{BAT}]_t = [\mathrm{TsNH_2Br^+}][\mathrm{TsNHBr}] \tag{4}$$

Solving for $[\mathrm{TsNH_2Br^+}]$ from step (i) of Scheme 1 and substituting in Equation (4), we get [TsNHBr] as

$$[\mathrm{TsNHBr}] = \frac{K_1[\mathrm{BAT}]_t}{[\mathrm{H^+}] + K_1} \tag{5}$$

Step (ii) of Scheme 1 determines the overall rate, so,

$$\text{rate} = -d[\mathrm{BAT}]/dt = k_2[\mathrm{TsNHBr}][\mathrm{Ru(III)}] \tag{6}$$

Substituting for [TsNHBr] from Equation (5) into Equation (6), the following rate law can be derived

$$\text{rate} = \frac{K_1 k_2 [\mathrm{BAT}]_t [\mathrm{Ru(III)}]}{K_1 + [\mathrm{H^+}]} \tag{7}$$

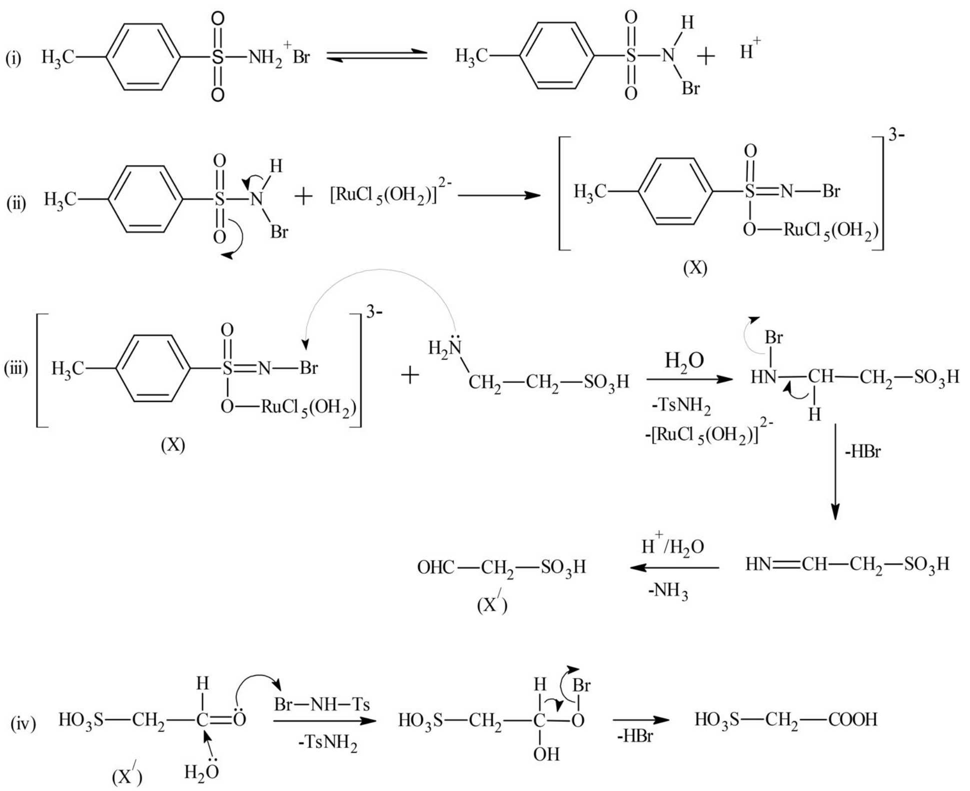
Above rate law is consistent with all the experimental results and can be written as:

$$\frac{1}{k'} = \frac{[\mathrm{H^+}]}{K_1 k_2 [\mathrm{Ru(III)}]} + \frac{1}{k_2[\mathrm{Ru(III)}]} \tag{8}$$

From Equation (8), plot of $1/k'$ versus $[H^+]$ (Figure 3) was found to be linear ($r = 0.9981$). From the slope and intercept of the above plot, the values of deprotonation constant K_1, protonation constant K_p ($1/K_1$), and decomposition constant k_2 have been evaluated and found to be 2.47×10^{-3} mol/dm^3, 4.1×10^2 dm^3/mol, and 69.1 dm^3/mol/s, respectively.

The proposed Scheme 1 and derived rate law (7) are substantiated by the following facts; a negative dielectric effect has been observed in the present studies indicating the negative ion–dipole interaction as seen in Scheme 2. For the limiting case of zero angle of approach between two dipoles or an ion–dipole system, the plot of log k' versus $1/D$ is linear[32] with negative slope for reaction between negative ion and a dipole or between two dipoles, while a positive ion and dipole interaction[33] results positive slope.

The observed retardation of reaction rate by solvent isotope effect in D_2O medium is due to the stronger acidity of D_3O^+ than hydronium ion.[34] No effect of added halide ions on the rate, indicating no inter halogen is formed. Addition of p-toluenesulfonamide has no significant effect on the rate, showing that it is not involved in any pre-equilibrium. The moderate values of $\Delta H^{\#}$ and $\Delta S^{\#}$ are favorable



Scheme 2. Oxidation of taurine by BAT in acidic medium catalyzed by $RuCl_3$.

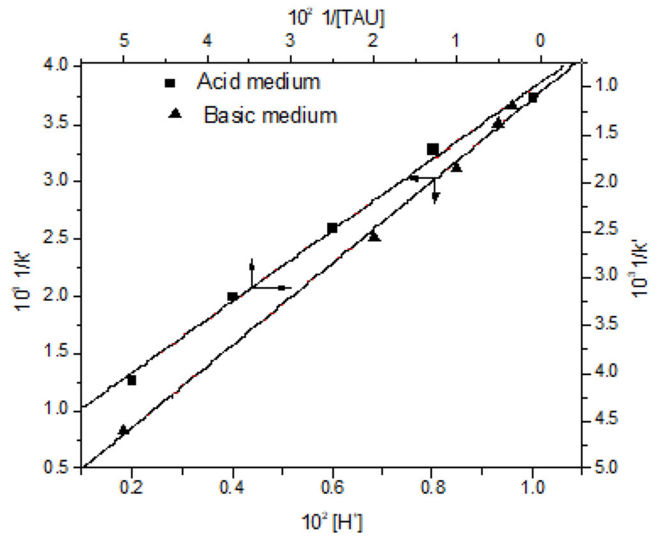


Figure 3. Plots of ■ $1/k'$ versus $[H^+]$ for Equation (8) and ▲ $1/k'$ versus $1/[TAU]$ for Equation (18).

$$TsNBr^- + H_2O \underset{}{\overset{K_5}{\rightleftharpoons}} TsNHBr + OH^- \qquad \text{(i) fast}$$

$$TsNHBr + TAU \overset{K_6}{\rightleftharpoons} (X^{//}) \qquad \text{(ii) fast}$$

$$(X^{//}) + OsO_4 \xrightarrow{k_7} (X^{///}) \qquad \text{(iii) slow and r.d.s}$$

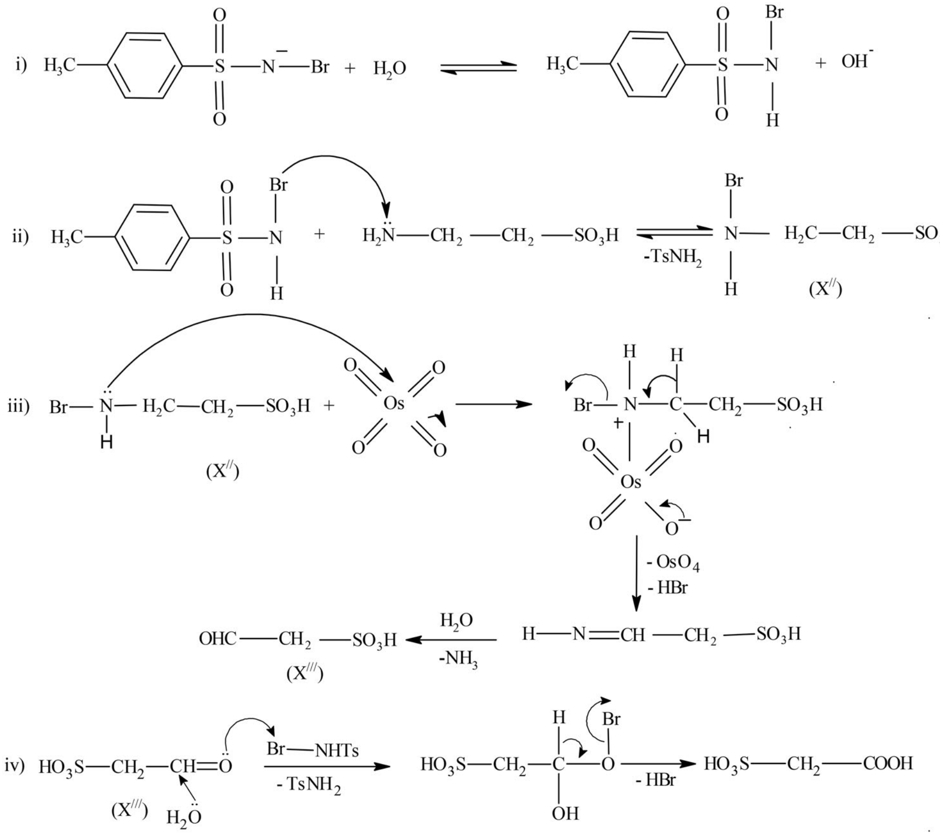
$$(X^{///}) + TsNHBr \xrightarrow{k_8} \text{Products} \qquad \text{(iv) fast}$$

Scheme 3. General mechanism in basic medium.

for electron transfer reaction. The fairly high positive value of $\Delta H^{\#}$ shows that the transition state is more solvated. The high negative value of $\Delta S^{\#}$ indicate that the intermediate complex is more ordered than the reactants.[35] The observed high rate constant for the slow step suggests that the oxidation presumably occurs *via* an inner-sphere mechanism. The activation parameters calculated for catalyzed and uncatalyzed reactions explain the catalytic effect on the reaction rate. The catalyst, Ru(III), form complex (X) with the oxidant and enhances the oxidizing property of the oxidant than that without catalyst. Further, the catalyst modifies the reaction path by lowering the energy of activation.

Mechanism and rate law for Os(VIII) catalyzed reactions in basic medium

The oxidation potential of haloamine–sulfonamide system is pH dependent and it decreases with an increase in pH of the medium. H_2OBr^+ does not exist at higher alkaline concentration.[36] An alkaline solution of BAT furnishes the oxidizing species[37] *viz.*, TsNHBr, $TsNBr^-$, HOBr, and OBr^-. The alkaline solutions where pH < 11, the most likely reactive species of BAT is TsNHBr. Further, it has been reported[38] that the retarding influence of OH^- ions on the rate of BAT reactions attributed to the formation of TsNHBr from $TsNBr^-$ in base retarding step. In the present investigations, HOBr as the oxidizing species is ruled out because of first-order retardation of rate was not noticed with the addition of $TsNH_2$ to the reaction mixture. Hence, the conjugate free acid TsNHBr is the most probable



Scheme 4. Oxidation of Taurine by BAT in alkaline medium catalyzed by OsO_4.

Table 4. Values of catalytic constant (K_c) at different temperatures and activation parameters calculated using K_c values.

Temperature (K)	K_c Ru(III)	K_c Os(VIII)	Activation parameters	Values Ru(III)	Values Os(VIII)
303	6.89	11.43	E_a (kJ mol^{-1})	70.25	63.87
308	10.88	16.89	$\Delta H^{\#}$ (kJ mol^{-1})	68.63	61.26
313	18.65	26.83	$\Delta S^{\#}$ (J K^{-1} mol^{-1})	−10.34	−22.52
318	28.19	39.26	$\Delta G^{\#}$ (kJ mol^{-1})	69.32	68.31
323	44.66	60.42	–	–	–

oxidizing species of BAT in the present study. A fractional order dependence of rate on $[TAU]_o$ indicates a pre-equilibrium before the rate-limiting step.

Osmium is stable in its +8 oxidation state and exists in the following equilibria:[39,40]

$$OsO_4 + OH^- + H_2O \leftrightarrow [OsO_4(OH)(H_2O)]^- \tag{9}$$

$$[OsO_4(OH)(H_2O)]^- + OH^- \leftrightarrow [OsO_4(OH_2)]^{2-} + H_2O \tag{10}$$

The species $[OsO_4(OH)(H_2O)]^-$ and $[OsO_4(OH_2)]^{2-}$ with octahedral geometries are likely to form coordination species with intermediate complex (X″) formed from taurine and oxidant. But, it is more convenient to postulate that OsO_4 with tetrahedral geometry can efficiently form complex with X″. Hence, bearing the preceding discussions in mind *viz.*, first-order dependence of rate on each of [BAT] and [Os(VIII)], inverse fractional order dependence of rate on $[OH^-]$ and fractional order on $[TAU]_o$, a general mechanism shown in Scheme 3 is proposed.

A detailed mechanistic interpretation of Os(VIII) catalyzed oxidation of TAU in NaOH medium is proposed in Scheme 4, in which the structure of intermediate species X″ and X‴ are depicted. In the initial fast equilibrium, the anion $TsNBr^-$ is protonated to form TsNHBr. In the next fast equilibrium, nucleophilic attack by the nitrogen of TAU on electron deficient bromine of the oxidant to form intermediate complex X″. In the next slow step, the complex X″ coordinates to the central metal of catalyst which activates X″ by stabilizing the charge on its nitrogen and X″ undergoes subsequent hydrolysis to form another intermediate complex X‴ with the elimination of NH_3 and regenerating the catalyst. In the next fast step, intermediate complex X‴ reacts with another mole of oxidant to form the final product sulfoacetic acid.

If $[BAT]_t$ denotes the total concentration of BAT, then,

$$[BAT]_t = [TsNBr^-] + [TsNHBr] + [X''] \tag{11}$$

From steps (i) and (ii) of Scheme 3, we have

$$[TsNBr^-] = \frac{[X''][OH^-]}{K_5K_6[TAU][H_2O]} \tag{12}$$

$$[TsNHBr] = \frac{[X'']}{K_6[TAU]} \tag{13}$$

Substituting for $[TsNBr^-]$ and [TsNHBr] from Equations (12) and (13) into Equation (11), solving for $[X'']$, one can get,

$$[X''] = \frac{K_5K_6[BAT]_t[TAU][H_2O]}{[OH^-] + K_5[H_2O] + K_5K_6[TAU][H_2O]} \tag{14}$$

From rate-limiting step (iii),

$$\text{rate} \ = k_7[X''][Os(VIII)] \tag{15}$$

Substituting for $[X'']$ from Equation (14) into Equation (15) and solving, we get

$$\text{rate} \ = \frac{K_5K_6k_7[BAT]_t[TAU][Os(VIII)][H_2O]}{[OH^-] + K_5[H_2O] + K_5K_6[TAU][H_2O]} \tag{16}$$

Since rate $= k'[BAT]_t$, under pseudo-first order conditions of $[TAU]_o \gg [BAT]_o$, rate law (16) can leads to Equation (17)

$$k' = \frac{K_5K_6k_7[TAU][Os(VIII)][H_2O]}{[OH^-] + K_5[H_2O] + K_5K_6[TAU][H_2O]} \tag{17}$$

The rate law (17) is in good agreement with all the observed results and it can be rewritten as:

$$\frac{1}{k'} = \frac{[OH^-] + K_5}{K_5K_6k_7[TAU][Os(VIII)]} + \frac{1}{k_7[Os(VIII)]} \tag{18}$$

The double reciprocal plot of $1/k'$ versus $1/[TAU]$ (Figure 3) of Equation (18) is linear ($r = 0.9830$) and from the intercept, the value of decomposition constant (k_7) has been evaluated and found to be $1.8\,dm^3/mol/s$. If K_5 is assumed to be small, the slope $([OH^-] + K_5)/K_5K_6k_7[TAU][Os(VIII)]$ of Equation (18) becomes $[OH^-]/K_5K_6k_7[TAU][Os(VII)]$. From this slope, the value of K_5K_6 is calculated and found to be $0.80\,dm^3/mol$.

The proposed Scheme 3 and derived rate law (16) are supported by the following facts; the negative dielectric effect observed indicates the dipole–dipole interaction in the rate determining step. The solvent isotope effect $k'(H_2O)/k'(D_2O) > 1$ in Os(VIII) catalyzed reaction, is generally correlated with greater basicity of OD^- as compared to OH^-.[41,42] The mechanism is supported by the moderate values of energy of activation and thermodynamic parameters (Table 3). The fairly high positive values of free energy of activation and enthalpy of activation indicating the transition state is more solvated. The high rate constant for the slow step indicates that the oxidation presumably occurs *via* an inner-sphere mechanism.[43,44] The activation parameters calculated for catalyzed and uncatalyzed reactions explain the catalytic effect on the reaction rate. The catalyst, Os(VIII), coordinates to the complex (X'') and activates it by stabilizing the charge on its nitrogen than that without catalyst.

It has been observed by Moelwyn-Hughes[45] that in the presence of catalyst, the uncatalyzed and catalyzed reactions proceed simultaneously so that:

$$k_1 = k_0 + K_C[\text{catalyst}]x \tag{19}$$

Here, k_1 and k_0 are the rate constants for catalyzed and uncatalyzed reactions, respectively, Kc is catalytic constant and x is the order of the reaction with respect to catalyst. In the present studies, '*x*' value was found to be unity for both Ru(III) and Os(VIII) catalysts. From the calculated values of K_C at different temperatures, the corresponding activation parameters (Table 4) have been deduced from the linear plots of $\log Kc$ versus $1/T$ ($r > 0.9998$). Further, for standard run at 313 K, plots of k' versus [Ru(III)] and k' versus [Os(VIII)] were found to be linear ($r > 0.9986$) leading to an intercept equal to $0.21 \times 10^{-4}\,s^{-1}$ and $0.16 \times 10^{-4}\,s^{-1}$ for Ru(III) and Os(VIII), respectively. These values are highly comparable with the rate constants obtained experimentally for the uncatalyzed reactions at 313 K (Table 3). This indicates that both catalyzed and uncatalyzed reactions proceed in parallel way. Furthermore, the observed kinetic results indicate that the Ru(III) and Os(VIII) catalyzed reactions are, respectively, about 16-fold and 28-fold faster than their corresponding uncatalyzed reactions. The difference in the reactivity of Ru(III) and Os(VIII) catalysts toward the oxidation of TAU by BAT is due to the electrons present in the d-orbital. The greater efficiency of osmium to catalyze the oxidation of TAU by BAT is because of its d^o electronic configuration as compared to ruthenium having d^5 electronic configuration. Thus, the catalytic efficiency of metal ion decreases as the number of electrons in the d-orbital increases.[46] As seen in Schemes 2 and 4 the metal ion undergoes reduction momentarily when it is attached to oxidant/oxidant–substrate complex and after this the metal ion comes back to its original state. Hence, in the present study the observed trend is based on the d electronic configuration of the metal ions.

Conclusion

The kinetics of oxidation of taurine by BAT in HCl medium, catalyzed by Ru(III), and in NaOH medium, catalyzed by Os(VIII) has been studied at 313 K. The stoichiometry and oxidation products are same in both the media. But, their kinetic and mechanistic behaviors are found to be different under identical set of experimental conditions. Suitable reaction schemes and kinetic models have been designed in both the cases. Thermodynamic parameters have been evaluated for catalyzed and uncatalyzed reactions. Catalytic constants and activation parameters are also calculated with reference to Ru(III) and Os(VIII) catalysts. The observed kinetic results indicate that Ru(III) and Os(VIII) catalyzed reactions are 16-fold and 28-fold faster than the uncatalyzed reactions. This difference in the efficiency of catalysts in catalyzing the TAU-BAT redox system is attributed to the difference in d electronic configuration of metal ions. Further, it can be concluded that Ru(III) and Os(VIII) act as efficient catalysts for the oxidation of taurine in acid and alkaline media, respectively.

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Disclosure statement

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