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Catalytic Activity of Os(VIII) on the Oxidation of Sulfadiazine with Alkaline Chloramine-T: Kinetic and Mechanistic Chemistry

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ABSTRACT

Sulfadiazine [SD: 4-amino-N-(2-pyrimidinyl) benzenesulfonamide] is a sulfonamide antibiotic and is commonly used to treat urinary track infections. Literature survey revealed that there are no efforts being made from the kinetic and mechanistic viewpoints of this drug and also no one has examined the role of platinum group metal ions as catalyst for the oxidation of SD drug. The chemistry of chloramine-T (CAT) has evinced considerable interest due to its diverse behavior. For these reasons, we have taken up a systematic kinetic study on the oxidation of SD drug with CAT in aqueous alkaline medium catalyzed by Osmium tetroxide (Os (VIII)) at 303 K in order to unfold the mechanistic picture of this redox system. The reaction shows a first-order dependence of rate each on $[CAT]_o$ and [Os(VIII)], and less than unity order dependence on both $[SD]_o$ and [NaOH]. The reaction was subjected to changes in (i) ionic strength, ii) NaCl and iii) p-toluenesulfonamide, and the effect of these on the rate of the reaction have been investigated. The reaction fails to induce the polymerization of acrylonitrile. The reaction was studied at different temperatures and activation parameters have been evaluated. Oxidation products were identified by GC-MS analysis. Os(VIII) catalyzed reaction was found to proceed about nine-fold faster than the unanalyzed reaction and hence it justifies the use of Os(VIII) catalyst in the present redox system. The observed results have been explained by a plausible mechanism and the related rate law has been formulated.

Keywords: Chloramine-T, Sulfadiazine, Os (VIII) catalysis, Oxidation-kinetics, Mechanism.

INTRODUCTION

Sulfadiazine [SD] is a sulfonamide antibiotic which is widely used in the treatment of urinary-tract-infections, pneumocystis, pneumonia, chronic bronchitis and toxoplasmosis [1]. Hence, it finds extensive applications in pharmaceutical industries. It is noted that despite the importance of this drug, there seems to be no reports available on the oxidation of this drug by any oxidant from its kinetic and mechanistic aspects. Additionally, no one has examined the catalytic activity of platinum metal ions on the oxidation of this drug.

The chemistry of sodium-N-haloarenesulfonamidates (N-haloamines) has evinced keen interest, as they are the precursors of halonium cations, hypohalite species, and N-anions which are capable of acting both as

bases and as nucleophiles [2]. Consequently, these compounds react with a wide range of functional groups affecting an array of molecular transformations [3-11]. The prominent member of this class of compounds is sodium N-chloro-p-toluenesulfonamide, commonly known as chloramine-T (CAT), is a well known analytical/oxidizing reagent. Chloramine T is a mild, efficient, stable and inexpensive oxidant [5], and the kinetic and mechanistic aspects of this reagent have been well documented [3-11].

Platinum metal ion catalyzed reactions from its use in many important industrial processes have generated an interest among researchers due to their significance in understanding the mechanistic chemistry of a particular redox reaction [12]. The mechanism of catalysis is quite complicated due to the formation of different intermediate complexes, free radicals, and different oxidizing states. Various platinum metal ions such as osmium(VIII) oxide, ruthenium(III) chloride, palladium(II) chloride, platinum(IV) chloride and iridium(III) chloride have been extensively employed as homogeneous catalysts in many redox reactions and some of these systems have been proved suitable for kinetic analysis [7,13-14]. Among platinum metal ions, Os (VIII) is the most effective catalyst in alkaline medium and has been widely used as catalyst in many redox reactions [8, 13].

Our preliminary kinetic studies revealed that the SD-CAT redox reaction is sluggish to be measured kinetically in alkaline medium. However, a trace quantity of Os (VIII) catalyst brings about rapid oxidation to a large extent. In view of this, we have taken up a systematic kinetic study on the oxidation of SD with CAT in NaOH medium with Os (VIII) as a catalyst in order to understand the mechanistic aspects of this redox system. The other aim of the study is to formulate the kinetic modeling and also to get a glimpse of the catalytic redox chemistry of this reaction in presence of Os (VIII) catalyst.

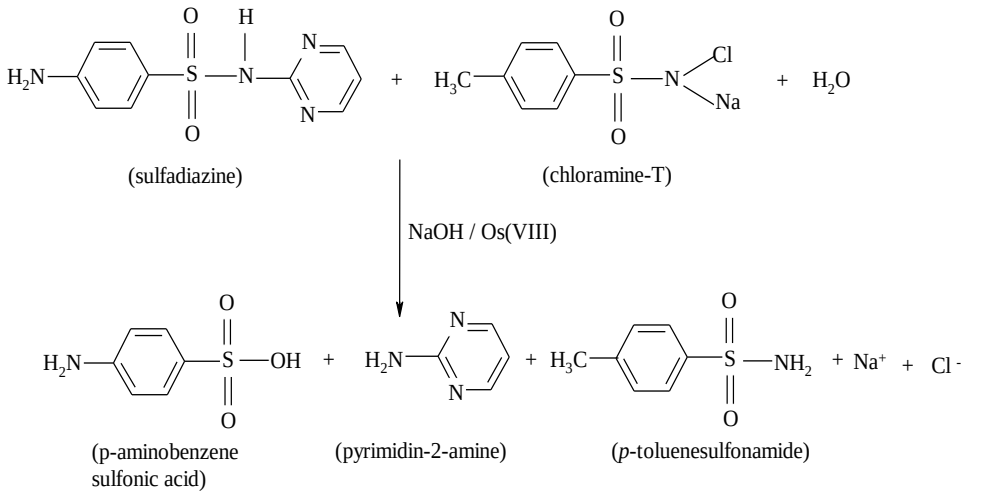
MATERIALS AND METHODS

Materials: The drug sulfadiazine (Aldrich) of analytical grade purity was used as obtained. Aqueous solutions of desired strength of the drug were prepared and employed. Chloramine T (Merck) was purified by the method mentioned in Morris *et al* [15]. An aqueous solution of CAT was prepared, standardized iodometrically and stored in amber colored bottles until further use. The concentration of stock solutions was periodically checked. All other chemicals used were of Analytical grade. Double distilled water was used throughout the work. The regression coefficients (R^2) were calculated for all linear plots using fx-100Z scientific calculator.

Kinetic measurements: The kinetic experiments were performed under pseudo-first-order conditions by keeping an excess of $[SD]_o$ over $[CAT]_o$. The kinetic runs were carried out in glass stoppered Pyrex boiling tubes whose outer surface was coated black to eliminate photochemical effects. Appropriate amounts of the drug, NaOH, Os (VIII) solutions and water (to maintain a constant total volume of 50 mL) were taken in a boiling tube and thermostated at 303 K for thermal equilibrium. A known amount of CAT solution also thermostated at the same temperature was rapidly added to the mixture in the boiling tube. The mixture was periodically shaken to ensure uniform concentration and the progress of the reaction was monitored by iodometric determination of unreacted CAT in a measured aliquot (5 mL each) of the reaction mixture at different intervals of time. The course of the reaction was studied for more than two half-lives. The pseudo-first-order rate constants ($k^{/}$ s^{-1}), calculated from linear plots of log [CAT] versus time were reproducible within 2-6%.

RESULTS AND DISCUSSION

Stoichiometry: The stoichiometry of the reaction was determined by equilibrating varying ratios of $[CAT]_o$ and $[SD]_o$ in presence of 6.0×10^{-2} mol dm^{-3} NaOH and 8.0×10^{-6}mol dm^{-3} Os(VIII) at 303 K for 24 h and then by determining the unreacted oxidant by iodometry. The results obtained indicate that one mole of SD required one mole of CAT and hence the following stoichiometric equation can be formulated.



(1)

Product analysis: The reaction mixture in the stoichiometric ratio was allowed to progress for 24 h in presence of NaOH and Os (VIII) catalyst at 303 K under stirred conditions. After completion of the reaction (monitored by TLC), the reaction products were neutralized with dilute $HClO_4$ and extracted with ethyl acetate. Separation of oxidation products was achieved using silica gel (60-100 mesh) column chromatography using hexane/ethyl acetate (8:6 v/v) as mobile phase. The oxidation products were identified as *p*-aminobenzensulfonic acid and pyrimidin-2-amine which were confirmed by GC-MS analysis. GC-MS data were obtained on a 17A Shimadzu gas chromatograph with a QP-5050 Shimadzu mass spectrometer. The mass spectra showed a molecular ion peak at 173 and 95amu, clearly conforming *p*-aminobenzenesulfonic acid and pyrimidin-2-amine, respectively (Figures 1 and 2). It was also noticed that there was no further reaction of these oxidation products under the present set of experimental conditions. The reduction product of CAT, *p*-toluenesulfonamide (PTS or $TsNH_2$), was extracted with ethyl acetate and detected by paper chromatography [10] using $PhCH_2OH$ saturated with H_2O as the solvent with 0.5% vanillin in 1% HCl solution in EtOH as the spray reagent (R_f = 0.905).

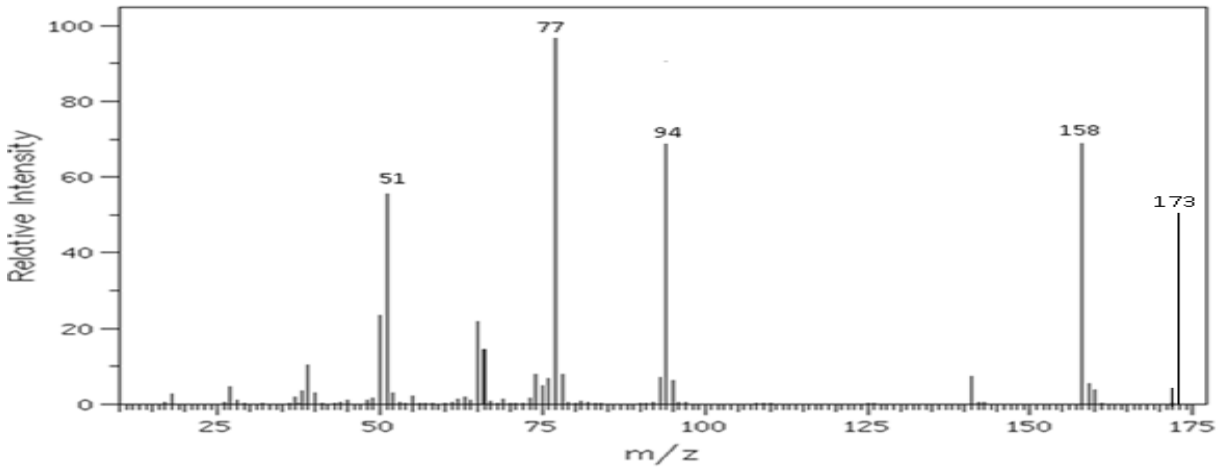


Figure 1: Mass spectrum of *p*-aminobenzenesulfonic acid with its molecular ion peak at m/z 173 amu.

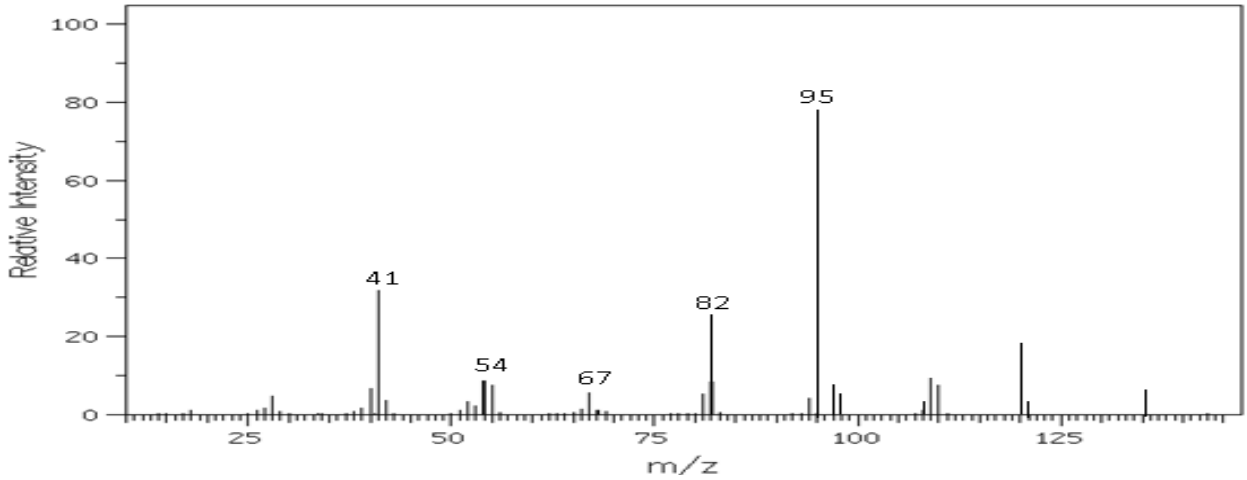


Figure 2: Mass spectrum of pyrimidin-2-amine with its molecular ion peak at m/z 95 amu.

Kinetic orders: The oxidation of sulfadiazine SD with CAT has been kinetically investigated at several initial concentrations of the reactants in the presence of NaOH and Os (VIII) catalyst at 303 K. The following effects on the rate of the reaction have been studied.

Effect of concentration of CAT on the reaction rate: The reaction carried out in the presence of NaOH and Os(VIII) catalyst, under pseudo-first-order conditions of $[SD]_o \gg [CAT]_o$, gave linear plots of log[CAT] versus time ($R^2 > 0.9914$). The linearity of these plots together with the consistency of the slopes obtained at various $[CAT]_o$, indicate a first-order dependence of the reaction rate on $[CAT]_o$. The pseudo-first-order rate constants ($k^/s^{-1}$) obtained are reported in table 1.

Effect of concentration of SD on the reaction rate: Under the similar experimental conditions, an increase in $[SD]_o$ increased the $k^/$ values (Table 1). A plot of log $k^/$ versus log [SD] was linear ($R^2 = 0.9835$) with a slope of 0.58, showing a fractional-order dependence of rate on $[SD]_o$. Further, a plot of $k^/$ versus [SD] was linear ($R^2 = 0.9910$) with a y-intercept, confirming the fractional-order dependence of rate on $[SD]_o$.

Effect of concentration of NaOH on the reaction rate: The rate increases with increase in [NaOH] (Table 1) and a plot of log $k^/$ versus log [NaOH] was linear ($R^2 = 0.9962$) with a slope of 0.60. This indicates a fractional-order dependence of rate on [NaOH].

Effect of concentration of Os(VIII) on the reaction rate: The reaction rate increased with increase in [Os(VIII)] (Table 1) and a log-log plot of $k^/$ and [Os(VIII)] yields a straight line with unity slope, suggesting the first-order dependence of rate on [Os(VIII)].

Effect of concentration of *p*-toluenesulfonamide on the reaction rate: Addition of 5.0×10^{-3} mol dm^{-3} *p*-toluenesulfonamide (PTS) to the reaction mixture did not alter the rate of the reaction. This indicates that PTS is not involved in any step prior to the rate-determining step in the scheme proposed.

Effect of concentration of NaCl on the reaction rate: Addition of Cl^- ion in the form of NaCl (2.0×10^{-3} mol dm^{-3}) had no significant effect on the rate of the reaction, suggesting that no interhalogen compound or free chlorine was formed in the reaction sequence.

Effect of ionic strength on the reaction rate: The effect of the ionic strength of the medium was studied by adding 0.20 mol dm^{-3} $NaClO_4$ solution to the reaction mixture. It was found that ionic strength has a negligible effect on the reaction rate. Hence, the ionic strength of the system was not kept constant for kinetic runs.

Table 1: Effect of varying $[CAT]_o$, $[SD]_o$, [NaOH] and [Os(VIII)] on the rate of the reaction at 303 K.

$[CAT]_o \times 10^4$ (mol dm^{-3})	$[SD]_o \times 10^3$ (mol dm^{-3})	$[NaOH] \times 10^2$ (mol dm^{-3})	$[Os(VIII)] \times 10^6$ (mol dm^{-3})	$k^{/} \times 10^4 (s^{-1})$
0.5	4.0	6.0	8.0	3.27
0.8	4.0	6.0	8.0	3.25
1.2	4.0	6.0	8.0	3.30
1.5	4.0	6.0	8.0	3.38
2.0	4.0	6.0	8.0	3.22
1.2	0.2	6.0	8.0	2.15
1.2	0.4	6.0	8.0	3.30
1.2	0.8	6.0	8.0	5.68
1.2	1.5	6.0	8.0	6.90
1.2	2.5	6.0	8.0	8.10
1.2	4.0	2.0	8.0	1.65
1.2	4.0	4.0	8.0	2.52
1.2	4.0	6.0	8.0	3.30
1.2	4.0	10.0	8.0	4.82
1.2	4.0	20.0	8.0	6.50
1.2	4.0	6.0	2.0	0.85
1.2	4.0	6.0	4.0	1.62
1.2	4.0	6.0	8.0	3.30
1.2	4.0	6.0	16.0	6.54
1.2	4.0	6.0	25.0	10.82

Effect of varying temperature on the reaction rate: The reaction was studied at different temperatures (298-313 K) by keeping other experimental conditions constant. From the linear Arrehenius plot of log $k^{/}$ versus 1/T, values of activation parameters (Ea, $\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$ and log A) were computed. All these results are tabulated in table2.

Test for free radicals: Addition of the reaction mixture to aqueous acrylamide solution did not initiate polymerization indicating the non-involvement of free radicals.

Table 2: Effect of varying temperature on the rate of reaction and activation parameters for the oxidation of SD by CAT in alkaline medium catalyzed by Os(VIII).

Temperature (K)	$k^{/} \times 10^4 (s^{-1})$
298	2.12
303	3.30 (0.38)
308	5.04
313	13.2
E_a (kJ mol^{-1})	72.4
$\Delta H^{\neq}$ (kJ mol^{-1})	69.8
$\Delta G^{\neq}$ (kJ mol^{-1})	93.4
$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	-78.2
Log A	9.18

value in parenthesis refers to the uncatalyzed reaction.
$[CAT]_o = 1.2 \times 10^{-4}$ mol dm^{-3} : $[SD]_o = 4.0 \times 10^{-3}$ mol dm^{-3} : [NaOH] = 6.0×10^{-2}mol dm^{-3}: [Os(VIII)] = 8.0×10^{-6} mol dm^{-3}.

Reactive species of chloramine-T: Chloramine-T (TsNClNa) acts as an oxidizing agent in both acidic and alkaline media [16]. In general CAT undergoes a two electron change in its reactions forming the reduction products, p-toluenesulfonamide (PTS) and NaCl. The redox potential of CAT-PTS system is pH dependent and decreases with an increase in pH of the medium having values of 1.138V at pH 0.65, 0.778 V at pH 7.0, 0.614 V at pH 9.7 and 0.50 V at pH 12. Chloramine-T behaves like a strong electrolyte [16] and depending on the pH of the medium, it furnishes the following types of reactive species in solutions [15-19].

$$TsNClNa \rightleftharpoons TsNCl^- + Na^+ \quad (2)$$

$$TsNCl^- + H^+ \rightleftharpoons TsNHCl \quad (3)$$

$$2\ TsNHCl \rightleftharpoons TsNH_2 + TsNCl_2 \quad (4)$$

$$TsNHCl + H_2O \rightleftharpoons TsNH_2 + HOCl \quad (5)$$

$$TsNCl_2 + H_2O \rightleftharpoons TsNHCl + HOCl \quad (6)$$

$$HOCl \rightleftharpoons H^+ + ClO^- \quad (7)$$

$$HOCl + H^+ \rightleftharpoons H_2O^+Cl \quad (8)$$

(here Ts = $CH_3C_6H_4SO_2$-)

Therefore, the possible oxidizing species in acidified CAT solutions are TsNHCl, $TsNCl_2$, HOCl and possibly H_2O^+Cl. In alkaline solutions of CAT, $TsNCl_2$ does not exist and the predominant species are TsNHCl, $TsNCl^-$, HOCl and OCl^-. Out of the aforesaid four possible oxidizing species of CAT in alkaline medium, the reactive species in the present case will be decided by the observed kinetic results. Further, Hardy and Johnston [17] have reported the following equilibria in alkaline solutions of CAT:

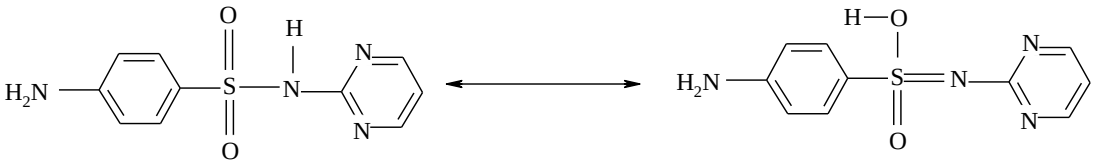
$$TsNCl^- + H_2O \rightleftharpoons TsNHCl + OH^- \quad (9)$$

$$TsNHCl + H_2O \rightleftharpoons TsNH_2 + HOCl \quad (10)$$

$$TsNHCl + OH^- \rightleftharpoons TsNH_2 + OCl^- \quad (11)$$

If TsNHCl, HOCl and OCl^- are considered to be the reactive oxidizing species, then the retardation of rate by the added $TsNH_2$ (p-toluenesulfonamide) and $[OH^-]$ would be expected according to Eqs. (9) – (11). No such effects were observed in the present case and hence these species can be ruled out as reactive oxidizing species. Therefore, the anion $TsNCl^-$ is most likely to be the oxidizing species in alkali accelerating reactions.

Reactive species of SD: The drug SD can tautomerize and exists in following two forms:



(Amide form) (Iminolic form)

In the present case, the drug SD reacts with CAT in its iminolic form

Reactive species of (Os (VIII): Osmium tetroxide is known to be an efficient catalyst in the oxidation of several organic compounds by various oxidants in aqueous alkaline medium [8,13]. It has been shown that osmium is stable in its +8 oxidation state and exists in the following equilibria [20].

$$OsO_4 + OH^- + H_2O \rightleftharpoons [OsO_4(OH)(H_2O)]^- \quad (12)$$

$$[OsO_4(OH)(H_2O)]^- + OH^- \rightleftharpoons [OsO_4(OH)_2]^{2-} + H_2O \quad (13)$$

The complexes $[OsO_4(OH)(H_2O)]^-$ and $[OsO_4(OH)_2]^{2-}$, which can be reduced to $[OsO_2(OH)_4]^{2-}$ with octahedral geometries seem to be less likely to form higher coordination species with the oxidant/substrate. It is more realistic to postulate OsO_4, which has tetrahedral geometry [21], as the active catalyst species that can effectively form a complex with the oxidant/substrate species.

Reaction scheme: Considering the above facts and all the experimental data the following mechanism (Scheme 1) may be suggested for Os(VIII) catalyzed oxidation of SD by CAT in alkaline medium.

$$\text{(i)}\ TsNHCl + OH^- \overset{K_1}{\rightleftharpoons} TsNCl^- + H_2O \qquad \text{fast}$$

$$\text{(ii)}\ TsNCl^- + SD \overset{K_2}{\rightleftharpoons} \text{Complex-I} \qquad \text{fast}$$

$$\text{(iii)}\ \text{Complex-I} + Os(VIII) \xrightarrow{k_3} \text{Complex-II} \qquad \text{slow and rds}$$

$$\text{(iv)}\ \text{Complex-II} \xrightarrow{k_4} \text{Products} \qquad \text{fast}$$

Scheme 1: A general reaction scheme for the oxidation of SD with CAT in presence of NaOH and Os (VIII) catalyst. The electron flow and structures of complexes I and II have been depicted in Scheme 2. In step (i) of Scheme 1, in alkali accelerating initial equilibrium fast step, the conjugate acid of CAT (TsNHCl) yields the reactive oxidizing species $TsNCl^-$. This anion, in the next fast pre-equilibrium step (step (ii)), reacts with the drug SD forming an intermediate complex-I. In the next slow/rds (step (iii)), complex-I interacts with the catalyst species and gives another intermediate complex-II. In the next fast step (step (iv)), complex-II hydrolyses to the formation of the ultimate products with the regeneration of catalyst.

Kinetic rate law: The kinetic rate law for the Scheme 1 can be formulated as follows:
The total effective concentration of CAT is

$$[CAT]_t = [TsNHCl] + [TsNCl^-] + [Complex\text{-}I] \quad (14)$$

By substituting for [TsNHCl]] and [$TsNCl^-$] from steps (i) and (ii) of Scheme 1 in Eq. (14) and solving for complex-I, we get

$$[Complex\text{-}I] = \frac{K_1K_2\,[CAT]_t\,[SD]\,[OH^-]}{[H_2O] + K_1[OH^-] + K_1K_2\,[SD]\,[OH^-]} \quad (15)$$

From the slow and rds of Scheme 1,

$$Rate = k_3\,[Complex\text{-}I]\,[Os(VIII)] \quad (16)$$

Upon substituting for [Complex-I] from Eq. (15) into Eq. (16), the following rate law is obtained:

$$Rate = \frac{K_1K_2k_3\,[CAT]_t\,[SD]\,[Os(VIII)]\,[OH^-]}{[H_2O] + K_1[OH^-] + K_1K_2\,[SD]\,[OH^-]} \quad (17)$$

The rate law (17) satisfies all the experimental observations, wherein first-order dependence of rate on each $[CAT]_o$ and [Os(VIII)], and fractional-order with respect to both $[SD]_o$ and [NaOH] were noted.

Catalytic efficiency of Os (VIII): In order to know the catalytic efficiency of Os (VIII) towards this redox system, the reaction was studied at 303 K with out Os(VIII) catalyst under the similar experimental conditions (Table 2). Os (VIII) catalyzed reaction was found to be about nine-fold faster than the uncatalyzed reaction. The catalyst Os (VIII) forms a complex (Complex-II) with the oxidant-substrate complex (Complex–I). This complex makes the reducing property of the substrate more effective than in the absence of catalyst. Further the Os (VIII) catalyst alters the reaction path by stabilizing the transition state, which in turn provides an alternate pathway having lower activation energy for the reaction. This justifies the use of Os (VIII) catalyst towards the present redox system.

Ionic strength effect: The proposed reaction mechanism is also evinced by the observed effect of ionic strength on the rate of the reaction. The primary salt effect on the reaction rates has been described by Bronsted and Bjerrum [22]. In the present case, neutral molecules are involved in the rate determining step (step (iii)) of Scheme 2. Hence, variation of ionic strength of the medium does not alter the rate and it is in accordance with the Bronsted -Bjerrum theory.

Activation parameters: The proposed mechanism and derived rate law are also supported by the moderate values of energy of activation and other thermodynamic parameters. The fairly high positive values of free energy of activation and enthalpy of activation indicate that the transition state is highly solvated. The high negative entropy of activation suggests the formation of a rigid associative transition state with a reduction in the degree of freedom of molecules. The constancy of the rate constants on addition of $NaClO_4$, PTS and NaCl provide additional evidence for the reaction mechanism proposed.

APPLICATIONS

CIn the present research, the kinetic and mechanistic picture of SD-CAT redox system in presence of NaOH and Os (VIII) catalyst has been clarified to a large extent. The knowledge generated through this research would be beneficial to the researchers who are working on the kinetic and mechanistic aspects of the biological activity of SD drug.

CONCLUSIONS

The kinetics of oxidation of SD with CAT in presence of NaOH and Os(VIII) catalyst obeys the rate law :- $d[CAT]/dt = k[CAT]^1\,[SD]^{0.58}\,[NaOH]^{0.60}[Os(VIII)]^1$. Oxidation products were characterized. Activation parameters for the overall reaction have been computed. It was found that Os(VIII) catalyzed reaction is about nine–fold faster than the uncatalyzed reaction. Hence, it can be said that Os(VIII) is an efficient

catalyst in the facile oxidation of SD with CAT in alkaline medium. Suitable mechanism and appropriate rate law have been worked out to account for the observed kinetics.

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REFERENCES

[1] J. Fan, Y. Chem, S. feng, C. Ye and J. Wang, *Analytical sciences*, **2003**, 19, 419-421.
[2] M.M. Campbell and G. Johnson, *Chem. Rev*. **1978**, 78, 65-79.
[3] K.K. Banerji, B. Jayaram and D.S. Mahadevappa, *J. Sci. Ind. Res*. **1987**, 46, 65-76.
[4] E. Kolvari, A. Ghorbani-Choghamarani, P. Salehi, F. Shirni and M.A. Zolfigol, *J. Iran.Chem. Soc*. **2007,** 4, 126-174.
[5] G. Agnihothri, *Synlett*, **2005**, 18, 2857-2858.
[6] Puttaswamy and Nirmala Vaz, *Bull. Chem. Soc. Jpn*, **2003**, 76, 73-80.
[7] D.S. Mahadevappa, K.S. Rangappa, N.M.M. Gowda and B.T. Gowda. *J. Phy. Chem.* **1981**, 85, 3651–3658.
[8] R.V. Jagadeesh and Puttaswamy, *J. Phy. Org. Chem*. **2008**, 21, 844-858.
[9] Puttaswamy, Anu Sukhdev and J.P. Shubha, *J. Mole. Catal A: Chem.* **2010,** 332, 113-121.
[10] K.N. Vinod, Puttaswamy and K. N. N. Gowda, *Ind. Eng. Chem. Res*, **2010**, 49, 3137–3145.
[11] Nirmala Vaz, K.N. Vinod, Puttaswamy and N.M.M. Gowda, *Am. J. Chem*, **2012,** 2, 12-17.
[12] N. Kambo and S.K Upadhyay, *Indian J. Chem*, **2004**, 43A, 1210–1215.
[13] Puttaswamy and Nirmala Vaz, *Trans. Met. Chem*, **2003**, 28, 409-417.
[14] Puttaswamy, R.V. Jagadeesh, Nirmala Vaz and A. Radakrishna, *J. Mole. Catal A: Chem* **2005,** 229, 211-222.
[15] J. C. Morris, J.A. Salazar and M. A. Wineman, *J. Am. Chem. Soc*. **1948,** 70, 2036-2041.
[16] E .Bishop and V.J. Jennings, *Talanta*, **1958**, 1, 197-212.
[17] F. F. Hardy and J. P. Johnston *J. Chem. Soc. Perkin. Trans*, **1973**, 2, 742-746.
[18] M.M. Natarajan and V. Thyagarajan, *J. Chem. Soc. Perkin Trans*, **1975**, 2, 1590-1594
[19] B.G. Pryde and F.G. Soper, *J. Chem. Soc*, **1962,** 1582-1588.
[20] A. M. Mackay and R. A. Mackay, *Introduction to Modern Inorganic Chemistry*, IV edn. Pentice-Harl, Englewood Cliffs, USA, **1989**, p 259.
[21] J.S. Mayell, *Ind. Eng. Chem. Res*. **1968**, 7(2), 129-136.
[22] K. J. Laidler. *Chemical Kinetics*, IIIedn. Pearson, New Delhi (**1987**) p 205.